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The qualitative characterization of '*Sangiovese*' grapevine according to the area and cultivation conditions

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Life is wonderful
all you need is to look at it with the
'right eyes'

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1. INTRODUCTION

1.1 Sangiovese cultivar

Sangiovese is the base vine variety of Tuscan enology as it is the main component of the 7 Tuscan DOCG, since its presence varies from a minimum of 50% to a maximum of 100%: 'Brunello di Montalcino' (100%), 'Carmignano' (50%), 'Chianti' (70-100%), 'Chianti Classico' (80-100%), 'Morellino di Scansano' (85%), 'Montecucco' (90%) and 'Nobile di Montepulciano' (70%). It has many synonyms, the official one reported in National Register of the Varieties of Vines, 'Sangioveto', and others certified as 'Brunello' (Tuscany), 'Morellino' (Scansano-Grosseto), 'Nielluccio' (Corse, FR), 'Prugnolo' (Tuscany), 'Prugnole gentile', 'Sangiogheto', 'Sangiovese grosso', 'Sangiovese piccolo', 'Sangioveto montanino', 'San Zoveto', 'Uvetta' (www.vitisdb.it). Reconstructing the origin of this vine is not easy since there is a lack of historical reference antecedent the XVI century. The importance of this variety in wine production in central Italy and its leading role today in Italian enology justifies the interest in searching the origin of its name. Due to lack of accurate references it was first thought that it recalled the idea of blood, one of the symbols linked to wine and to offering sacrifices to the gods, the blood of Jove (sanguis Jovis). The semantics of the word recalls a game (jugum), and sustains the hypothesis of sangue-gio-vese, hill games; another hypothesis is that of wine 'giovevole al sangue' (Mainardi 2001). Other connections have been hypothesized with language and popular customs, between the Etruscan language, religious aspects and the meaning of the term 'Sangiovese'. An Etruscan phrase was found on a bandage used to wrap an Egyptian mummy of the first century AD, it read 's'antist'celi' with the word 'vinum' and it is thought that it referred to a type of wine as it is very close in assonance to terms that describe 'Sangiovese'. Other assonances linked to rituals and 'Sangiovese', as in *thana-chvil* (votive offering*)*, *tbcms.zusleva* (ritual offering), *thezin-eis* (offering to the god), which is very close to the Romagnolo term sanzve used for 'Sangiovese', this term means father or ancestor to mean the wine of my father's or an offering to the fathers (Mainardi, 2001).

Linking the origin of the Sangiovese vine variety to the Etruscan culture is fascinating, recent discoveries, the close relationship between 'Ciliegiolo' e 'Calabrese di Montenuovo'(Vouillamoz et al., 2007) and (Bergamini et al., 2012), do not concord with these hypothesis even if they do not totally negate them as shown in other research (Di Vecchi et. al, 2007). A current hypothesis associates the name of the vine to 'sangiovannese' as in

originating in 'San Giovanni Valdarno', others believe the origin of the name to come from dialect 'sangiovannina' early grapes. The first reference to the existence of this vine variety in Tuscany dates back to Soderini (1590) who calls it 'Sangiogheto'. At the end of the sixteenth century it appears in a painting by Bartolomeo del Bimbo known as 'il Bimbi' by the name 'Sangioeto' (Basso, 1982), while Trinci (1738) describes the 'SanZoveto' as 'a fine quality grape and bountiful in production'. Moreover the reliable productivity characteristics of the 'San Gioveto' are praised by the Villifranchi in his 'Oenologia Toscana' (1773) defining it 'the protagonist of Tuscan wine superb in taste and generous'. Villifranchi (1773) also refers to 'San Gioveto' strong (synonymous of dog deceiver) and 'San Gioveto romano' that is cultivated in Marca and in particular in the Faentino area where the wine produced is generous 'call it San Gioveto'. The existence of the 'Sangovese' wine and the description of its qualities are found in convivial texts and in the dithyramb of 1818 'Il Bacco in Romagna' by the abbot Piolanti (Mainardi, l.c.).

From Tuscany and 'Romagna' the elected areas the cultivation on 'Sangiovese' spread progressively to other Italian regions, 'Marche', 'Umbria', 'Abruzzo', 'Lazio' and 'Puglia' (Mainardi l.c.) and 'Corsica'. Most of this growth occurred at the end of the nineteenth century and the beginning of the twentieth century with the reconstruction post phylloxeras.

A large scale renovation of the plants took place in the 60s and 70s thanks to the 'Piano Verde', that gave incentives to expand vineyards. The setting for quantity and choice of plant sites which were not always the best did not help the development of this vine variety, but have indeed limited it. The obsolescence of these vineyards has requested renovation, paying particular attention to choice of soil, cloning material and plant design. The latter has been orientated towards an increase in plant density and the accomplishment of management techniques to obtain high quality grapes, able to produce important red wines. (Loreti and Scalabrelli, 2007). At present the 'Sangiovese' vine is the most diffused in Italy, and according to the ISTAT (General Census Survey), in the year 2000 about 70.000 hectares were cultivated covering over 10% of the total surface in vineyards; this data is also confirmed in the 2010 statistics. In Tuscany it is the most diffused vine variety, covering 37.170 ha 67,4% of the regional viticulture surface. As for the agronomic properties, the 'Sangiovese' variety is characterized by a rather early bud burst, found along the Tuscan coastal areas in the last 10 days of March and about a week later in the inner areas. This vine needs high temperatures for ripening (Turri and Intrieri, 1988), reaching its peak around the last 10 days of September in the coastal areas while inland and hilly areas early to mid October. Adaptation to colder climes is linked to rainfall in the month preceding harvest. The

high fertility of the base gems accounts for the spur pruning which can be very short in the hottest areas ('Montalcino', 'Maremma'). Many types of training system can be practiced, short pruning (tree-like, spur pruned cordon, GDC), mixed (Guyot, 'capovolto'), long ('tendone'): these are chosen on the basis of climatic conditions and soil fertility. Rootstocks are now more used than in the past in areas where there are no risks of prolonged drought, high density plantations are employed choosing less vigorous subjects (161/49,101,14), to 110R where there is a need for more drought tolerance, while in the most difficult conditions 1103P is used.

The bunch (fig. 1) is average size, conic in shape and average compactness.

The sugar levels reached in the right conditions is high, while the anthocyanins content of the skins is greatly influenced by the site, the cultivation technique and in particular by the vigour.

The different clones offer a variety of choice according to the morphology and the qualitative characteristics of the bunch (Moretti et al., 2007; Tamai, 2009), so as to allow the realization of polyclonal vineyards.

Figure 1. Sangiovese's bunch.

It is greatly adaptable to diverse environments, even if in coastal areas it can suffer from late frosts. High quality grapes are produced in low fertility soils, well drained and dry climes, with moderate lack of water from veraison to ripening. For a better aroma complexity it is also important to have good temperature range. The terroir effect is well shown by the particular characteristics of wines from different areas. As already stated the 'Sangiovese' is the base vine variety in Tuscan oenology besides being the king of wines like 'Chianti', 'Brunello di Montalcino', 'Nobile di Montepulciano' and 'Morellino di Scansano' (fig. 2), it is the main vine variety in the production of almost all red DOC and IGT wines in Tuscany.

Figure 2. Consortium Logos of some DOCG produced with Sangiovese.

Among the DOC there are 'Barco Reale di Carmignano', 'Bolgheri rosso', 'Candia dei Colli Apuani', 'Capalbio', 'Colli dell'Etruria Centrale', 'Colli di Luni', 'Colline Lucchesi', 'Cortona', 'Elba', 'Montecarlo', 'Montecucco', 'Monteregio di Massa Marittima', 'Montescudaio', 'Orcia', 'Parrina', 'Pietraviva', 'Pomino', 'Rosso di Montalcino', 'Rosso di Montepulciano', 'San Gimignano rosso', 'Sant'Antimo', 'Sovana', 'Terratico di Bibbona', 'Val di Cornia', 'Valdichiana', 'Vin Santo Occhio di Pernice'. Among the IGT 'Sangiovese' is among the components of: 'Alta Valle del Greve', 'Colli della Toscana centrale', 'Maremma Toscana', 'Montecastelli', 'Toscana', 'Val di Magra'.

'Sangiovese' is also used in the production of DOP and IGP wines in other regions too; 'Bardolino', 'Garda Est,' 'Valdadige,' 'Valpolicella', 'Sangiovese di Romagna', 'Montefalco', 'Rosso piceno', 'Rosso Conero', 'Velletri' and 'Gioia del Colle'.

Depending on the area, grape characteristics and level of phenol ripening, it is possible to obtain rosé wines, young red wines ready to be drunk and wines suited to short, mid or long maturation. One of the problems with 'Sangiovese' is linked to the quality of the grapes which are heavily dependent on the climatic course of the year. The grapes can be turned into wine in blend with other vine varieties according to the objectives desired. Grapes that are in a

good healthy state give a tannic product needing refinement before it can be consumed. The colour stability greatly depends on the anthocyanic composition, that in the 'Sangiovese' is not optimal for lack of malvidin; however this problem has been mitigated improving the production techniques (minor yield per plant) and by using qualitative clones. 'Sangiovese' is also a blend vine, as shown by the formula in 'Chianti' del 'Barone Bettino Ricasoli' (7/10 of 'Sangiovese', 2/10 od 'Canaiolo nero' and 1/10 of 'Malvasia bianca lunga'), and it has evolved from being a year wine to refined wine with the progressive reduction of white berry vines. The red berry vines used in the blend are there to integrate the characteristics of the 'Sangiovese' wines in particular years or in less favourable conditions to give greater colour stability, greater sense of smell and mellowness. The young wine is an intense rich red colour, red fruit scented and at times floral and or vegetable, dry tasting, correctly tannic. Wines that are to be refined are more structured and have a higher acidity level. With ageing the colour tends to garnet and with the fruity note there are the evolved scents of tobacco, balsamic and liquorices.

1.1.1 Adaptability of the soil

Tests conducted on the influence of the soil on the quality of 'Sangiovese' grapes in the 'Chianti Classico' area, have shown a link between the sugar content of the grapes and nature and soil composition and in particular the organic and clay content. The best soils are those with average fertility, clayey-chalky and well framed, that dry quickly during ripening and as such in these soils the vegetative development of the plants is more balanced. According to Bertuccioli (2000) the most interesting values of the chemical parameters linked to quality, were found in areas with a higher percentage of sand and with a lower rate of phosphorous and potassium that can be assimilated. Tomasi and others (2006), have pointed out that in cases of grapes from non chalky soils, in the corresponding wines there was a strong spicy scent, cinnamon and cherry, but above all they presented a fullness of taste that was not present in chalky soils. In these soils however, the aromatic fineness and persistence triumphed, and the scent of violets and white flowers. At high temperatures the monoterpenic substances are lower. The reduction of aromatic content of the grapes, due to high temperatures, is so strong so as to also cancel the positive action linked to water content of the soil. It was also possible to note the norisoprenoids components present in the grapes grown in quite damp soils. The high temperatures therefore compromised the aromatic quality, independently from the water content in the soils.

From a survey carried out by the CRA-VIT (Sebastiani and Storchi, 2004) on a number of vineyards in the 'Arezzo' province, the influence of soil management relative to a number of vegetal-productive plant response emerged. Therefore, the positive response of 'Sangiovese' to grass cover became obvious, even if limited to alternate rows. In particular, with this technique the result was a lower average weight of the bunch and of the berries, but with positive effects on sugar content and colouring substances and on the state of health of the grapes at harvest. All this had already been noted by Egger et al., (1996). These results have also been confirmed in other research by Bertuccioli et al., (2000) carried out on the grass cover in two areas of the 'Chianti Classico'. The wines from grass covered vineyards have clearly shown the positive influence of this technique on the quality of the product having higher alcohol content and greater net extract, total polyphenols and anthocyanins compared to vineyards situated on land worked so as to support the vigour of the vine (Pisani et al., 2000). Triolo and Materazzi (Triolo et al., 2000) too have noted how grass cover favours significant reduction in Botrytis, particularly in years of low rainfall.

1.1.2 Adaptability to temperatures

Intrieri, already in the 1980s, underlined the resistance to the cold of the main buds of the 'Sangiovese'. After the bad frost in January 1985 at -18°C, the bud mortality was just over 20%,but with the further fall of 1°C the mortality rose to 90% thus setting the critical threshold to the winter cold at an interesting -18°, -19°C. In tests in the 1970s the environmental stability in the phonological phase was evaluated and variable behaviour per bud, flower and veraison was observed in that the vine often suffers environment conditions but not always in an univocal way (Calò et al., 1977). Test Results carried out in 2004 have underlined the importance of high thermal summing for the perfect completion of the vegetative cycle and that the best quality is determined by temperature along with water availability in the fruit set- veraison period, so much so that the best years are correlated to higher average temperatures summing and lower rainfall values in the vegetative period. In the 'Montepulciano' area there was a positive correlation between the altitude of the vineyards and malic acid content in the must, as late harvesting occurs in altitude and this confirms the temperature needs of this vine variety during ripening (Egger et al., 1986). Systematic research conducted since 1987 on the relationship between variety and environment, has shown that the 'Sangiovese' is more reactive to pedoclimatic and cultivation solicitations. Results from four different years (1987-1990) from the main vine growing areas

of Tuscany ('Chianti Classico', 'Montalcino' and 'Montepulciano'), show higher sugar levels in areas where the mean temperatures are higher and rainfall levels are lower during the vegetative period. The values obtained from the Huglin index, on the other hand, appeared less correlated to the sugar content at harvest. In the 'Montepulciano' area there was a positive close correlation between the altitude of the vineyards and the malic acid content and the titratable acid of the must. In relation to altitude the ripening period too is later due to the lower temperature levels in the period preceding harvest. Research in the 'Chianti Classico' area clearly show the vine sensitivity to rising temperatures. In particular, comparing the two maturation curves obtained from vines with the same productive weight but in different altitude environments (600 and 350 m. above sea level) showed for the latter a constant higher sugar level (Scalabrelli et al.,1996). This difference is to be attributed presumably to the beneficial effects that rising temperatures together with periods of sun exposition, can have on the total photosynthetic yield of the foliage as a consequence and the ability to accumulate dry substance in the bunches.

Bunch size is determined by climate and temperature and is one of the determining factors in the synthesis processes, accumulation and conservation inside the berry of the aromatic mixtures. Another important positive link is between climatic parameters and aromatic substances between the norisoprenoids content and potential value of photo- synthetically active radiation. It is necessary to add the effect of the active limestone content in the soils, in fact in equal active photo synthetic radiation the norisoprenoids content is distinctly higher in vineyards with greater limestone content (Failla, 2006).

1.1.3 Adaptability to rootstock

The adoption of rootstock suitable in different ecopedologic and cultural conditions and productive typologies is of crucial importance in order to obtain the qual-quantitative results desired. Even in this sector there is much reliable data from research carried out on the 'Sangiovese'. In the area of the 'Morellino di Scansano', Di Collato et al., (2000) noted the tendency of higher sugar concentration levels in grapes in vines grafted on 110R followed by SO4 and 41B. A good hold on acidity levels was observed in combinations with rootstock 140 Ru, 3309C and 41B, while in most of the other thesis the values registered were much lower. Taking into account the generalized tendency to the decreasing productive yields in the areas of Denomination of Origin, where red wines are produced, it is worthwhile noting that lower productivity induced by 41B, differently from other rootstocks, determined some of the

highest sugar gradation, while keeping a good hold on acidity levels. In the 'Chianti Classico' the experimental trials carried out on rootstocks by Scalabrelli and Loreti (Scalabrelli et al., 2000) evidenced the different influence on 'Sangiovese' both in the vegetative-productive performances and in qualitative aspect. On the basis of the results the SO4 is not the ideal rootstock for the pedoclimatic characteristics of this area. With this rootstock, the vines often produce an excessive quantity of grapes with a mediocre sugar level.

The rootstocks by V. Berlandieri x V. Rupestris (775P, 779P, 1103P), even if producing a certain vigour and productivity, have also determined a reasonable sugar gradation of the grapes. However, some years it has been necessary to reduce the quantities produced. The 140Ru, 110R, 225Ru, 420A, 34EM, rootstocks have induced average to low vigour and quite good sugar gradation and production. Rootstocks 101.14 and 3309C have induced lower vigour, higher sugar gradation and relatively low productivity even lower than the regulatory foreseen for the 'Chianti Classico' DOCG. From this we can ascertain that the 110R is the best rootstock for the global performance of the 'Sangiovese' in the 'Chianti Classico' soil conditions Scalabrelli et al., l.c.).

1.1.4 Adaptation to the training system and density of plantation

Intrieri points out 'the high fertility of the basal buds of the 'Sangiovese' vine shoot offers a wide range of choice in terms of pruning lengths and consequently training systems. On this premise the author carried out many tests to observe the behavior of different systems with long pruning with annual renewing of shoots (Guyot unilateral or bilateral) and with permanent cordon with long pruning ('Casarsa' type) or short (spur pruned cordon type, single and double T, short and long GDC, single 'Cortina') (Filippetti et al., 2000. Intrieri et al,. 1985, 1992, 1993, 2000).

In the results the 'Sangiovese' has always shown a tendency to stay on high unitary yield levels and above all the remarkable capacity for productive compensation, if blocked on rather modest bud weight. From the systems observed, only the long GDC and vertical cordon have resulted in lower than the average production remembering that this system (in the case of GDC) lowers the vigour. In the vertical cordon, acrotonic gradient has brought physiological imbalance, shading from the excessive bud growth and resulting in product penalization. The result highlighted even by the author of the test, is that the 'Sangiovese' vine is adaptable to training systems that can be diversified per vine structure, bud weight and crown architecture.

Varying these conditions, the vine maintains a strong productive capacity with appreciable qualitative levels. However there is also the need to find systems that can contain the natural tendency of the vine to let the vegetative phase prevail; this phenomenon has also been found in other tests by Intrieri et al., 2000.

Bertuccioli et al., (2000), in a study, noted that average-low density plantation determined a likely physiological imbalance of the vines in favour of vegetative growth, penalizing the quality of the production.

Moreover, according to Bertuccioli (2000), plantation density, showed significant effects on the quality of the 'Sangiovese' grapes. In particular, the most interesting values of the chemical parameters linked to quality have been observed, in the area characterized by a higher percentage of sand and lower values of phosphorous and potassium that can be assimilated and by the catatonic exchange in the higher densities, while on the richer soil they coincide with the average-low densities, which as a result of the excessive soil exploitation determines a physiological imbalance of the vines in favour of vegetative growth.

Scalabrelli, et al., (2000) have noted that even in diverse environments and wine typology, density of around 5.000 stumps per hectare in general determines a better balanced plant growth. Higher density do not offer advantages, that can be generalized, on the vegetal-productive behavior and on the quality of the grapes. Indeed, depending on the ecopedologic conditions problems can arise due to the alteration of the vegetative balance if a low number of buds per plant is chosen, or production increase if buds with a greater weight are chosen.

1.1.5 Adaptability to summer pruning

Shoot thinning the vine during the vegetative cycle, is quite diffused and this has posed and poses many physiology problems, particularly concerning the flow of the elaborates at the time of intervention.

Several works conducted by Calò (1975-1976) clarified the balance in the vegetative and accumulation phase, and how it can be compromised in relation to trimming, which cannot be considered as the operation that reduces the surface foliage of the plant.

In some studies by Intrieri and collaborators (Intrieri et al., 1983, 1985) confirmed that good results were obtained by trimming 12 days after flowering. By stimulating the development of the laterals shoots able to reach physiologic ripening at veraison and thus in time to contribute to nourishing the bunch, has given rise to a good level of ripeness. On the other hand, a late

trimming, that is at the time when the push in the development of the shoots is inferior, has brought about a slowing down in the growth of the berries and their ripening.

Experiments by Palliotti (2000) the trimming of the shoots carried out prematurely has resulted in the early development of the shoots, in the building sufficient surface foliage sufficiently to guarantee in an optimal way the ripening processes of the grapes, without modifying vine productivity and improving grape quality. Various factors contribute in reaching such results: foliage reduction of the crown resulting in better light penetration; to the source of the shoots thereby improving light intensity and the radiation red ratio far away in the grape area, rejuvenating the crown with early shoots whose leaves have shown since veraison up to their abscission, higher photosynthetic activity than the main leaves. This has drastically reduced foliage surface necessary to bring into full maturation the weight unit of the grapes. After defoliation, Ferrante et al., (1999) did not observe production compromise neither in qualitative nor quantitative levels, not even with intensity over 60 %. Late trimming caused the slowing down of the sugar accumulation and the acidity degradation, thereby delaying the best time to harvest and induced product quality deterioration. These results backed by other authors, are probably due to the late trimming of the vines, laterals shoots development continues even after veraison, thereby reducing sugar in the bunches. This new vegetative development delays the accumulation phase and consequently the best harvest time. Another in summer pruning studied was defoliation. In 2012 studies were made by D'Onofrio et al. on the effects of defoliation carried out in different periods, on the characteristics of the berries and on the aromatic quality of the 'Sangiovese'. These experiments reported how the berries from the non defoliated sample had a higher greater berry weight compared to the two thesis defoliated at pre-flowering and ay veraison. With reference to the aromatic component of the grapes a progressive accumulation of diverse class aromas reaching peak point, from which it starts decreasing up to harvest time. Such a decrease is probably due to the degradation of the aromatic composites induced by the high temperatures recorded in the last phases of ripening.

The fruit set defoliation determines an increase in content of aromatic composites, compared to the non defoliated sample. A significant increase was noted in the monoterpenols and C13 norisoprenoids, a slight increase in benzene derivatives and a decrease in the aliphatic alcohols. The veraison defoliation thesis, presented on the other hand, aromatic composites content inferior to the non defoliated control thesis. Early defoliation is therefore an important and effective in increasing aroma concentrations and, as a result for the aromatic quality of the grapes. The same vineyard was monitored in 2009. This time the thesis analyzed were

two: non defoliated control and fruit set defoliation. In the defoliated sample an increase was noted in all the composite classes, above all at the expense of the C13-norisoprenoidi, exception made for aliphatic alcohol class. The experiment was also carried out the following year with the addition of a thesis created by covering some bunches. It was highlighted how the defoliated thesis at flowering and the fruit set defoliated thesis, had at harvest a higher concentration of all the aromatic composite classes studied. Among these the greatest increase was reached in the fruit set thesis where there was a significant increase in the concentration of all the composite classes. In the defoliated at flowering thesis and later covered it was noted that the bunch temperature was about the same as the temperature of the defoliated at flowering thesis and therefore the only variable, at the base of the significant reduction of monoterpenols and C13-norisoprenoids concentrations, can be attributed to the absence of light.

Reduced leaf layer numbers in a vine may have many beneficial impacts greater anthocyanins and phenolics in Sangiovese harvested after leaf removal (Poni et al., 2006).

In 2008 Intrieri and Filippetti, compared manual and mechanical defoliation on a 'Sangiovese' cultivar: the first six basal leaves and any laterals were removed by hand, and the same area was subjected to mechanical defoliation, the latter removing 48.3% of the leaf area removed manually. Both treatments significantly reduced fruit-set, yield per shoot, bunch weight, berries per bunch and bunch compactness. Yield/ha declined from 32.8 tons in control vines to 24.4 and 19.0 tons for mechanical defoliation and hand defoliation (pre and post bloom treatment means), respectively. Leaf to fruit ratios were unaffected by defoliation as source loss was fully offset by yield decline. Soluble solid concentration and total anthocyanins on a fresh-weight basis increased by 2.4°Brix and 0.2 mg/g in hand defoliation and by 2.2°Brix and 0.08 mg/g in mechanical defoliation as compared with that in non-defoliated control. Although results from hand defoliation reinforce the physiological basis of the technique's effectiveness, mechanical defoliation proved likewise effective in reducing yield and improving grape quality.

1.2 The terroir

Even in well known and prestigious 'denomination of origin' vine growing areas there are different vine behavior patterns and therefore the grape and wine characteristics in time and area. It is a well known fact that soil, climate, vine variety and cultivation technique are the main factors in influencing the productive and qualitative result of the vines.

Appraising the cultivation vocation of the territory is one of the best instruments in safeguarding the typicality of the products and the risks involved in soil degradation. In particular, studies on the correlation between the quality of the environment and the quality of the product show the good use of local resources which is strictly connected the specificity of the environment of origin and that must be safeguarded. Such specificity is usually known by the term 'cultivation vocation' and this is regarded as one of the most important success factors in national agriculture in the global market because very often quality cultivation becomes a reference point and a leading image of the territory. Indeed, the term 'total quality of the territory' refers to territory managed in function of product quality, soil and ecosystem conservation, healthy environment and landscape beauty. The acknowledgement of the 'vocation' of a territory is needy of research into its peculiarities which exalt its 'exclusiveness'. In other words, it is the peculiarities of a territory and its functionality, the influence that determines the variability of response, the quality of a wine or of an olive oil for example, that determines the uniqueness of that particular production area. The uniqueness of a production area is thus and added value to the quality that can be crucial for the success of a cultivation. The distinguishing characteristics that determine a production area suited to quality food producing are better explained and detailed in the single functional components of the territory, the 'terroir'.

1.2.1 The terroir and its evolution

The French term *terroir* which is difficult be to translated in other languages it nowadays utilized in the wine world communication, its meaning can be described as a complex combination of factors that determine a specific wine characteristics not repeatable elsewhere. Regarding the roots of this term it is useful to remember that over a century ago its meaning was very different, as revealed by Lawely (1870): '*it is to be remembered that our hills created by terrestrial clay-limestone white grapevine varieties perform very well because*

they can acquire a perfect maturity, that elsewhere it is not possible: cultivated black grapes in that soil could equally produce good wines , if these didn't receive from the soil a particular taste of terrain, that French call terroir'.

The term *terroir* has since been modified and enriched with other meanings, especially in consequence of the intensification of viticulture and wine research and for the its wide use by producers, researchers, journalists, wine critics and wine consumers. Today this word contains at least the following four specifications Origin, Specificity, Perennial and Typical (fig. 3).
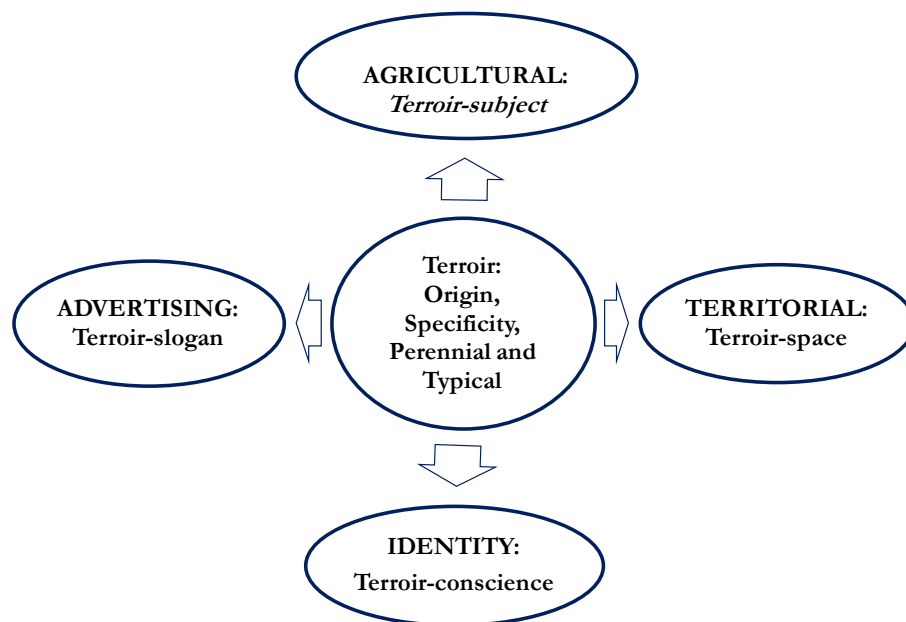
Figure 3. The multiple meaning of Terroir (Scalabrelli, 2013).

The AGRICULTURAL or *Terroir-subject* is identified by the *Taste* (sensory characteristic) and from the consequent *Instrumental Quality,* the complex features due to relationships between plant and environment. The TERRITORIAL concept or *Terroir-space*, concerns the delimitation of a territory, with the relative Denominations and their specificities recognised by the Unity of landscape that are also referred to as historical Geography of the territory.

The *terroir* IDENTITY or *Terroir-conscience*, constitute the immaterial part that is present in a determined country, represented by identity and by the sense of affiliation of the inhabitants, in relationship to their genealogical origin and their traditions.

The ADVERTISING *terroir* or *Terroir-slogan* constitutes the communicative part of the rural world which needs to express certain values and to transmit one specific image. This means searching meanings that are patrimony of the producers and that must be rendered explicitly well through communication in order to offer a better understanding of the essence and the specificity of the viticulturists job.

The *terroir* can be considered a complex system where the genotypes (rootstock, variety and clone) interact with the soil, the macro-meso-climate (Carbonneau, 2000) and the viticulture model (planting design and density, training system, geometry and canopy extension) determining a functioning ecosystem, modulated by techniques of management (fig. 4).
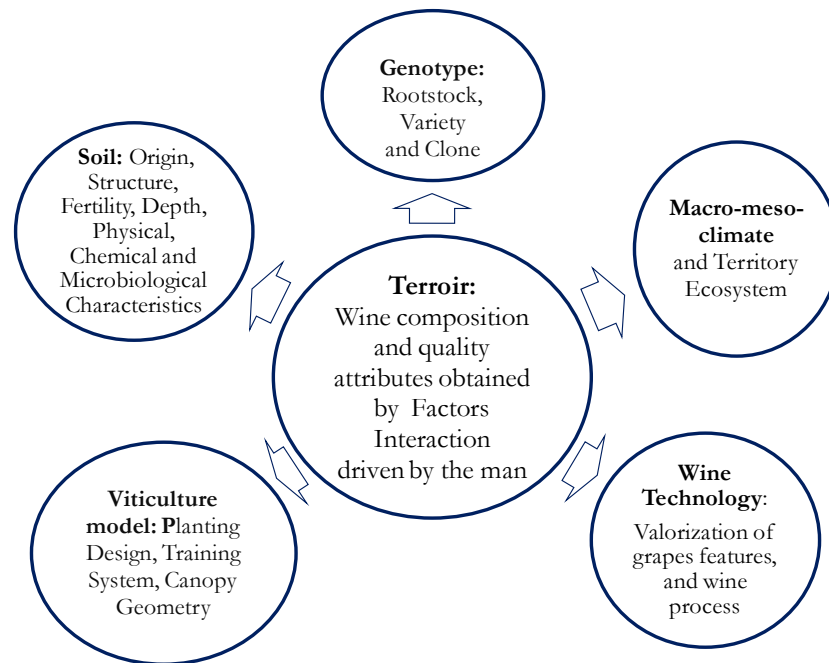
Figure 4. Factors involved into the Terroir effect (Scalabrelli, 2013).

The interaction genotype environment, influences the vine sink/source relationships and, in general, the production efficiency of the canopy. Therefore the quality and the composition of grapes depend on vine equilibrium, or rather from the correct relationship between the leaf functioning area and the amount of yield (Casternan, 1971; Scalabrelli et al., 2001; 2003; Fregoni, 2005).

The knowledge of the vocation of the territory is acquired through interdisciplinary studies of zoning, that through an integrated approach (Morlat et al., 1989) they aim to understand the mechanisms of interaction *environment x macro-meso-climate* that affect the grapevine physiology (Asselin 2001, Asselin et al., 2003). The system *terroir*/vine/wine can be represented by a pyramid constituted by variables of simple and composite state, parameters of functioning, and variables of operation, vintage and wine. All these aspects, in relationship, define the system *terroir*/vine/wine (fig. 5).

Wine

Harvest

Variabiles of Functioning
(earliness, water nutrition..)

Parameter of functiong
(pedoclimate, mesoclimate)

State Composed Variables
(permeability, porosity)

State Simple variables
(altitude, mineralology, granulometry,
chemical composition..)

Characteristics
of
the
production

Plants Characteristics

Environmental
features
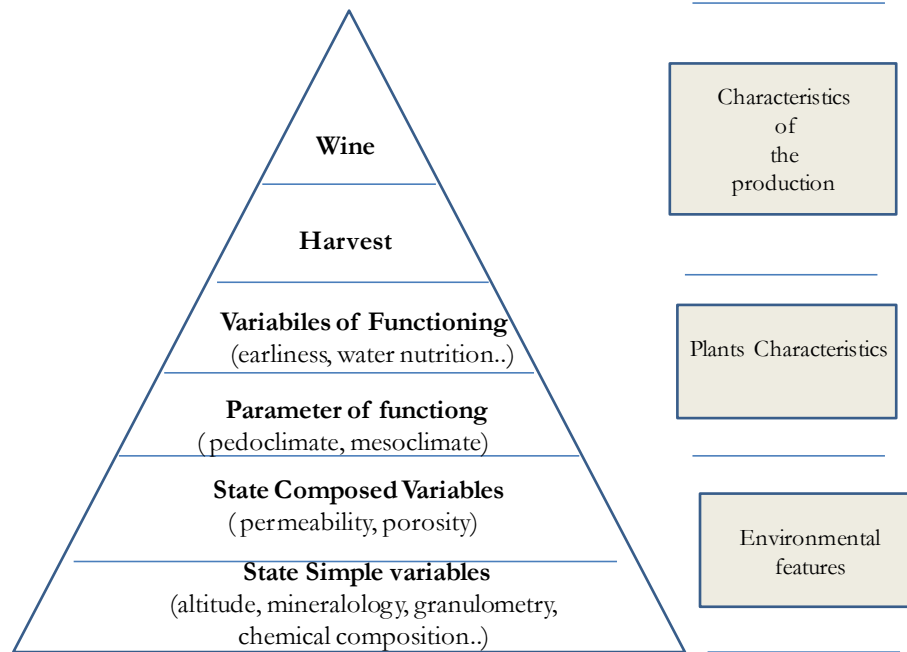
Figure 5. Chain of influences involved in the Terroir effect. Redrawn from Asselin (2001) and Scalabrelli, (2013).

Hence this system implicates the impossibility to expound the elaboration of the wine quality and the operation of the *terroir* through the simple measurement of the influence of a single factor (Morlat, 2001).

Through an integrated approach it was initially defined the scientific concept of *terroir* (Asselin, l.c.) as the basic unit *terroir* (UTB), which can be defined as '*the smallest vineyard area used by the grower in which the response of the vine is reproducible through the wine*', or 't*he smallest physical unit homogeneous that we can usefully differentiate, for practical or for scientific purposes*', which is a separate operating unit agro-ecosystem '*physical site x vine*' (Riou et al., 1995). The unit of viticulture terroir (UTV) is the smallest unit that can be formed by UTB, locally defined (Carbonneau, 1993) with the variety, cultivation techniques and wine (Deloire et al., 2002). Moreover when the base of the UTV group are identical or similar and associated with a strong personality of the wines (sometimes without complexity), they give rise to a homogeneous viticulture *terroir*. If several UTV are different, they form a '*composite terroir*'. In this case the personality of the wines is based on the diversity, the assemblage and regularity according to the vintage year.

In recent years the eco physiological approach of vine-environment interaction, as assessed by the phenotypic expression of the production and quality, has led to a better assessment of the

factors that contribute to the wine *terroirs*. Many of the investigations conducted under conditions comparable of vineyard model and management system were aimed at the identification of vocational units (UV) characterized by vegetative performance, production and quality consistently homogeneous.

The variety 'Sangiovese' is a genotype characterized by a wide variation of expression due to its high responsiveness to the environment (Egger et al., 1999; Bandinelli et al., 2001; Bertuccioli et al., 2001; Giannetti et al., 2001; Scalabrelli et al., 2006), so it would be possible to obtain in different areas wines with very similar quality levels , though differentiated , thus expressing the varietal potential in response to a specific *terroir* (Brancadoro et al., 2006).

1.2.2 The vineyard factors

The 'Sangiovese' with over 67.4% of the vineyard surface cultivated represents the main variety for wine production in Tuscany (ARTEA, 2008).

Without a doubt the wines produced with this variety (pure or base for blend) are famous above all for their geographic origin, thanks to the influence of the environment that modulates their characteristics (Brancadoro et al., 2006; Storchi et al., 2006). Several Tuscan Denominations of Origin (DOCG) thanks to their peculiar aspects are distinguished and have acquired reputation and notoriety abroad (tab. 1), according to several strategies of wine valorisation (Cotarella, 2001; Gallenti and Cosmina, 2001). Only 'Brunello di Montalcino' and few other famous red wines are produced with 100% of 'Sangiovese' while many other red wines, including those reporting the indication 'Sangiovese', are produced mainly by this grape which is integrated with other local or international varieties (Boselli, 2006; Fregoni, 2006; Zampi, 2006). This choice depends on several reasons, to note, problems of inconstant quality levels to produce aging wines due to insufficient content of anthocyanins and polyphenols or aromatic pattern, which could occur in some vintage years or in territory with fair vocation.

Denomination	Main variety	Number of Inscription	Vineyard area (hectare)	Maximum yield of grape (Ton/hectare)
BOLGHERI	Cabernet Sauvignon, Cabernet franc, Merlot, Sangiovese, Sirah	263	1.927,18	10
BRUNELLO DI MONTALCINO	Sangiovese	311	2.020,11	8
CARMIGNANO	Sangiovese + other varieties	34	215,72	10
CHIANTI	Sangiovese	6160	23.585,45	9
CHIANTI CLASSICO	Sangiovese	1178	7.559,14	7,5
MONTECUCCO SANGIOVESE	Sangiovese	317	687,14	9
MORELLINO DI SCANSANO	Sangiovese	412	1.543,54	9
SUVERETO	Sangiovese, Cabernet Sauvignon, Merlot,	100	239,03	9
VERNACCIA DI SAN GIMIGNANO	Vernaccia di San Gimignano	180	777,88	9
VINO NOBILE DI MONTEPULCIANO	Sangiovese	318	1.286,18	8

Table 1. Wines of excellence produced in Tuscany (DOCG in 2011).

The vineyard model (rootstock, density of plantation, training and pruning system, and type of management) is of great importance on vine production equilibrium and therefore on the vineyard ecosystem functioning. Although the 'Sangiovese' grapevine was well studied, it is not possible to indicate a generalized vineyard model suited to all situations (Intrieri, 1995; Loreti and Scalabrelli, 2007). Holding into account the vineyards renewal initiated from 1990' with the objective to avoid vine vigour excesses, in the new vineyards established in Tuscany less vigorous rootstocks and close distances of plantation were used to achieve root competition and decrease vine vigour, which unfortunately not always reached the desired goal. The rootstocks can offer interesting opportunities for modulating vegetative, yield and quality performances of vines, especially in difficult situations. In presence of not limiting conditions less vigorous rootstocks like 3309C and 101-14 can be used, while it would be more appropriate to use 110R when there is the risk of summer water deficit (Di Collalto et al., 2001; Scalabrelli et al., 2001; 2003; Palliotti et al., 2006).

During the last phase of vineyards renewal in Tuscany the dominant tendency has been to adopt planting models with middle or high density planting to achieve better light interception

and improve the vine efficiency. This choice is nearly always a result of a compromise between the best solution from the physiological point of view and the management costs, which can vary according to the conditions of the territory, the size of the farm and the type of enterprise. In this region the tendency to adopt a vertical canopy with horizontal cordon spur pruning or Guyot (less used) is quite generalized, while other innovative systems are introduced only on a small scale (Intrieri and Poni, 2000; Loreti and Scalabrelli). The optimal plantation density from the physiological and qualitative point of view for the most part are intermediate (5000 - 6000 vines/ha), while only in poor soil, is it possible to plant vines at closer spacing (Scalabrelli et al., 2001; Bertuccioli et al., 2001; Bagnoli et al., 2001; Loreti at. al., Mattii et al., 2005). Narrow spacing between lines often induces canopy height to decrease too much with negative effects on grape quality (Scalabrelli et al., 2006). Moreover the model of vineyard must always be adequate to the environment and technical conditions so as to obtain a high grape quality potential. Hence much more the behaviour of the vineyard is approached to the optimal one, the less management actions to equilibrate the system will be required (fig. 6).
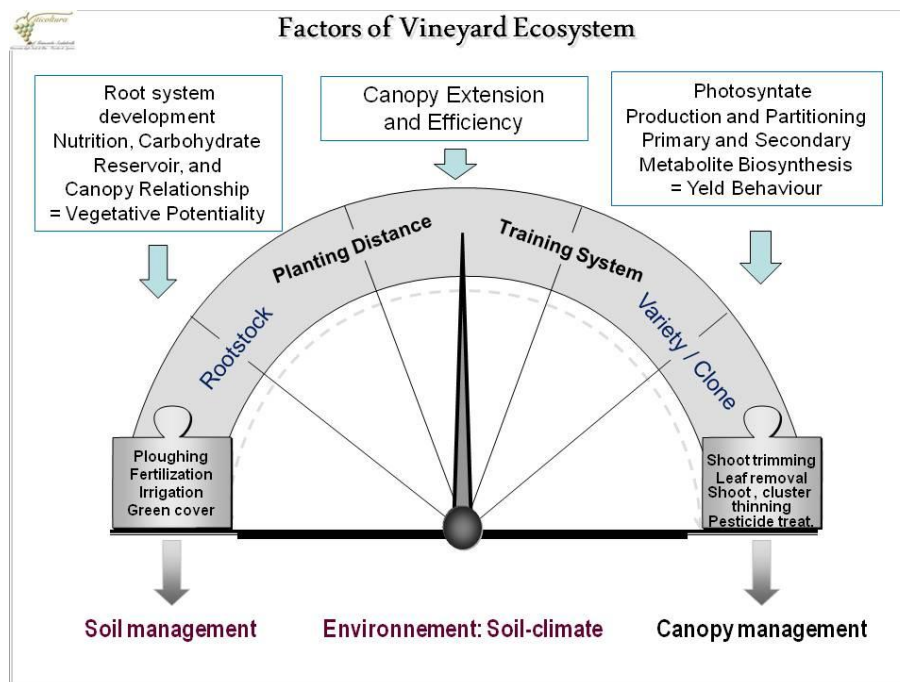
Figure 6. Balance of factors in vineyard ecosystem (Scalabrelli, 2013).

1.2.3 Terroir of Tuscany

The spatial soil and climate variability of the different appellation of origin contributes to the different expression of 'Sangiovese' has been highlighted by a series of works of characterization and zoning .This has led to the definition of specific territorial units (UT) and the drafting of maps of soil landscape to different scales within which a large number of vineyards were researched in detail (Brancadoro et al., 2006). The climatic survey, fundamental for the knowledge of *terroir*, proposes to draw up a climatic map organised into levels of the territory space, in order to find microclimates of the vineyard, the local climate and the regional climate (Zamboni, 2003; Carbonneau, 2003; Orlandini et al., 2003). The use of simple and complex variables or climatic indices, useful for identifying homogeneous areas requires well distributed information systems and weather stations on the territory and the adoption of a different scale of reference (Vaudour, 2005; Costantini et al., 2006). The work conducted in Tuscany by ARSIA meteorological service does not highlight uniform conditions between the various areas with the possibility of a strong influence of the variable climate the behaviour of 'Sangiovese' performances (Scalabrelli, 2008).

The geologic and climatic survey has proved crucial in zoning studies to identify the UTB and the soil map. In these studies the selected data for physical and chemical analysis of the soil, the morphological interpretation of horizons, the roots profiles, the micro morphological analysis and the study of the water functioning or heat of the soil (soil maps with their properties) were separated from the spatial data (Costantini et al., 2006).

The experiences carried out on various scales in the territory of the provinces of Florence and Siena showed great differences in the territory regarding to the climate and soil type profiles and in the behaviour of the productive performance of 'Sangiovese' variety in several vineyards included in the main zones of Denomination of Origin: 'Chianti', 'Chianti Classico', 'Chianti Colli Senesi', 'Chianti Colli Fiorentini', 'Orcia', 'Nobile di Montepulciano' and 'Brunello di Montalcino' (Campostrini e Costantini, 1996; Costantini et al., 1996; Bogoni, 1998; Cricco e Toninato, 2004; Storchi et al., 2005). Climatic variables and altitude were useful in characterizing only partially the zones having viticulture vocation, while the mean soil temperature well characterized soils of the 'Montalcino' vineyards. From the geologic point of view the viticulture areas of 'Montepulciano' and 'Colli senesi' (Siena hills) proved to be more homogenous, followed by those of Montalcino, while the 'Chianti Classico' and the 'Orcia' resulted much more variable (Costantini et al., 2008). The soils of 'Montalcino' and in the 'Chianti Classico' area were found stoniest and less deep, the latter

were also sandiest and could lesser withhold water although exhibiting the best inner water-drainage, which is considered a key soil factor for the health of the vine root system (Costantini et al., 2006; Costantini e Bucelli, 2008).

Other soil features like the cationic exchange capacity, the apparent density and the stability of structure, were found to be quite different in the examined zones. The best vine responses were observed in selected sites of 'Montalcino', compared to 'Chianti Classico'. In several viticulture zones in Tuscany, having the same meteorological conditions, we can find soils with different physical and chemical characteristics (texture, water-drainage, water content) that can characterize various units of soil landscape (USL). Examples are furnished by 'Cerreto Guidi' (Cricco and Toninato, 2000), and 'Bolgheri' (Bogoni, 1999) where the expression of 'Sangiovese' is identified by different wine sensory profiles.

In a study carried out in the 'Arezzo' province, 33 vineyards of `Sangiovese' were subdivided into groups of premature sugar accumulation underlining the greater importance of the inner soil water-drainage (26%), followed by altitude (16%) and water availability (11%) (AWC = Available Water Content). The factors water-drainage, AWC and altitude well discriminate the performances of the vineyards, important too are the depth of soil and the texture (Fig. 11). In particular the water-drainage and the AWC influenced significantly the kinetic of sugar accumulation and the main qualitative grape parameters at harvest. The early ripening vineyards achieved the best grape quality (higher anthocyanins and polyphenols content) and also gave wines more interesting sensory profiles and of greater amplitude. Surveying has permitted a subdivision of the territory into territorial units (UT) having similar characteristics of soil, landscape and climatic conditions, and productive and qualitative expressions (Toninato et al. 2005).

Several soils identified in 'Montalcino' area having different water available in the ground during ripening proved to significantly influence most characteristics (sugars, pH and acidity) according to the year, while the extractable anthocyanins and polyphenols content were influenced only by vintage year. It appeared obvious that in order to obtain the best characteristics from `Sangiovese, soil water content is crucial during the period between veraison to ripening, during which a moderated water deficiency is positive, while excesses or drastic reductions of water available are both negative (Storchi et al., 2000).

Work conducted on small scale zoning in 'Montalcino' area allowed to identify territorial units (UT) characterized by soil chemical and physical parameters (table 3) eg. texture and electrical conductivity, an indirect evaluation of AWC. In this case the UT richer in clay was able to assure the greater AWC in the ground during maturation, while the other UT induced

in `Sangiovese' conditions of water stress from severe to light. Such conditions have influenced meaningfully the kinetic of ripening and particularly increasing the sugar accumulation and the content of extractable anthocyanins (Brancadoro et al., 2006). These results are in agreement with several papers which have underlined that a moderated water stress occurring in the period between veraison and ripening, induces favourable characteristics of the grapes and the wine (Scalabrelli, 2006; Remorini et al., 2007).

Extensive research activities performed in the province of Siena have confirmed that the vine root depth and AWC are significantly correlated with viticulture parameters while the vine performances were mainly influenced by the annual variables like the temperatures of the ground and the air, the rainfall and the number of days without rain (Costantini et al., l.c.). At the end of a series of surveys led in this province an innovative methodology for the *terroir* definition was proposed which previewed the construction of a soil information GIS which collected data in geographic form (scale 1:100.000) and alphanumeric (DB) data. Moreover a DB of viticulture and oenological data, monitored in 70 vineyards for several years, was created. On the basis of these results in this province 363 *terroir* were thus characterized that have an average extension of 46 hectares, varying from a minimum of 2 to a maximum of 474 hectares (Costantini et al., l.c.). Therefore, it can be noted how in Tuscany there are many viticulture *terroir* although very few are really homogenous. The majority of the *terroir* can be considered multiple sites, in which the meaningful effect of the soil and climatic factors, utilized to characterize the UV, on the qualitative characteristics of the grapes and wines, can determine a compensatory effect in areas of non homogenous production supplying however wines having similar characteristics (Brancadoro et al. l.c.).

Recent studies on grapes were able to predict wine characteristics (Bucelli et al., 2010), while berry sensorial analysis was used as a complementary method to determine berry quality (Ducci et al., 2012) and the study of the aromatic profile as well (D'Onofrio et al., 2012).

1.3 Aim of the thesis

The variety 'Sangiovese' is a genotype characterized by a wide variation of expression due to its high responsiveness to the environment so it is possible to obtain in different areas wines with quality standards very similar, though differentiated between them, thus expressing the varietal potential in response to a specific *terroir*. Although the 'Sangiovese' grapevine was well studied, it is not possible to indicate a generalized vineyard model adapt to all situations.

The project, through a structured study wants to proceed first to the chemical-physical and sensory characterization of 'Sangiovese' grapes produced in some representative production's areas of Tuscany. Through a detailed study on the main components responsible for the quality of grapes, especially aroma compounds, based on eco- pedological factors, it will deepen the knowledge of the factors that in the vineyard are the source of differentiation in order to provide the necessary tools to operate more efficiently technical choices that can make a valuable contribution to the diversification and the identification of the wines produced. These investigations, does not aim to make a hierarchical scale of oenological products of a specific territory, but to provide a way to understand the potential of a territory. In this work a particular attention was dedicated to the areas of 'Montecucco' and 'Brunello di Montalcino' making a focus on vineyard effect ('ColleMassari' estate) and on clone effect ('Col d'Orcia' estate).

2. MATERIALS AND METHODS

2.1 Plant material

The research was conducted in three consecutive years (2009, 2010 and 2011), on 'Sangiovese' vineyards in five areas of production located in 'Grosseto', 'Pisa', and 'Siena' provinces, involving a total of 17 theses (fig. 7 and tab. 2).

The corresponding Denomination areas of wine production were: 'Brunello di Montalcino', 'Chianti Classico', 'Chianti Colline Pisane', 'Montecucco' and 'Morellino di Scansano'. On 'Montecucco' and 'Brunello di Montalcino' the study were focused on several vineyards and the clonal effect was also studied. The vineyards in our study were planted in 2000-2001, at a density of 4000-5000 plants per hectare, trained to horizontal spur pruned cordon. The use of cloned material has almost always been identified, most of these clones are 'R24' and 'SS-F9-A548' grafted on 420A or 1103P rootstock depending on the cultivation area (tab. 3).
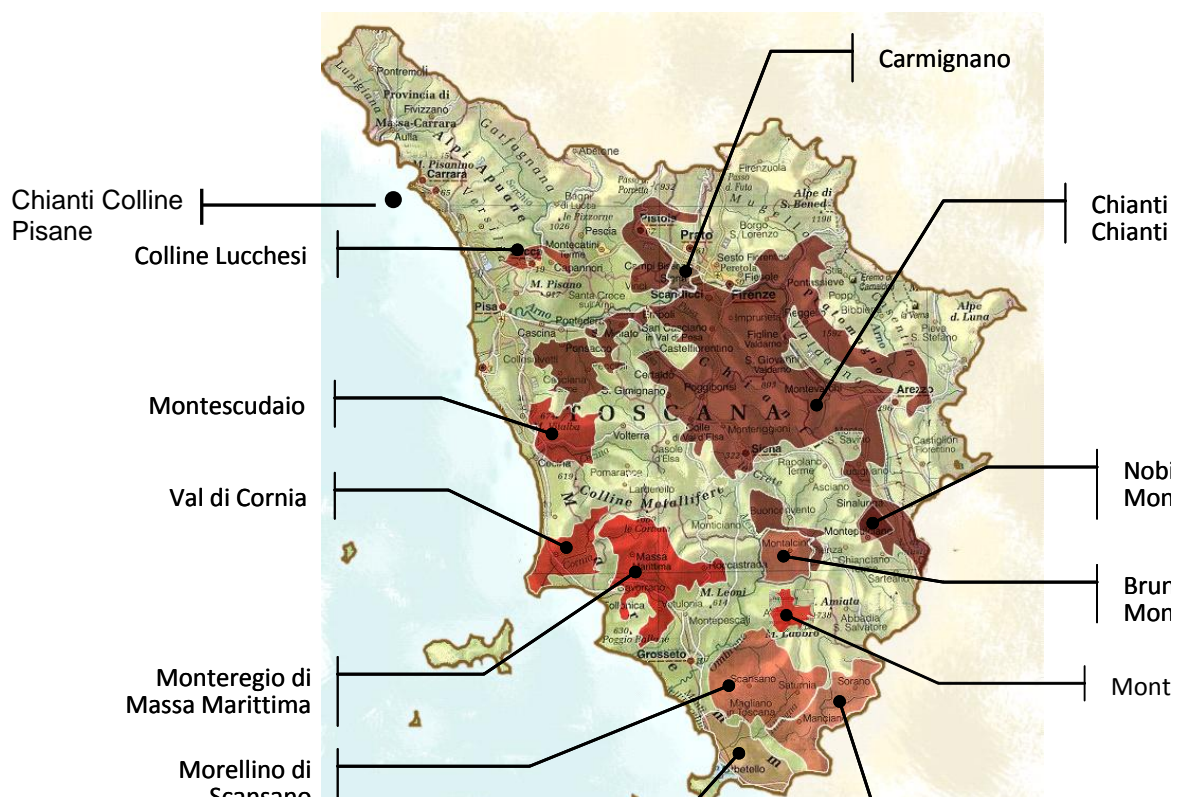
Figure 7. Main D.O. and D.O.C.G. areas in Tuscany on Sangiovese vines.

Thesis	Code	Company - Vineyards	Denomination Area	Town	Prov.	Site
1	CCP 1	Beconcini	Chianti Colline Pisane	S. Miniato	Pi	1
2	MC 1	ColleMassari Campo La Mora F9	Montecucco	Cinigiano	Gr	2
3	MC 2	ColleMassari Campo La Mora Sal	"	Cinigiano	Gr	2
4	MC 3	ColleMassari Cerrete	"	Cinigiano	Gr	2
5	MC 4	ColleMassari Orto del Prete	"	Cinigiano	Gr	2
6	MC 5	ColleMassari Vigna Vecchia	"	Cinigiano	Gr	2
7	MC 6	Salustri	"	Cinigiano	Gr	3
8	MS 1	Fattoria di Magliano	Morellino Scansano	Magliano	Gr	4
9	BM 1	Col D'Orcia	Brunello di Montalcino	Montalcino	Si	5
10	BM 2	Col D'Orcia	"	Montalcino	Si	5
11	BM 3	Col D'Orcia	"	Montalcino	Si	5
12	BM 4	Col D'Orcia	"	Montalcino	Si	5
13	BM 5	Col D'Orcia	"	Montalcino	Si	5
14	BM 6	Casanova Di Neri	"	Montalcino	Si	5
15	BM 7	La Mannella Terra Bianca	"	Montalcino	Si	6
16	CC 1	Capannelle	Chianti Classico	Gaiole	Si	7
17	CC 2	Castello di Albola	Chianti Classico	Radda	Si	8

Table 2. Prospect of vineyards chosen for the study.

Thesis	Code	Clone	Rootstock	Training system	Age	Conduct
1	CCP 1	F9	1103P	SPC	10	C
2	MC 1	F9	161-49 C	Guyot	9	B
3	MC 2	Sel. Salustri	161-49 C	Guyot	9	B
4	MC 3	Sel. Salustri	110 R	Guyot	8	B
5	MC 4	Sel. Talenti	157-11	SPC	9	B
6	MC 5	Sel Col D'Orcia	775 P	SPC	10	B
7	MC 6	Sel. Salustri	110 R	Guyot	10	B
8	MS 1	R 24	110 R	SPC	10	C
9	BM 1	Clone 1	420A	SPC	10	C
10	BM 2	Clone 2	420A	SPC	10	C
11	BM 3	Clone 3	420A	SPC	10	C
12	BM 4	Clone 4	420A	SPC	10	C
13	BM 5	Clone 5	420A	SPC	10	C
14	BM 6	VCR 5	110 R	SPC	9	C
15	BM 7	R 24	1103P	SPC	10	C
16	CC 1	R 24	420A	SPC	10	C
17	CC 2	R 24	420A	SPC	9	C

Table 3. Main characteristics of the vineyards (SPC = Spur pruned cordon; C= Current; B=Biologic; BD= Biodinamic.).

2.2 Technological maturity

At harvest time, sets of 10-12 bunches for thesis were sampled and subjected to sensorial, physical-chemical, and aromatic analyses. Crashed bunches were used to determine the concentration of total soluble solids (°Brix) by a digital refractometer (Model 53011, TR, Forlì, Italy), the pH by a bench pH-meter (Hanna Instruments, Milano, Italy) and total acidity by a digital burette (Brand, Wertheim ,Germany) by titration with NaOH 0.1 N.

2.3 Sensory analysis on grapes

Evaluating the quality of the grapes before harvest is very important for the decision making of the vine technician and the enologist, as they can better direct the growing techniques in vineyard and better select the grapes for the wine making based on quality and suitability in the production of specific wines. Moreover it is possible to adjust the winemaking technology on the basis of the characteristics of the raw material. The ICV has in the last ten years developed a sensorial method of analysis in order to satisfy the above needs (www.icv.fr). This method, slightly modified (Scalabrelli et al., 2010) can be used with good results at contained costs, above all because it represents a complementary technique to the chemical-physical analysis of the grapes (sugar, acidity, phenolic ripeness).

Sensorial analysis of the grapes consists in the evaluation of the visual and tactile characteristics of the berry by the sequential tasting of the skin, the pulp and seeds.

The method used obtains the evaluation by one test: a) the mechanical characteristics of the single berry, acid balance, aromatic strength, quantity and quality of polyphenol and the respective localization; possible imbalance in ripeness levels of the different parts of the berry; c) the variation of the technological ripeness in different periods and years. The procedure expects that every wine taster on the panel assigns for every single descriptor a mark from 1 to 4 corresponding to a level of increasing ripeness (tab. 4-5).

However it must be noted that for some parameters higher values correspond to an advanced level of berry ripeness. This is the reason for the astringency of the tannin and the sensation of bitterness.

Such requirements from a technical point of view are very important in the life of the vine and in the conditions in which ripening occurs, as out of phase ripening can be important from a technological point. Therefore from a sensorial analysis by a trained panel of tasters, it is possible to understand the differences in the stage of ripeness of the different parts of the berry, that can be difficult to determine analytically. For example the sensation of astringency

bitterness and aroma can be quantified immediately without turning to laboratory analysis, but for sweetness and acidity of the must laboratory analysis is needed.

The panel of tasters were five and they were specifically trained in the tasting procedure.

Part/Score	Sensorial descriptors				
Berry	**Skin color**	**Plasticity**	**Pedicel detachment**		
1	Pink	Hard	Very difficult		
2	Red	Elastic	Difficult		
3	Red dark	Plastic	Easy		
4	Blue - black	Easy to break	Very easy		
Skin	**Aptitude to the Skin grinding**	**Tannins astringency**	**Aromatic dominant notes**	**Bitter sensation**	
1	Very difficult	Strong	Herbaceous	Strong	
2	Difficult	Medium	Neutral	Medium	
3	Little hard	Light	Fruity	Light	
4	Tender	Nothing	Marmalade	Little	
Pulp	**Flesh - Skin separation**	**Sweet sensation**	**Acid sensation**	**Aromatic dominant notes**	
1	Very tight	Little	High	Herbaceous	
2	Middle tight	Medium	Medium	Neutral	
3	Tight	Sweet	Little	Fruity	
4	Not tight	Very sweet	Nothing	Marmalade	
Seed	**Colour**	**Hardness**	**Tannins astringency**	**Aromatic dominant notes**	**Bitter sensation**
1	Green	Soft	High	Herbaceous	Strong
2	Green -brown	Little soft	Medium	Neutral	Medium
3	Brown	Hard	Little	Little roasted	Light
4	Brown dark	Lignified	Nothing	Roasted	Little

Table 4. Synthetic sheet of sensorial descriptors and relative score attributed to each level perceived during tasting of the berry parts. (Method proposed by Department of Fruit Science and Plant Protection of Woody Species: Scalabrelli, 2008).

Score	Skin color	Skin	Flesh	Grape-seed	Technological evaluation
1	Little colored	Tight to pulp, herbaceous taste, astringent	Hard, acid, and herbaceous taste	Green, gummy, astringent and bitter	Unripe
2	Incomplete coloration with green veins	Tight to pulp, lightly herbaceous, thick, astringent	Thick, acid, herbaceous taste	Brown with green veins partially lignified astringent and bitter	In progress of ripening: not to harvest
3	Red, enough uniform	Thick, a little bit fragile, lightly fruity with final herbaceous taste	Little thick, lightly acid	Brown, lignified and little astringent	Almost ripe, to vinification with particular attention
4	Bleu - Black	Easy to remove, fragile, strong	Sweet juicy flesh, fruity	Lignified, spiced or lightly hot,	Ripe: suitable to make wine

		fruity notes without final herbaceous taste	and/or marmalade taste	almond taste, not bitter and not astringent.	

Table 5. Sensorial analysis of berry parts (with black skin) during ripening: score and synthetic description of perceived sensations.

2.4 Phenolic compounds analysis

For each sampling, 60 berries were randomly chosen, divided into three groups of 20 berries, which were used as triplicates, and processed according to the method of Di Stefano et al. (2008) slightly modified as follows. Berry skins of each replicate were manually separated from pulp and seeds, and skins and seed were separately weighed and extracted for 4 h at 25°C in 25 mL of a pH 3.2 tartaric buffer solution. This solution contained 12% (v/v) ethanol, 2 g/L sodium metabisulphite, 5 g/L tartaric acid and 22 mL/L NaOH 1 N. After grounding in a mortar and pestle, the extract was separated by centrifugation (R-9M: Remi Motors TD, Vasai India) for 10 min at 3000 rpm. The pellet was re-suspended in 20 mL of buffer and centrifuged for 5 min. The final two pooled supernatants were adjusted to 50 mL with the buffer solution. The skins extract was measured by UV-Vis absorption (Spectrophotometer HITACHI U-2000) at 540 nm after dilution (1:20) with ethanol: water : HCl (70:30:1) and at 750 nm as the seeds extract in the following solution: 0.1 mL of the extract, 6 mL H_2O, 1 mL Folin-Ciocalteu reactive, 4 mL 10% Sodium Carbonate (after 5 min) and H_2O up to 20 mL. Anthocyanins were expressed as mg of equivalents of malvidin 3-O-glucoside and phenolic compounds as mg of equivalents of (+)-catechin.

2.5 Aroma compounds analysis

Aroma compounds originating from the enzymatic hydrolysis of glycosidic precursors (aldehydes, benzene derivates, monoterpenes, norisoprenoids) were extracted from fresh berries by Solid Phase Extraction (SPE) according to the protocol described by Di Stefano *et al*. (1998).

Moreover to reproduce changes in compounds occurring during ageing, hydrolysis of the extract was performed under similar acidic conditions of wines. In order to have a total overview and concentration of aroma compounds, we decided to carry out hydrolysis reaction on the methanolic extract obtained after enzymatic hydrolysis.

Preliminary investigations, considering the use of SPE or SPME procedure for the separation and analysis of the formed compounds, showed SPME technique more suitable because of its efficiency in the extraction, taking into account also the very low concentration of the revealed compounds.

Free compounds were not considered in this work because usually their contribution in neutral grapes, as 'Sangiovese', is very limited.

2.5.1 Preparation of grape sample

Skins of 100 berries were separated from the pulp and extracted with 20 mL of methanol for 1 hour while the pulps were put in a glass containing 100 mg of sodium metabisulfite. After 1 hour pulp and juice were reunited with 150 mL of a pH 3.2 tartaric buffer solution (2 g/L sodium metabisulphite, 5 g/L tartaric acid and 22 mL/L NaOH 1 N). After homogenization by Ultra - Turrax and centrifugation at 7000 g for 5 minutes, solid parts were washed with 100 mL of pH 3.2 tartaric buffer solution and again centrifuged, and the clear liquid was reunited to the first one. The obtained extract was treated with pectolytic enzyme (Vinozym FCEG) for 1 night at room temperature and finally filtered (Whatman 42).

2.5.2 Enzymatic hydrolysis of glycosides

The extract was added to 200 μL of 1-heptanol (40 mg/L in ethanol) as internal standard, and the solution was passed through a cartridge 5 g C_{18} Sep Pak (WAT 036795) previously activated by 20 mL methanol, and 50 mL water. After the sample loading, salts, sugars, and more polar compounds were removed by washing the cartridge with 100 mL of water, and the fraction containing free compounds was recovered by elution with 30 mL of dichloromethane. A second fraction containing glycoside compounds was recovered with 30 mL of methanol.

The methanolic solution was evaporated to dryness under vacuum at 40 ° C, the residue was dissolved in 5 mL of a citrate – phosphate buffer pH 5 (2.04 g of citric acid, 2.92 g of hydrogen phosphate monoacid), then it was added to 200 μL of a glycosidic enzyme with strong glycosidase activity and kept at 40 °C overnight. Then, the solution was centrifuged, added to 200 μL of a 1-heptanol (40 mg/L), and the resulting solution was passed through a 1 g cartridge C_{18} Sep Pak (WAT 036795) cartridge previously activated by 5 mL methanol and 10 mL water. After cartridge washing with 10 mL of water, the fraction containing the aglycones was eluted with 6 mL of dichloromethane, dehydrated with sodium sulfate anhydrous, and concentrated to 200 μL before analysis. A last fraction, containing the

potentially aromatic precursor compounds, was recovered from the cartridge by elution with 5 mL methanol.

2.5.3. Acid hydrolysis of glycosides

The methanolic solution, was evaporated to dryness under vacuum at 40 ° C and the residue was dissolved in 10 mL of tartrate buffer at pH 3.

1g of sodium chloride and 8μL of a 40 mg/L solution of 1-heptanol were added to this solution and the mixture was heated in a water bath to 100°C for 1 h, in an encapsulated vial under a nitrogen atmosphere. After cooling, 2.5 mL of the resulting reaction mixture was transferred in a 20 ml headspace vial and extracted with a SPME fiber (DVB/CAR/PDMS) using an automatic CombiPal system (CTC analytics) under the following conditions: incubation at 60°C for 20 min.; extraction for 35 min.; desorption in the GC injector at 240°C for 6 min in pulsed splitless mode (25 psi for 5 min).

2.5.4. Gas chromatography – mass spectrometry

Chromatographic analysis were carried out using a Agilent 7890A gas-chromatograph coupled with a Agilent 5975C quadrupole mass spectrometer. The carrier gas was helium at a constant flow rate of 1 mL/min. The capillary column was a HP-Innowax (30 m length, 0.25 mm i.d., 0.25 mm film thickness) from Agilent. The temperature programme of the column oven started at 30 °C, then increased at 30 °C/min to 60 °C for 2 min, at 2 °C/min to 190 °C, and at 5 °C/min to 230 °C for 10 min. The MS detector scanned within a mass range of *m/z* 30-450.

Compounds were identified by a combination of matching retention indices with library matches (Nist 08) and authentic standards, which were available for the compounds of interest. The quantification was carried out comparing the peak area of each compound with that of the internal standard.

2.6 Statistical analysis

The resulting data was then analyzed statistically using SPSS130 software. In detail, the climatic data underwent cluster analysis and discriminating analysis and the visual results by centroids which report the first two canonical functions. The macro and microstructural characteristics data of the grapes at harvest were analyzed using the MANOVA test and the differences highlighted two by two by the Tukey test.

With the statistical analysis by placing the three factors thesis, year, and the interaction thesis by year, it was calculated the percentage of variance due to each factor relative to the total variance, obviously including the error.

A factorial statistic analysis was also carried out to reduce the wide variability range of descriptors and constitute complex variables that could well represent the theories examined and to highlight the substantial differences that exist among them. Subsequently the results underwent multiple linear regression to show the possible correlation between the parameters examined.

The evaluation given in the berry sensorial analysis were transformed in percentages before statistical analysis.

Statistical significance was accepted at $P < 0,05$.

3. RESULTS

3.1 Weather station location and study of the historical sequences

The ARSIA archive provided the data relative to the areas under study by selecting six weather huts that were close to each other and that were representative of the production area. The climatic characteristics of the areas were analyzed by studying the following parameters: min-max temperatures, temperature range and rainfall. Average values were calculated for the period April–October and the bioclimatic index Growing Degree Days using the total daily temperatures >10°C. As regards the station chosen on a specific site corresponding to n°2 ('ColleMassari', 'Montecucco'), the climatic findings were collected from weather huts installed on the company.

The localization of the weather huts (fig. 8) and the climatic characteristics of the different areas of Tuscany can be seen in fig. 9-11 relative to average annual temperatures, annual rainfall (mm) and to the hydroclimatic balance (mm) up to the year 2007 (the difference between the total rainfall and the total ETP).
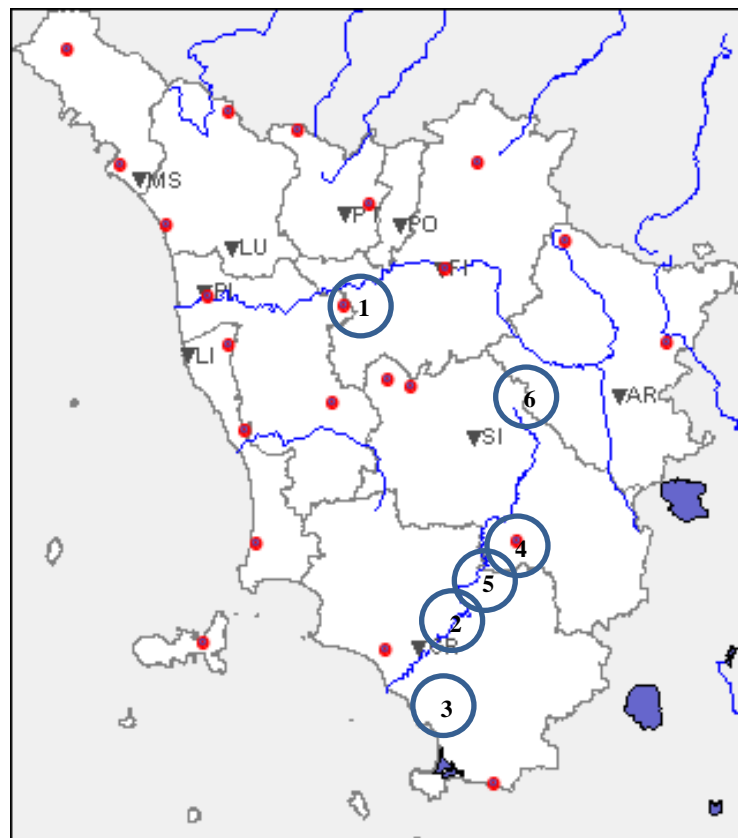
Figure 8. Weather stations used (initials corresponding to table 6).

The data collected is in tabulate and graphic format so as to compare the different areas (tab. 6 a,b,c,d).

n	Station	Temp max (°C)	Temp min (°C)	Temp media (°C)	Daily excursion (°C)	Rainfall (mm)	Growing Degree Days (°C)	Huglin Index
1	San Miniato	26,2	14,7	21,5	11,5	234	2.043	2915,4
2	Cinigiano*	25,6	14,6	20,6	11	254	1.943	2548,8
3	Magliano	26,8	16,3	21,8	10,5	275	2.159	3206,8
4	Montalcino	23,8	14,3	19,5	9,5	331	1.750	2315,8
5	Montalcino**	25,6	13,7	20,3	11,9	254	1.895	2776,9
6	Gaiole	26,0	9,5	18,7	16,5	292	1.608	2449,8

* Poggi del Sasso
** Argiano

Table 6 (a). Average data about weather trends in the year 2009 in the period April-October.

n	Station	Temp max (°C)	Temp min (°C)	Temp media (°C)	Daily excursion (°C)	Rainfall (mm)	Growing Degree Days (°C)	Huglin Index
1	San Miniato	24,1	13,0	19,2	11,1	450	1.688	2470,3
2	Cinigiano*	24,2	13,7	19,3	10,5	379	1.715	2243,8
3	Magliano	23,1	14,2	19,4	8,9	355	1.739	2991,8
4	Montalcino	22,4	13,2	18,2	9,2	449	1.509	1981,8
5	Montalcino**	23,7	12,7	19,0	11	442	1.732	2374,6
6	Gaiole	24,2	9,0	17,4	15,2	465	1.368	2081,9

* Poggi del Sasso
** Argiano

Table 6 (b). Average data about weather trends in the year 2010 in the period April-October.

n	Station	Temp max (°C)	Temp min (°C)	Temp media (°C)	Daily excursion (°C)	Rainfall (mm)	Growing Degree Days (°C)	Huglin Index
1	San Miniato	26,5	14,2	20,9	12,3	185	2.181	2902,2
2	Cinigiano*	25,6	14,3	19,5	11,3	344	2.051	2623,1
3	Magliano	27,1	15,1	21,8	12	227	2.791	3389,6
4	Montalcino	24,1	14,2	19,3	9,9	349	1.847	2389,6
5	Montalcino**	25,6	13,2	20,6	12,4	352	2.138	2753,3
6	Gaiole	26,4	9,3	18,7	17,1	249	1.662	2599,6

* Poggi del Sasso
** Argiano

Table 6 (c). Average data about weather trends in the year 2011 in the period April-October.

n	Stazione	Temp max (°C)	Temp min (°C)	Temp media (°C)	Daily excursion (°C)	Rainfall (mm)	Growing Degree Days (°C)	Huglin Index
1	San Miniato	25,6	14,0	20,5	11,6	290	1.971	2762,6
2	Cinigiano*	25,1	14,2	19,8	10,9	326	1.903	2471,9
3	Magliano	25,7	15,2	21,0	10,5	286	2.230	3196,1
4	Montalcino	23,4	13,9	19,0	9,5	376	1.702	2229,1
5	Montalcino**	25,0	13,2	20,0	11,8	349	1.922	2634,9
6	Gaiole	25,5	9,3	18,3	16,2	335	1.546	2377,1

* Poggi del Sasso

** Argiano

Table 6 (d). Average data relating to meteorological trends of 2009-2011 three-year period during the reference period April-October.
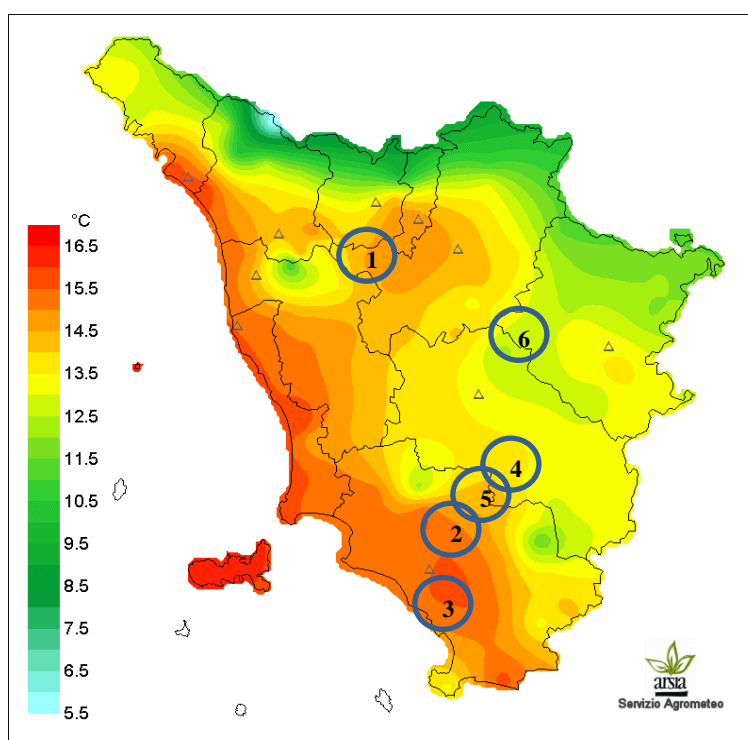
Figure 9. Territorial distribution of the average annual temperature (period 1998-2007). ARSIA source.
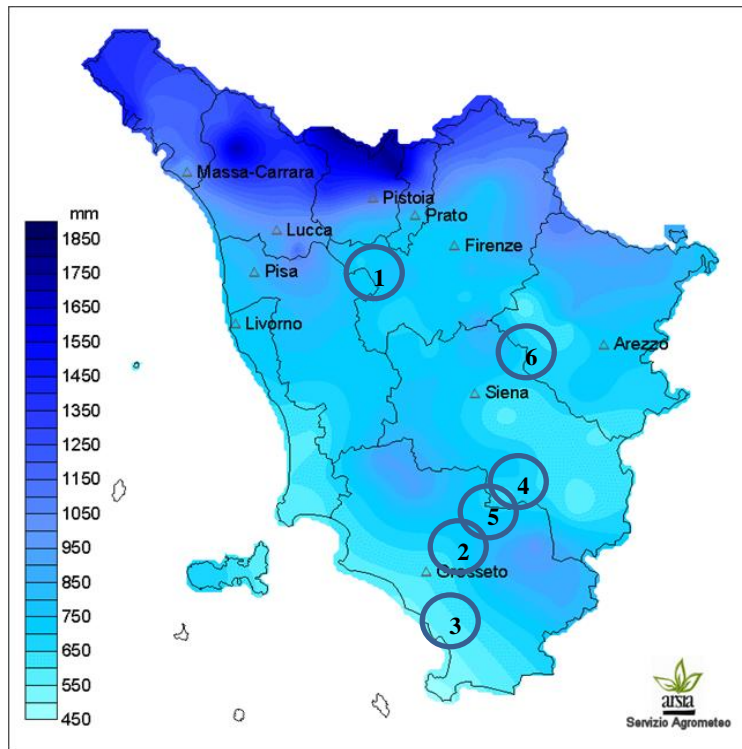
Figure 10. Territorial distribution of annual rainfall (mm/per year) (period 1998-2007).
ARSIA source.
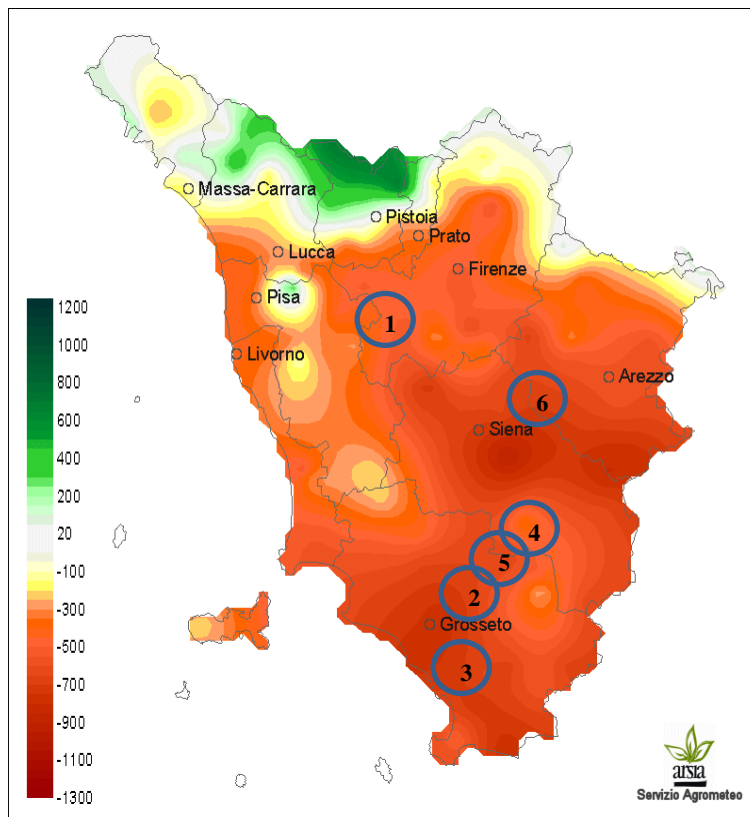
Figure 11. Regional distribution of the hydroclimatic balance (mm) for the year 2007 (the difference between the total rainfall and the total ETP). ARSIA source.

3.2 Climatic characteristics

The graphic representation of some averages highlight the differences between areas relative to average temperatures, temperature range, rainfall and total of Growing Degree Days. (figures 12-23).

The 'Gaiole' station shows in all the three years the lowest average temperature rates, while the province of 'Grosseto', with 'Magliano' in 2009 and 2011 and with 'Cinigiano' in 2010 reached the highest average temperatures in the period April-October. In addition 'Gaiole' differs greatly from the other stations for reaching the highest temperature range in the three year period, with temperatures close to 20°C in the main summer months. Growing Degree Days have shown different trends for the years 2009-2010 where there was an accumulation up to the month of August followed by a sharp fall; instead in 2011, the GDD do not all follow the same trend moving away from the values of the previous years. To note that 2010 represents the year with the highest rainfall in mm, with the exception of 'Argiano', where the mm rainfall is lower compared to the other two years studied.
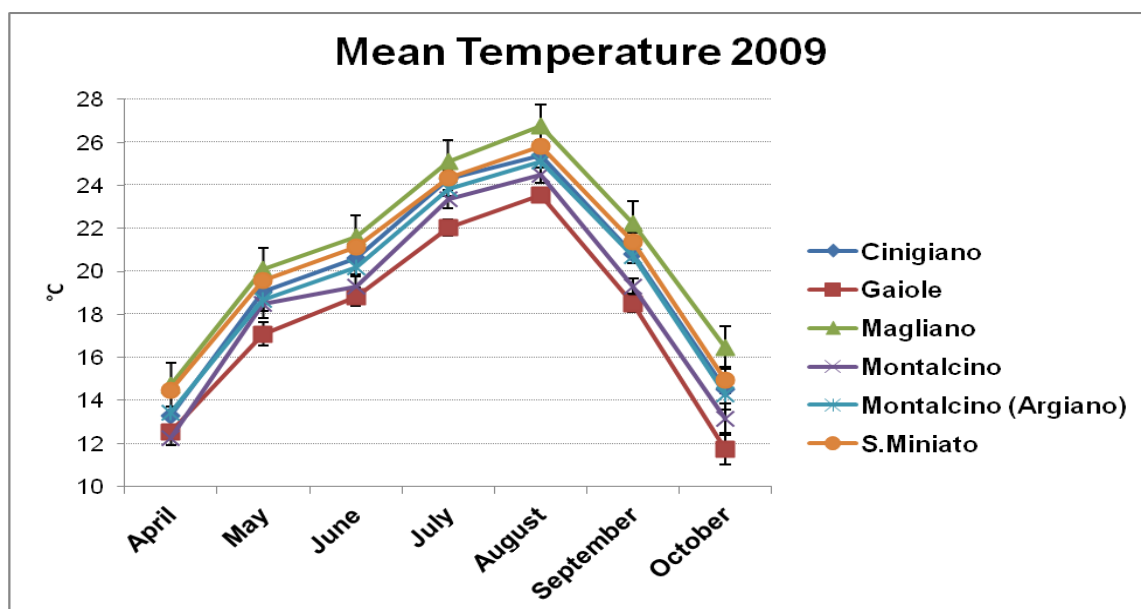
Figure 12. Average temperature trend in 2009 during the reference period April-October.
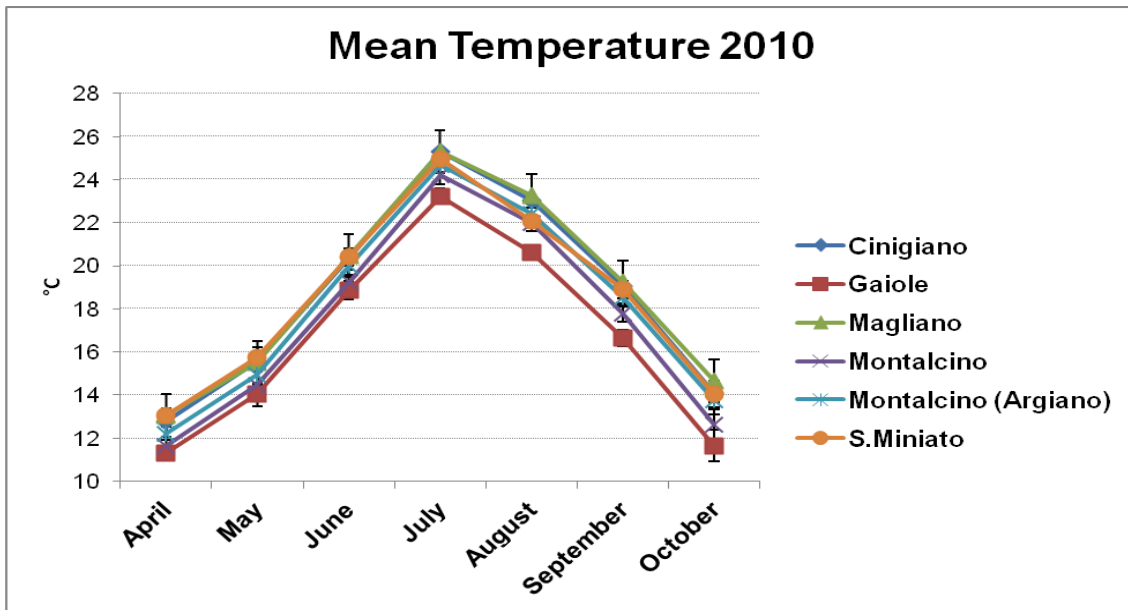
Figure 13. Average temperature trend in 2010 during the reference period April-October.
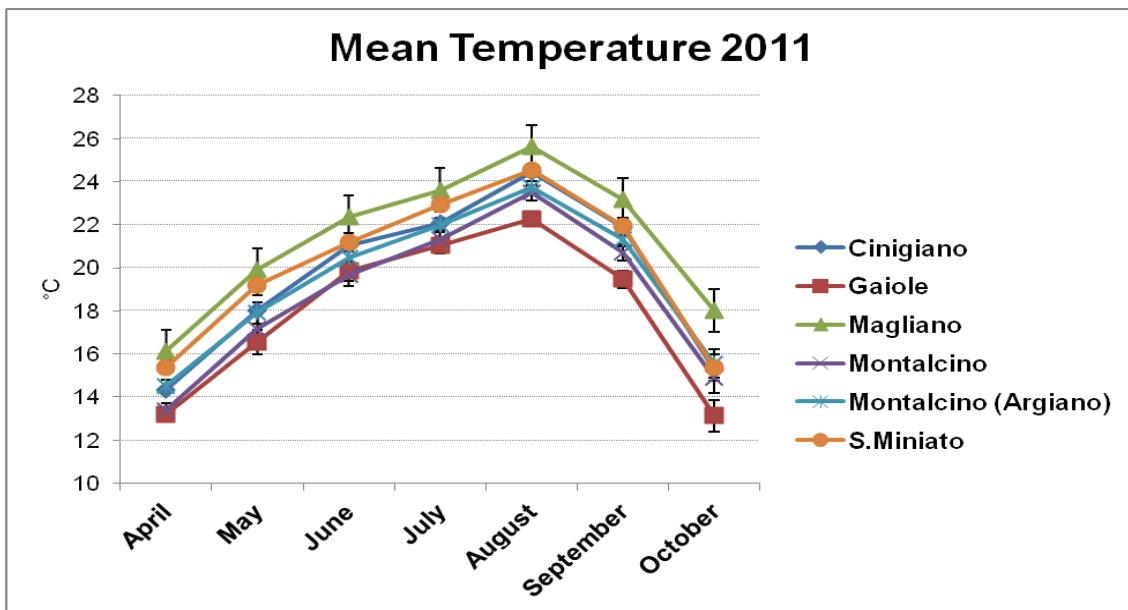
Figure 14. Average temperature trend in 2011 during the reference period April-October.
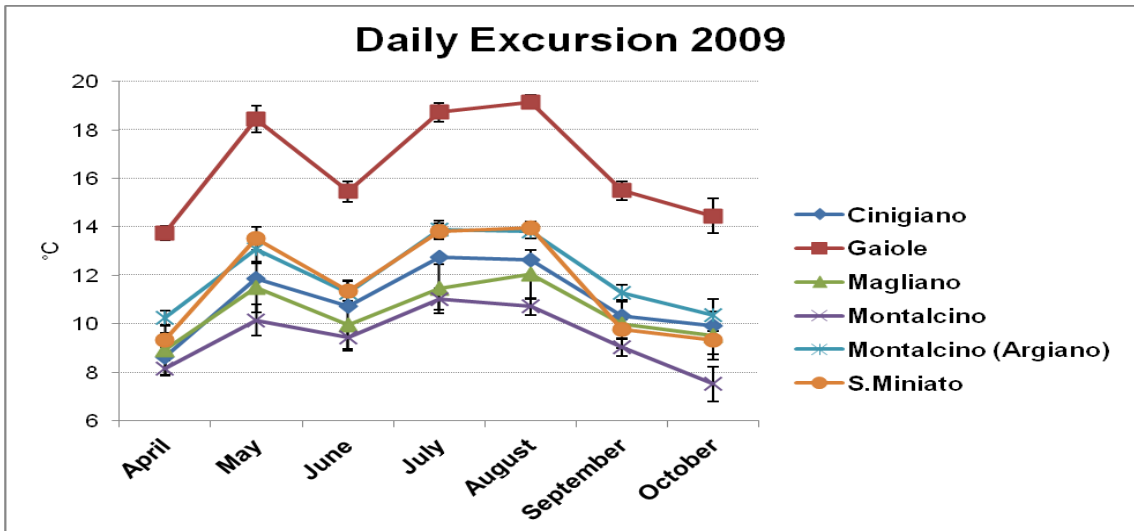
Figure 15. Daily excursion trend in 2009 during the reference period April-October.
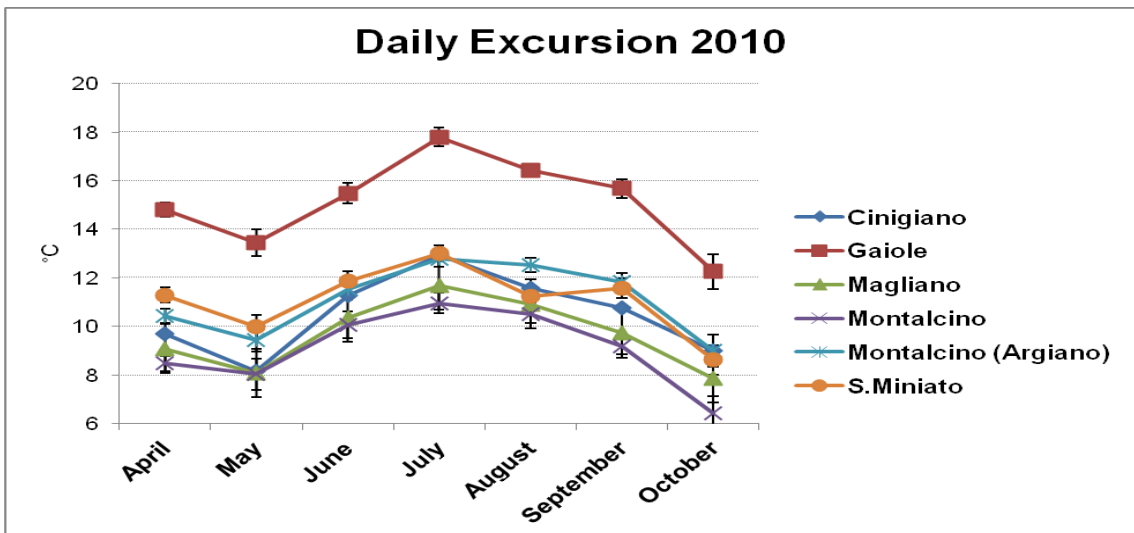
Figure 16. Daily excursion trend in 2010 during the reference period April-October.
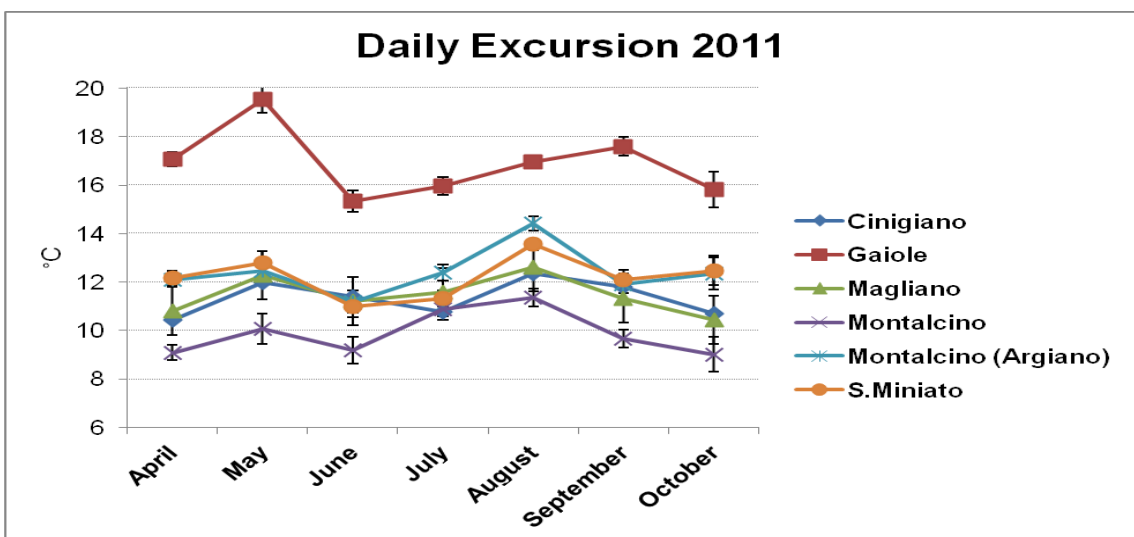
Figure 17. Daily excursion trend in 2011 during the reference period April-October.
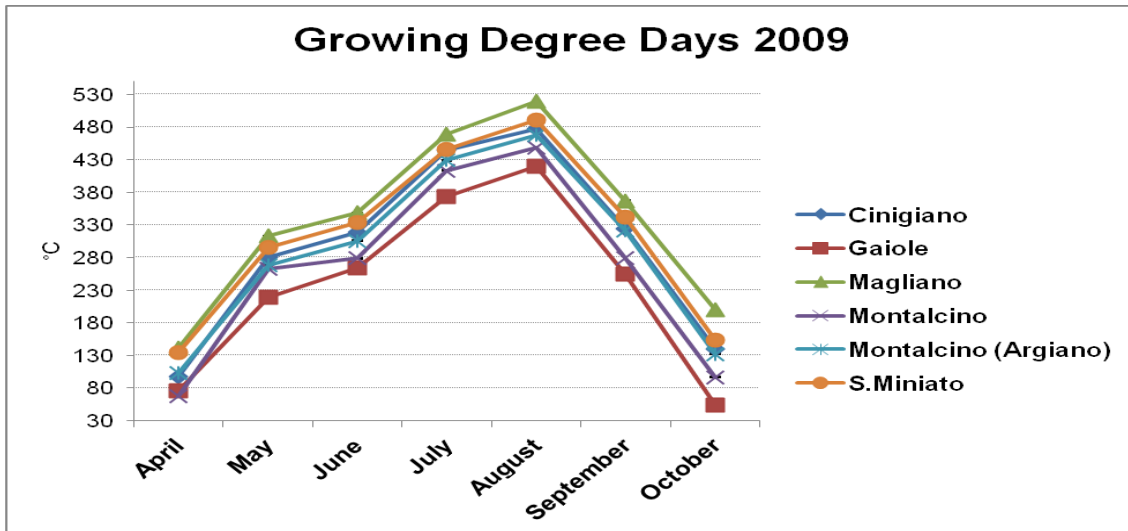
Figure 18. GDD trend in 2009 during the reference period April-October.
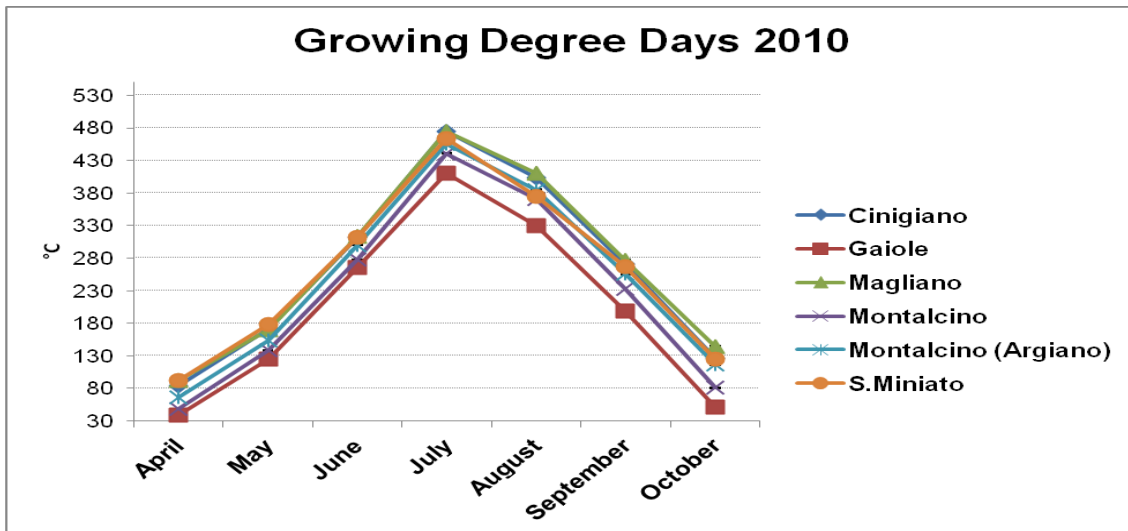
Figure 19. GDD trend in 2010 during the reference period April-October.
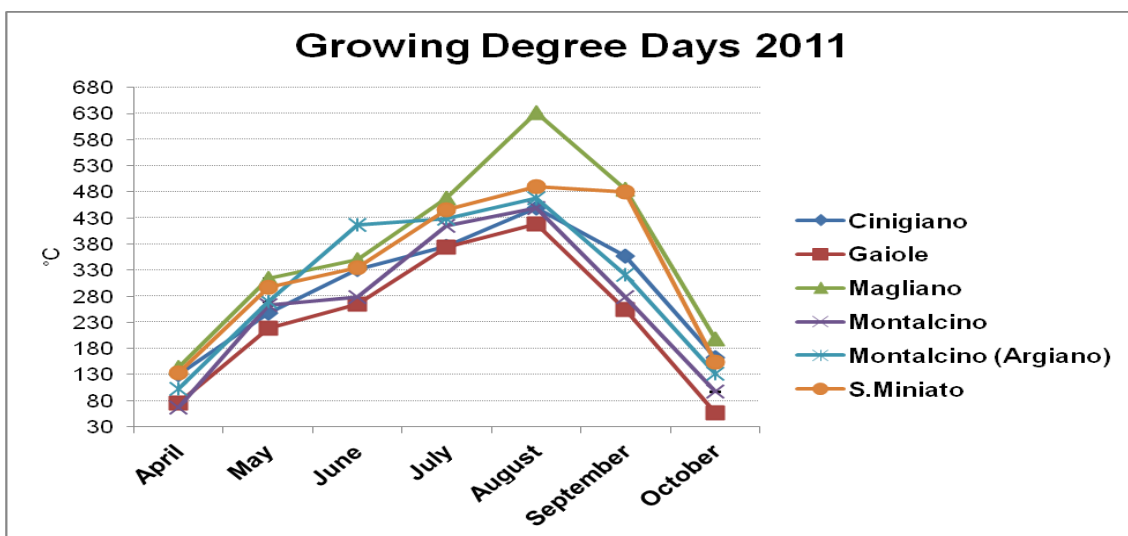
Figure 20. GDD trend in 2011 during the reference period April-October.
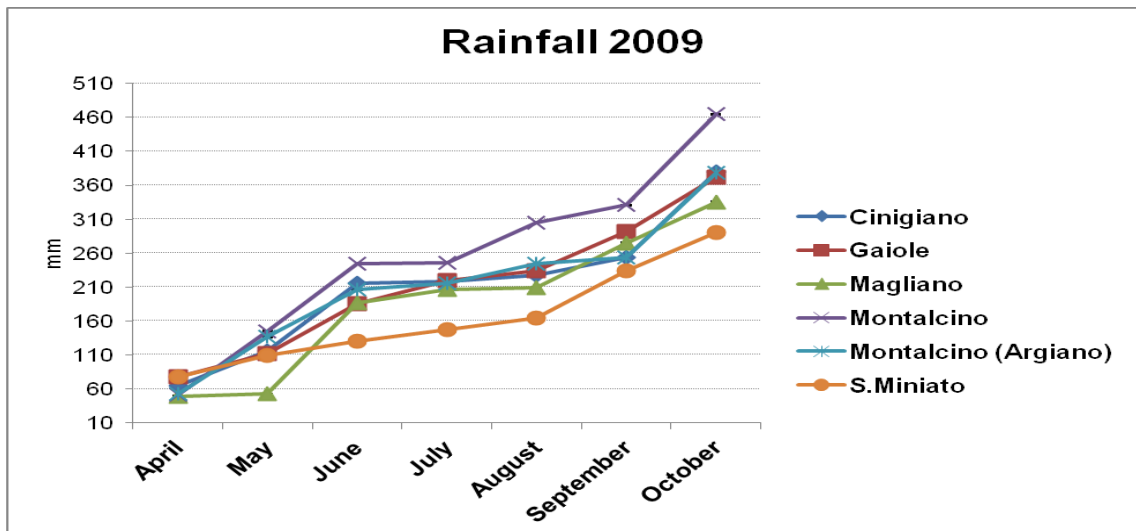
Figure 21. Rainfall trend in 2009 during the reference period April–October.
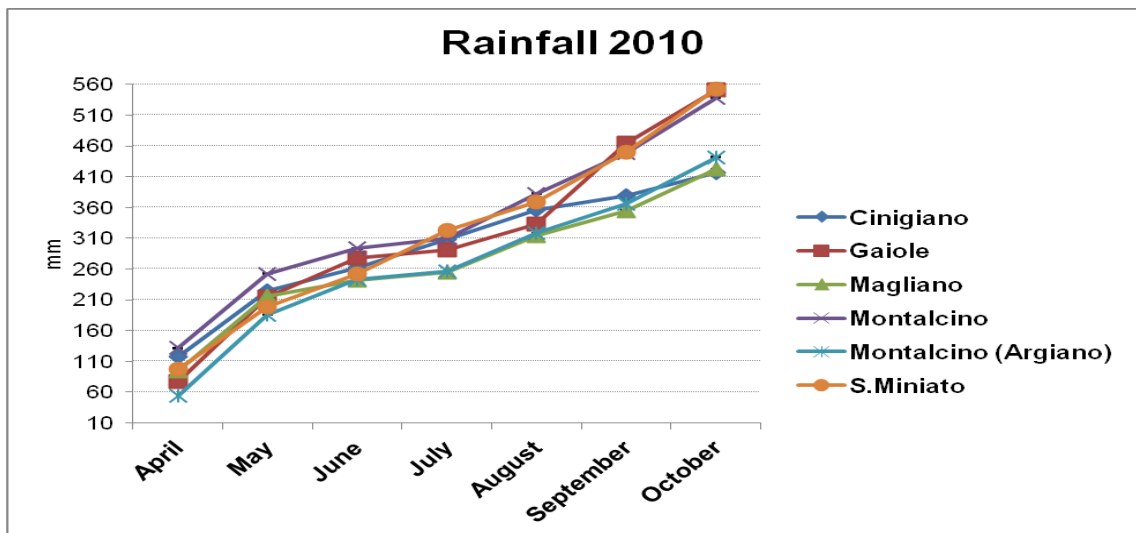
Figure 22. Rainfall trend in 2010 during the reference period April–October.
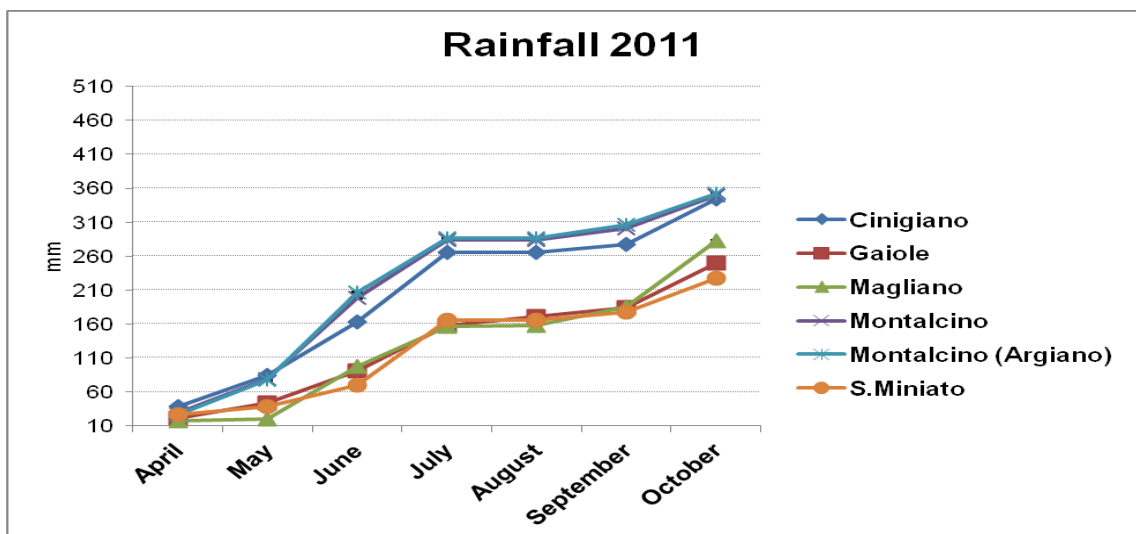
Figure 23. Rainfall trend in 2011 during the reference period April–October.

By cluster analysis of the variables noted it was possible to obtain a dendrogram where it was possible to see areas with similar climatic conditions on the basis of the mean climatic data observed in each year of the three years studied from the six stations (fig. 24). The sites in the study are grouped in cluster, the first being 'Col D'Orcia' 2010 ('Argiano') and the second all the other weather stations. In the second group only the 'Magliano' 2011 station is distinguishable from the others. The 'Gaiole' and 'Montalcino' stations, unlike the others, fall in the same group for all three years.

From the centroids graph obtained from the cluster analysis (fig. 25), which highlighted a significant result since the first two accepted functions represent 93,1% of the total variability, it is noted that the points relative to the groups show a limited dispersion with the exception of the 'Cinigiano' station. Three distinct groups appear in the centroid, the first the stations of 'San Miniato' and 'Magliano' that appear less distinct and the two belonging to the 'Montalcino' area; the second the station of 'Gaiole' very close to that of 'San Miniato' and the third 'Cinigiano' which is the most distinguishable.

The 91,3% of the original grouping are classified correctly, while 87,3% of the cases grouped cross-validated are reclassified correctly (tab. 8). From the test table of the effects among subjects, obtained from the multifactor analysis of the variables examined, differences between weather stations emerge (tab. 7). Analysing the station as a source, the dependent variables statistically different are maximum/minimum temperature and temperature range. If on the other hand it is the year as the source the temperature range remains statistically different together with the rainfall. From the interaction year by station however, the statistics on the parameters examined resulted negative, that is to say, there are no statistically significant differences between the stations studied.

Rescaled Distance Cluster Combine
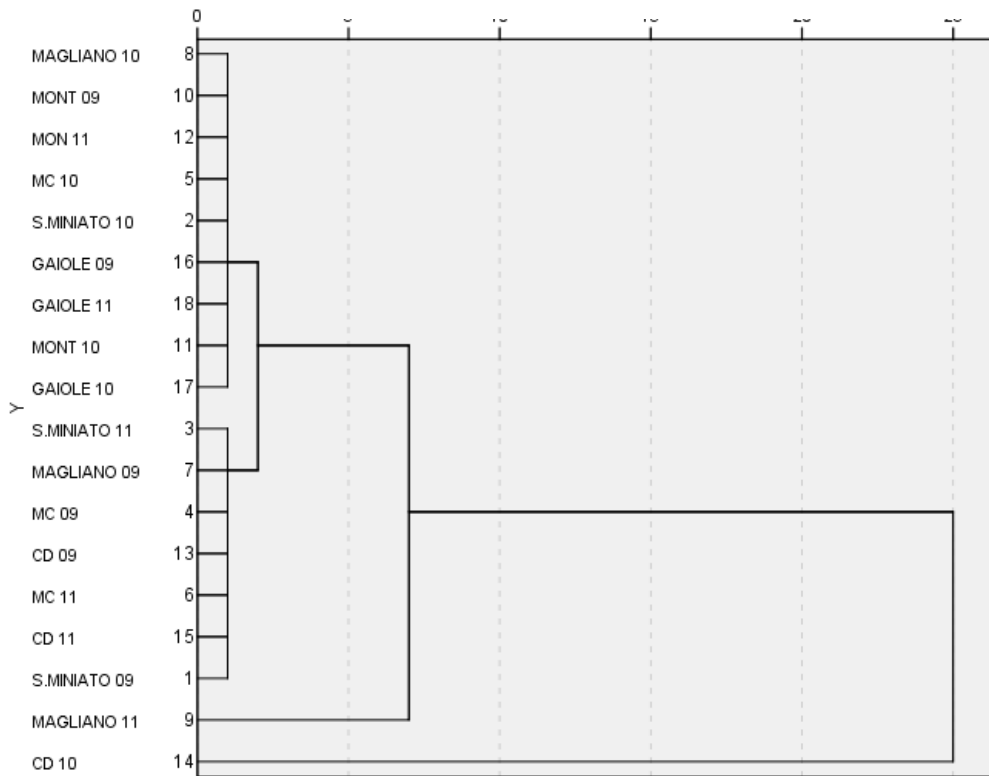
Figure 24. Dendrogram obtained from the hierarchical cluster analysis of the mean data of the six stations. Stations grouped on the basis of the average link between groups.
.
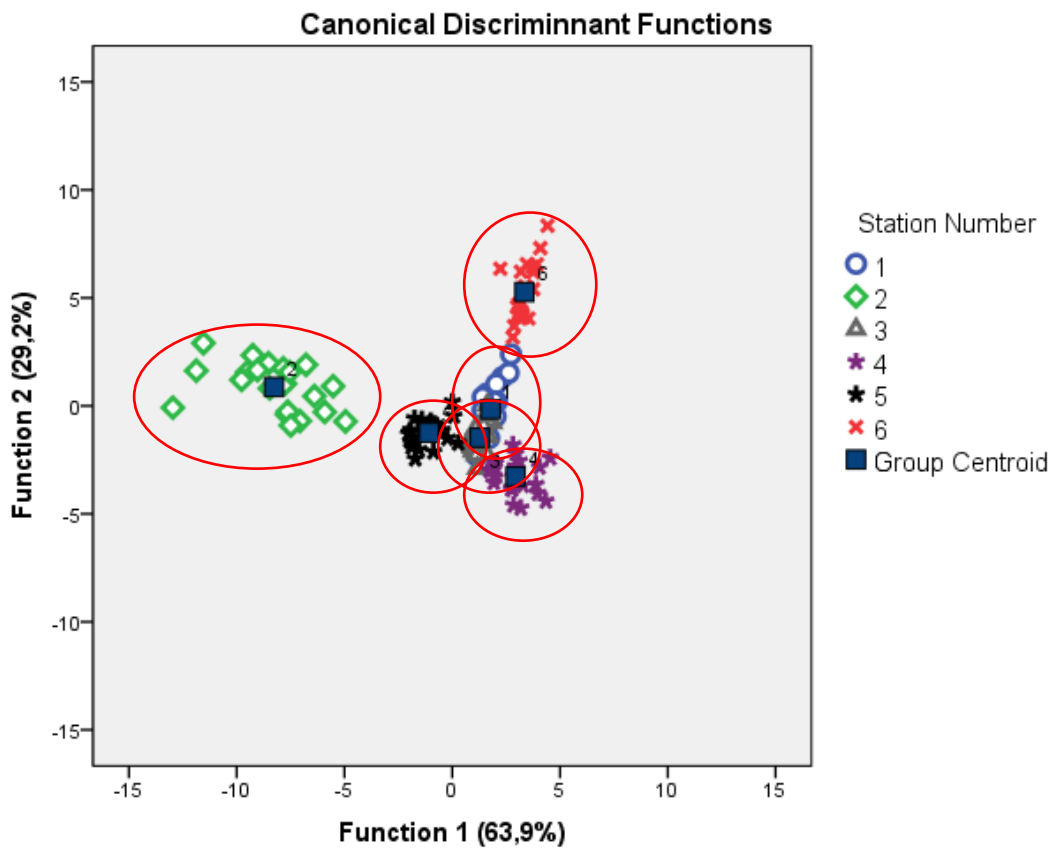
Figure 25. Centroids obtained from the cluster analysis of the climatic parameters.

Factor	Dependent Variable	F	Sig.
Station	T Max	5,717	,000
	T Min	9,235	,000
	T Med	1,615	,162
	Rainfall	,631	,677
	Excursion	58,455	,000
	GDD	1,783	,122
Year	T Max	2,759	,068
	T Min	1,384	,255
	T Med	2,135	,123
	Rainfall	6,359	,002
	Excursion	9,577	,000
	GDD	2,501	,087
Station * Year	T Max	,048	1,000
	T Min	,058	1,000
	T Med	,048	1,000
	Rainfall	,262	,988
	Excursion	,260	,988
	GDD	,174	,998

Table 7. Test of the effects between subjects (p=<0,05).

		Station Number	Group expected						Totals
			1	2	3	4	5	6	
Cross-validation	**%**	1	66,7	,0	33,3	,0	,0	,0	100,0
		2	,0	95,2	,0	,0	4,8	,0	100,0
		3	23,8	,0	76,2	,0	,0	,0	100,0
		4	,0	,0	4,8	95,2	,0	,0	100,0
		5	,0	,0	9,5	,0	90,5	,0	100,0
		6	,0	,0	,0	,0	,0	100,0	100,0

Table 8. Classification results.
a. Cross validation is done only for those cases in the analysis in cross validation, each case is classified by the functions derived from all cases other than that case.
b. 93,7% of original grouped cases correctly classified.
c. 87,3% of cross-validated grouped cases correctly classified.

3.3 Vineyards's characteristics

The main characteristics of the vineyards are reported as followed according to the denomination.

3.3.1 'Chianti Colline Pisane'

3.3.1.1 'Beconcini' estate

The main component of the soil where the vineyard is situated is the white sand. The other layers that make up these soils are varied, very thin and mostly consist of a series of marine fossils from the Pliocene age and of sandstone. So we can see shells of every size and in quantities such as to constitute, in some cases, the real skeleton of soils and also sands from the finest to the heaviest, arranged in thin layers and very unlike for salinity and fertility as the soil goes downwards. The soils are alkaline.

The vineyards are trained to spur pruned cordon with planting design of 1 meter on the row and 3 meters between rows. With this pruning, every plant presents four spurs with two buds and so, bud load of eight buds.

Figure 26. 'Sangiovese's vineyard in 'Beconcini' estate.

3.3.2.'Montecucco'

3.3.2.1 'ColleMassari' estate

The vineyards of our study are quite homogeneous in terms of conduct, training system, rootstock and age. Only in the case of 'Orto del Prete' vineyard, training system is spur pruned cordon unlike the system used mainly that is the Guyot. All the vineyards have a bud load of 10 buds per plant.

The main crop operations are performed in the same way in all the vineyards and the spontaneous grass cover among rows is used.

'ColleMassari' is conducted according to the organic protocol and then the pest protection is carried out exclusively by the use of copper-based and sulphur-based products according to the limits imposed by law. Shoot thinning is carried out only one time.

The widespread use of summer pruning and mechanic thinning restrict vegetation, which in itself would be very vigorous. Usually the cluster thinning takes place during the first week of September.

'Campo la Mora F9': sloping vineyard of around 15%, with 'rittochino' layout in north-east south-west row orientation and then east- west in the end. The plantation dates from 2003.

Training system: simple Guyot

Clone: clone F9

Rootstock: 161-49 Couderc

Planting design: 2.30 x 0.80 m

Vine density: 5435 vines/ha
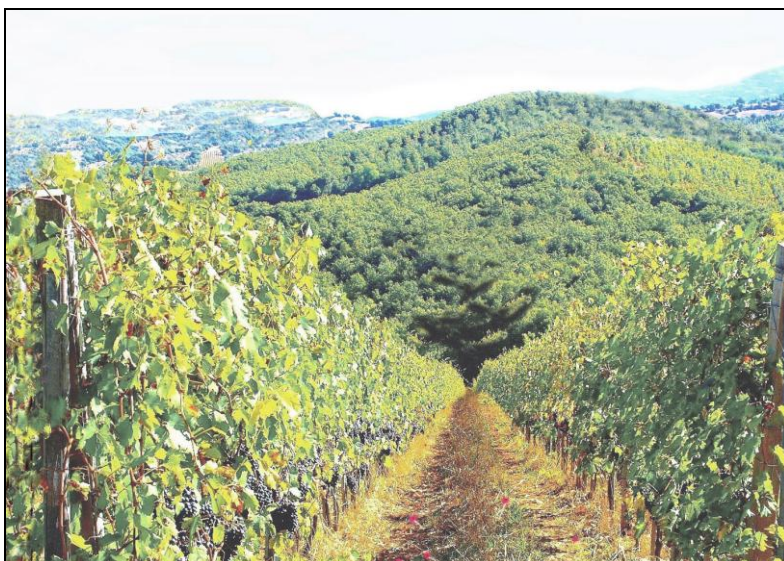
Figure 27. 'Campo la Mora F9' vineyard in 'ColleMassari' estate.

'Campo la Mora Sal.': sloping vineyard of around 15%, with 'rittochino' layout in a north-east south-west row orientation. The plantation dates from 2003.

Training system: simple Guyot

Clone: Salustri selection

Rootstock: 161 - 49 Couderc

Planting design: 2.30 x 0.80 m

Vine density: 5435 vines/ha

Figure 28. 'Campo la Mora Sal.' vineyard in 'ColleMassari' estate.

'Cerrete': sloping vineyard greater than 15%, with 'rittochino' layout and in north-east south-west row orientation. The plantation is the youngest among the six examined vineyards: it planted in 2005

Training system: simple Guyot

Clone: Salustri selection

Rootstock: 110 R.

Planting design: 2.30 x 0.80 m

Vine density: 5435 vines/ha

Figure 29. 'Cerrete' vineyard in 'ColleMassari' estate.

'Orto del Prete': sloping vineyard greater than 15%, with 'rittochino' layout and in east- west row orientation. The plantation dates from 2001.

Training system: spur pruned cordon

Clone: Talenti's selection

Rootstock: 157-11 Couderc

Planting design: 2.30 x 0.80 m

Vine density: 5435 vines/ha

Figure 30. 'Orto del Prete' vineyard in 'ColleMassari' estate.

'Vigna Vecchia': sloping vineyard with 'rittochino' layout and in north - south row orientation. The plantation dates from 2001 planting out five Sangiovese's selections.

Training system: simple Guyot

Clone: Col D'Orcia n°5 selectioned clones

Rootstock: 775 P

Planting design: 2.30 x 0.80 m

Vine density: 5435 vines/ha

Figure 31. Vigna Vecchia vineyard in ColleMassari estate.

3.3.2.2 'Salustri' estate

The farm is conducted according to the organic protocol. The ground belongs to those who present the surface layer from 0 to 30/40 cm, yellowish brown, dry, without any mottling, with small, common, scarce and medium pores. Besides it is neither very adhesive nor plastic, with sandy texture, frequent skeleton, devoid of concretions, non-calcareous with pH of 6,8.

The organic fraction of the soil is very low; thus microbial activity, physical structural characteristics and chemical fertility are adversely affected. The contribution of organic substance is therefore necessary. The cationic exchange capacity (C.E.C.) is average; the amount of nutrients kept in cationic form is good. Total nitrogen appears to be low; his contribution to nitrogenous nutrition of crop is modest. The phosphorus level is medium while the calcium level is low, as well compared with C.E.C.

The vineyard was established with a 'Sangiovese Salustri' selection at 0,8 meter on the row and 2,3 meters between rows (5700 vines/ha), trained to Guyot with 8 buds per plant.

Figure 32. Sangiovese's vineyard in 'Salustri' estate.

3.3.3 'Morellino di Scansano'

3.3.3.1 'Fattoria di Magliano estate'

The soil where the vineyard is situated has a moderately rich texture of skeleton and it is calcareous. Is situated at 150 m above sea level, in a south-west row orientation.

The pH of the soil is alkaline.

The vineyards in our study are trained to unilateral spur pruned cordon with planting design of 0,8 meter on the row and 2,2 meters between rows vines are hedged at 0,8 m in height. The average yield is 1 kg/vine.

Figure 33. Sangiovese's vineyard in 'Fattoria di Magliano' estate.

3.3.4 'Brunello di Montalcino'

3.3.4.1 'Col d'Orcia' estate

The vineyard is placed on a slight slope with 'rittochino' layout and in north - south row orientation. The soil is silty, sandy, alkaline, calcareous reaction with active medium lime, with a low content of organic substance and of potassium but is characterized by high strength of magnesium, and of calcium and medium C.E.C. The vineyard was planted in 2000 with planting design of 0,8 meter on the row and 2,35 meters between rows and 5319 vines/ha is the planting density.

In this vineyard there are five Sangiovese's clones in selection (virus-free) on 420A rootstock, this ensures a limited vigour, even considering the low amount of organic substance and total nitrogen.

The vineyard is trained to spur pruned cordon with four spurs per plant; cluster thinning is used to maintain production within disciplinary levels DOCG 'Brunello di Montalcino' cluster thinning is used.

Figure 34. Sangiovese's vineyard in 'Col D'Orcia' estate.

3.3.4.2 'La Mannella' estate

The vineyards is to the north-east of 'Montalcino', is trained to spur pruned cordon placed at at 0,8 m from the soil with rows in south east row orientation. The planting design is of 0,8 meter along the row and 3 meters between the rows. The 'Sangiovese' clone is R24 grafted on 1103P. The soil is stony and alkaline.

Figure 35. Sangiovese's vineyard in 'La Mannella' estate.

3.3.4.3 'Casanova di Neri' estate

The vineyard is trained to spur pruned cordon and vines are hedged at 0,55 m in height in south east row orientation. The planting design is of 0,8 meter on the row and 2,2 meters between rows. 'Sangiovese' is a mass selection grafted on 110R. The soil has a medium consistence and it is rich in stones.

Figure 36. Sangiovese's vineyard in 'Casanova di Neri' estate.

3.3.5 'Chianti Classico'

3.3.5.1 'Castello di Albola' estate

The vineyard with an east exposure, located in the hills, is placed at an altitude of 550 meters. The planting design is of 0,80 meter on the row and 2,50 meters between rows and 5000 vines/ha is the planting density.

'Albola's soils are characterized by the presence of pedological formations of limestone-marly nature and partly calcareous-clayey. Morphologically the rock comes from austro-alpine domain, with a place in the 'series of marly limestone'.

Figure 37. Sangiovese's vineyard in 'Castello di Albola' estate.

3.3.5.2 'Capannelle' estate

The vineyard is collocated on calcareous rocks and it is characterized by rich stones, of similar origin to the soil of 'Albola' estate, rows wirh east-west orientation. Vines are trained to horizontal spur cordon placed at 0,6 m from the ground. At distance of 0,8 x 2,5 m (5000 vine/ha).

Figure 38. Sangiovese's vineyard in 'Capannelle' estate.

3.4 Soil's characteristics

By cluster analysis of the chemical and physical characteristics of the experimental soils (tab. 10) it was possible to obtain dendrograms where it was possible to see theses (tab. 9) with similar pedologic conditions.

Thesis	Code	Vineyard	Estate	N° denomination	Denomination
1	CCP 1	Beconcini	Beconcini	1	Chianti Colline Pisane
2	MC 1	CM F9	ColleMassari	2	Montecucco
3	MC 2	CM Sal	ColleMassari	2	Montecucco
4	MC 3	Cer	ColleMassari	2	Montecucco
5	MC 4	O_P	ColleMassari	2	Montecucco
6	MC 5	V_Vec	ColleMassari	2	Montecucco
7	MC 6	S_Marta	Salustri	2	Montecucco
8	SC 1	Magliano	Magliano	3	Morellino Scansano
9	BM 1_5	CL 1	Col D'Orcia	4	Brunello di Montalcino
14	BM 6	Casanova	Casanova di Neri	4	Brunello di Montalcino
15	BM 7	La Mannella	La Mannella	4	Brunello di Montalcino
16	CC 1	Capannelle	Capannelle	5	Chianti Classico
17	CC 2	Albola	Albola	5	Chianti Classico

Table 9. Prospect of vineyards chosen for the statistical analysis of the soil.

Parameter	M.U.
pH	
Sand	%
Silt	%
Clay	%
Total limestone	%
Active limestone	%
Cation exange capacity	meq/100g
Electrical conducity	dS/m
Total nitrogen	g/Kg
Organic substance	%
P_2O_5	ppm
CaO	ppm
MgO	ppm
K_2O	ppm

Table 10. Prospect of parameters chosen for the statistical analysis of the soil.

Code	Sand	Silt	Clay	pH	Electrical conductivity	Cationic exange capacity	Organic matter
CCP 1	28,0	44,0	28,0	8,50	0,11	14,50	0,97
MC 1	49,0	26,0	25,0	7,90	0,16	17,40	1,46
MC 2	49,0	26,0	25,0	7,90	0,16	17,40	1,46
MC 3	37,0	36,0	27,0	7,80	0,45	14,60	1,12
MC 4	58,0	22,5	19,5	7,90	0,15	13,40	1,17
MC 6	67,0	19,0	14,0	7,90	0,13	9,47	0,88
MC 7	70,0	20,0	10,0	6,80	0,07	15,40	1,20
SC 1	29,0	39,0	32,0	8,30	0,14	14,60	2,30
BM 1_5	14,0	60,0	26,0	8,30	0,13	15,66	0,27
BM 6	42,4	21,6	36,0	8,15	0,44	18,80	0,53
BM 7	57,0	20,0	23,0	8,41	0,30	18,40	1,29
CC 1	61,7	21,3	17,0	8,40	0,13	16,20	1,22
CC 2	49,6	23,0	27,4	8,40	0,13	25,30	1,36

Table 11. Physical characteristics of the experimental soils.

Code	Total limestone	Active limestone	Tot. nitrogen	P_2O_5	CaO	Mg0	$K_2$0
CCP 1	21,00	14,50	0,06	10,80	3150	132	70
MC 1	5,90	1,90	0,09	4,00	3050	130	125
MC 2	5,90	1,90	0,09	4,00	3050	130	125
MC 3	39,70	8,00	0,07	5,00	2600	130	100
MC 4	0,22	2,85	0,05	4,50	2350	110	108
MC 6	23,50	3,80	0,06	5,00	1650	90	91
MC 7	0,70	0,10	0,10	21,50	1.684	490	181
SC 1	31,00	14,60	0,20	18,00	3650	320	141
BM 1_5	34,80	0,14	0,03	4,00	3400	185	90
BM 6	0,50	0,10	0,07	5,00	3212	1.135	324
BM 7	19,50	3,80	0,09	9,00	4796	181	98
CC 1	9,24	2,39	0,02	5,00	2760	161	410
CC 2	8,30	4,75	0,09	5,50	2930	154	322

Table 12. Chemical characteristics of the experimental soils.

```
Dendrogram using Average Linkage (Between Groups)
                     Rescaled Distance Cluster Combine
     C A S E       0         5        10        15        20        25
     Label   Num   +---------+---------+---------+---------+---------+

     MC  1     2    ─┐
     MC  2     3    ─┤
     CC  2    13    ─┤
     MC  4     5    ─┤
     BM  7    11    ─┤
     CC  1    12    ─┘
     BM  6    10    ──────
     MC  6     6    ─┐
     MC  7     7    ─┘
     CCP 1     1    ─┐
     SC  1     8    ─┤
     MC  3     4    ─┘
     BM  1_5   9    ────────
```
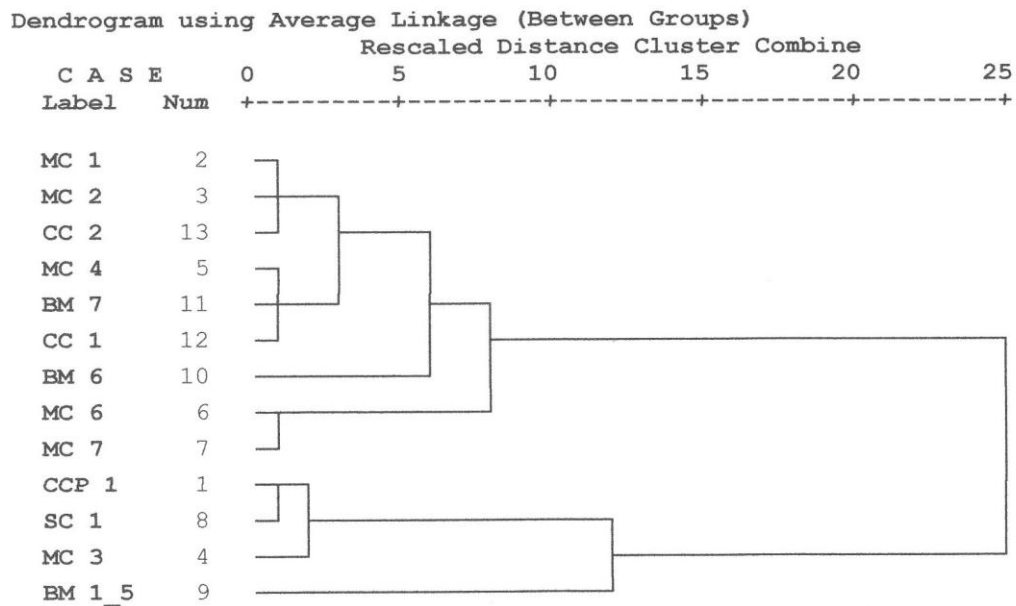
Figure 39. Dendrogram obtained from the texture analysis of the soils.

The dendrogram obtained from the texture analysis (fig. 39) showed that the soils were included into two large groups, in which we find in the first nine soils with a prevailing sandy composition, while in the second one mostly silty soils (4 vineyards).

```
Dendrogram using Average Linkage (Between Groups)
                     Rescaled Distance Cluster Combine
     C A S E       0         5        10        15        20        25
     Label   Num   +---------+---------+---------+---------+---------+

     MC  1     4    ─┐
     MC  2     5    ─┤
     CCP 1     1    ─┤
     CC  1    12    ─┤
     CC  2    13    ─┤
     MC  3     3    ─┤
     MC  4     6    ─┘
     SC  1     8    ─┐
     BM  1_5   9    ─┤
     BM  6    10    ──┤
     MC  6     2    ─┐
     MC  7     7    ─┘
     BM  7    11    ────────
```
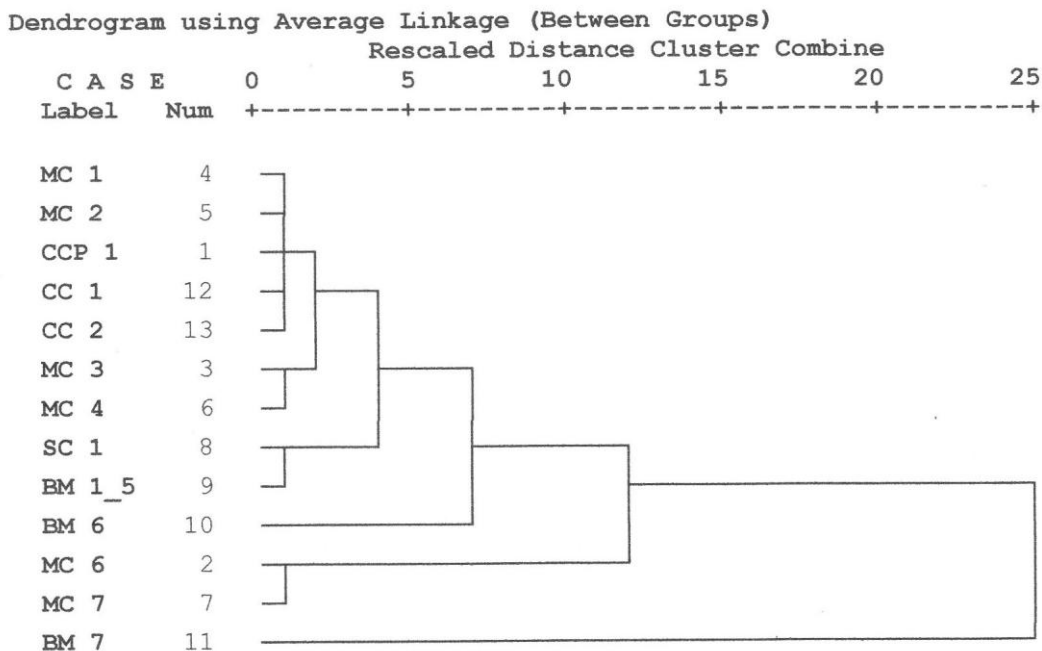
Figure 40. Dendrogram obtained from the physical and chemical analysis of the soils.

Examining chemical and physical characteristics of the soils was obtained the second dendrogram (fig. 40).

The soil of the vineyard located in the 'Chianti Colline Pisane' is a sandy, alkaline, calcareous soil, poor in organic matter and potassium, with a mean amount of magnesium and phosphorus (tab. 11-12).

The soils of the vineyards of 'Montecucco' area have several differences between them, so as they can be grouped into three clusters (tab. 11-12).

In the first one MC1 and MC 2, almost identical, are characterized by prevalence of sand, sub-acid pH, moderate presence of limestone, low organic substance, and average potassium, magnesium and exchange cation capacity. The MC3 and MC 4 even though appear in the same cluster have some differences, for example the MC4 has greater content of sand while the MC3 has equal proportions of sand, silt and clay. Different is the amount of total limestone but not the active limestone which is low, in addition pH, organic matter and the macro elements are at low or medium similar levels in both vineyards.

The third cluster is composed by MC5 and MC6 which have in common the high percentage of sand and the low amount of clay. The MC5 soil has a slight range of active lime and a low content of all the other elements. Soil of the vineyard MC6 has a lower pH, almost no limestone, low organic substance and available nitrogen, meanwhile it has a good amount in phosphorus, magnesium and potassium content.

The two vineyards located in the 'Chianti Classico' belong to the same cluster although are characterized by medium to high content of sand, medium silt and variable amount of clay. Both soils are alkaline, moderately rich in active limestone, organic substance and mineral elements (tab. 11-12).

The soil of the vineyard of 'Magliano' has some similarities to one of the 'Brunello di Montalcino' (BM1_5) vineyard ('Col D'Orcia' estate), for the prevalence of silty particles, the same alkaline pH and quantity of active limestone, while the soil of 'Magliano' estate is rich in organic matter and well provided by all the other elements, while the BM1_5, is poor of organic matter and by the other macro elements (tab. 11-12).

The soil of the other two vineyards of the 'Montalcino' area are very different, in particular BM6 ('Casanova di Neri') is clay-sandy, poor in organic matter and phosphorus, while is rich in potassium and showed an excess of magnesium. The soil of BM7 wich has a prevalence of sand, is calcareous and rich in magnesium and poor in potassium.

3.5 The study of geopedologic, orographic and viticultural aspects: the ColleMassari estate

As for data on soils (www.soilmaps.it) bibliographic data (Costantini et al.; 2006) and current database was used as well as specific analyses conducted on the soils of the specific territory. In depth study was carried out in the DOC 'Montecucco' area where six vineyards from the same wine farm were chosen, from which data on the geopedologic characteristics of the soils were obtained from a previous study (Lizio 1999).

In this case the chemical-physical characteristics of the soil, were obtained from soil samples analyzed in a special laboratory using methods approved by the 'Società Italiana di Scienza del Suolo'. The geopedologic study refers to the land in the 'ColleMassari' area, in the town of 'Cinigiano' (Gr) on a surface area of around 200 ha, where the six vineyards in question are located. A general geological and geopedologic survey was carried out first. A study on the soil type was carried out following the geological study of the area, using where possible a manual drill to the depth of 80-100 cm, as often there were strata of compact pebbles and clays. The limits between different soils are never clearly defined but the passage always occurs through transition forms. The open profiles have been marked on the topographic map to the scale of 1:5000, by enlarging the topographic base to the scale of 1:25.000 of the IGM. During this geopedologic survey the World Reference Base for Soil Resources (WRB) was used, which has led to the adoption of an innovative soil classification, already codified and used internationally for geopedologic surveys. This type of classification regards the functional characteristics of the soil as important without systematically subordinating it to climatic data which obviously must be part of the interpretative aims of a project of zoning but not necessarily be part of the geopedological definition of the interpretative model of the soil examined and least of all subordinating it (Costantini and Lizio, 1996). The observations transcriptions in the world soil classification (WRB) of the Fao, the last version of which was published in 2001, conforms to the geoviticulture (Vaudour E., 2005) prospective. The analysed data is always reinterpreted in the light of those modifying processes that occur on the soil, therefore, it would be good practice to inspect the soils in different periods of the year, as was done in this study. Studying the soil also means placing it in relation with the landscape in which it is found so as to understand how the pedogenesis factors act, ie. the climatic, biological, anthropical and geomorphologic processes occur on the territory (Costantini and Lizio, 1996).

For a better understanding of the pedologic data there is a list of suffixes used to describe the soil strata that for the most part traces the indications given by the 'Chiavi della Soil Taxonomy ed.1992'.

STRATA Ap: mineral strata that form on the surfaces interested by agricultural work (trenching – ploughing).

STRATA B: strata that form below strata Ap and that are well structured .

HORIZON or STRATA C: strata that are not so influenced by pedogenetic processes and lack the characteristics of strata Ap and B, but are made of hard rock.

HORIZON or STRATI R: presence of hard rock and impenetrable from the plant roots, the rock is not possible to dig out with a spade.

Suffix of the horizons:

g (gley) hydromorphia linked to the drainage limitations in the soils, or to a saturation of the horizons with stagnating water;

w (weathering) used to draw an alteration horizon B in which materials of soil origin are differentiated by colour, structure or both;

t horizon of alluvial clay cumulus;

k horizon of calcium carbonate cumulus;

r (rock) symbol used to characterize the horizons C, made of soft rock, partially cemented; in any case materials that can be dug up with a spade, but cannot be penetrated from the plant roots save through their fractures;

n exchangeable sodium cumulus.;

AWC (usable water): differences between field capacity and withering point.

Water reserve classes (A, W, C in mm):

Very high> 200 mm;

High 150-200 mm;

Moderate 100-150 mm;

Low 50-100 mm;

Very low < 50mm

In particular for this wine farm the study was carried out on soils from 4 specific vineyards that are identified and described in the units they belong to. Their physical characteristics have been determined by studying soil conduits, both by manual drill and by opening pedologic profile, with samples per soil strata (Lizio, 1999).

3.5.1 'Campo La Mora'

The soil where the vineyard is located falls within the cartographic unit called 'Unità Bocca Nera' which occupies the moderate convex slopes , with excessive internal drainage.

Lithology: Polygenic conglomerates of the Messinian sup.. The substrata is made up of pebbles and sand with areas where the pebble concentration prevails on the sandy part. The soils present a sequence Ap/C, are moderately deep with a skeleton of 35% to 40%.

The horizon from 0 to 40 cm light yellowy brown in colour has a structure that tends to be loose; an open sandy clayey texture, abundant skeleton, limestone, pH 7,9 ,a horizon from 40 to 110 cm pale brown in colour, bulky, open texture abundant skeleton; high in limestone and pH 8,1. The organic substance is low and the C.E.C. average on all the pedologic profile (tab. 13).

The apparent density is 1,4 gr/cmc, useful water calculated AWC is 95mm, belonging to the low water reserve (50-100mm). As for taxonomy the soils belong to the Xerorthents typical open skeleton .

Figure 41. Ground's surface of '*Campo la Mora'*.

Figure 42. Soil's profile of '*Campo la Mora'*.

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PHYSICAL AND CHEMICAL ANALYSIS	VALUE		JUDGMENT
Skeletron	Ab.		abundant
Sand	50%		
Silt	32%		
Clay	18%		
pH	8,1		medium alkaline
Electrical conducity	0,118 mS		normal
Total limestone	59,00%		calcareous
Active limestone	7,4		medium
Organic matter	0,14		medium-low
NUTRIENTS ANALYSIS	VALUE		JUDGMENT
Total N	0,02%		medium-low
Assimilable P	4 ppm		medium-low
Assimilable Fe	3 ppm		low
Assimilable Mn	8,2 ppm		medium
Assimilable Cu	0,2 ppm		medium-low
Assimilable Zn	0,3 ppm		medium-low
Soluble Bo	0,26 ppm		medium-low
Exchangeable Ca	1800 ppm		high
Exchangeable Mg	140 ppm		medium
Exchangeable K	80 ppm		low
Exchangeable Na	100 ppm		normal
C.E.C. ANALYSIS	VALUE (meq/100 g)		JUDGMENT
C.E.C.	10,80 meq		medium
Ca	9 meq	83,3%	high
Mg	1,17 meq	10,8%	high
K	0,20 meq	1,9%	low
Na	0,43 meq	4,0%	normal
Basic saturation	100%		high
mg/K ratio (meq/meq)	5,9		high

Table 13. Physical and chemical analysis of the soil of 'Campo la Mora'(profile 40-110 cm).

3.5.2 'Cerrete'

The soils relative to the vineyard of the same name are found between two cartographic units: 'Unità Poggi del Sasso' (fig. 46) and a second unit that represents a vertical discontinuity between 'Unità Colle Massari' and 'Unità Poggio Formicone'. The vineyard is situated on a 'rittochino' slope, the soil at the base of the plot is in the category of soils with discontinuous characteristics inside the 'Colle Massari' unit.

Such soils present probable water slump of contact between the pebbly part and the fine reddish part. Contact situations exist between sediments containing pebbles up to 100/110 cm and bulky reddish sediments.

Therefore there are notable differences between the deep strata and the superficial strata in terms of texture, limestone content and physical - chemical analyses (tab. 14).

PHYSICAL AND CHEMICAL ANALYSIS	VALUE	JUDGMENT
Skeletron	Ma.	marginal
Sand	42%	
Silt	28%	
Clay	30%	
pH	0,3	alkaline
Electrical conducity	0,132 mS	normal
Total limestone	27,50%	calcareous
Active limestone	4,3	low
Organic matter	0,33	medium-low
NUTRIENTS ANALYSIS	VALUE	JUDGMENT
Total N	0,03%	medium-low
Assimilable P	3 ppm	medium-low
Assimilable Fe	4,0 ppm	low
Assimilable Mn	4,6 ppm	medium
Assimilable Cu	0,5 ppm	medium-low
Assimilable Zn	0,3 ppm	medium-low
Soluble Bo	0,20 ppm	medium-low
Exchangeable Ca	2850 ppm	medium-high
Exchangeable Mg	175 ppm	high
Exchangeable K	80 ppm	low
Exchangeable Na	100 ppm	normal

C.E.C. ANALYSIS	VALUE (meq/100 g)		JUDGMENT
C.E.C.	16,34 meq		medium
Ca	14,25meq	87,30%	high
Mg	1,46 meq	8,9%	medium
K	0,20 meq	1,20%	low
Na	0,43meq	2,60%	normal
Basic saturation	100%		high

Table 14. Physical and chemical analysis of the soil of 'Cerrete'(profile 110-170 cm).

The soil upstream the plot falls within the 'Poggi del Sasso' unit (fig. 45) and occupies the sides with the low to moderate slopes badly drained. The substrata is made up of fine sandy silts sediment with calcium carbonate concentrations right up to the surface.

Figure 43. Ground's surface of '*Cerrete'*.

Figure 44.Vertical discontinuity between 'Unità ColleMassari' and 'Unità Poggio Formicone'.

Figure 45. 'Poggi del Sasso' unit..

The soils that fall in this category present a sequence Ap/CBgl/Cg2, are deep soils with a poor skeleton and with obvious signs of hydromorphia. The horizon from 0 to 20/30 cm light olive brown in colour, has an angular structure, moderately developed average, open texture, ordinary skeleton, very chalky, pH 8, modest ordinary small red and grey mottles and small ordinary limestone carbonate concretions. The horizon from 20/30 cm to 70 cm light olive brown in colour, with average angular multifaceted structure, moderately developed, poor skeleton, very calcareous, with pH 8,5, clear ordinary small red and grey mottles and small ordinary limestone carbonate concretions. The horizon from 70 to 120 cm grey brown in colour, lacking in structure and massive, open clayey texture, no skeleton, very calcareous, with pH8, clear, ordinary small red and grey mottles, sodium content slightly high. The organic matter is generally very low, average C.E.C., on all the pedologic profile. The apparent density is 1,35 g/cmc for the superficial horizon, 1,3 g/cmc for the horizon below, 1,4 g/cmc for the third horizon; useful water calculated AWC is 168 mm, belonging to the high water reserve class (150-200 mm).

The taxonomy of the soils belong to the Aquic Xerorthens, open fine on fine clay with soda clay.

Observations: as can be seen from the analysis the texture goes from sandy for the top soil to clay silt for the sub soil, here too the depth increases electric conductibility associated to high sodium content both in absolute value and in relation to C.E.C. .This is a soil characteristic of the 'Poggi del Sasso' that presents a finer texture than the other soils in the wine farm with a presence of sodium in the sub soil associated to a higher clay content and to clear hydromorphy, sign of imperfect drainage .

3.5.3 'Orto del prete'

The vineyard is located in a transition area between two cartographic units: 'Unità Colle Massari' and slight variation from the' Colle Massari' and 'Bocca Nera' units.

'Colle Massari' occupies the steep slopes, with excessive internal drainage .

Lithology: Polygenic Messinian sup. conglomerates.

The substrata is made up of pebbles in sandy soil with areas in which the pebbly part prevails on the fine sand, abundant presence of pebbles right from the surface. Such soils belong to the category of soils that have a sequence Ac/C/Cr, moderately deep with a rich skeleton from 35% to 40%.

The horizon from 0 to 30/40 cm yellowy brown in colour , presents a structure that tends to be loose, sandy texture, rich skeleton, very chalky with pH 7,9, the horizon 30/40 cm to 70/80 cm pale brown in colour, bulky, sandy franco texture, rich skeleton, with a pH 8,1; the strata from 70/80 cm to 110 cm is very pebbly with thin layers of chalky sand.

The organic substance is very low and low C.E.C., on all the pedologic profile.

The nutrients analyses show a low quota of macro elements nitrogen, phosphorous and potassium as well as inadequate secondary macro elements and microelements.

The apparent density is 1,4 gr/cmc, useful water calculated AWC is 72 mm, belonging to low water reserve class (50-100 mm).

Regarding taxonomy the soils belong to Xerorthents typical sandy skeleton.

The 'Bocca Nera' unit occupies the convex moderately steep slopes, with excessive internal drainage.

Lithology: Messiniano sup. Polygenic conglomerates.

The substrata is made up of pebbles in sandy soils with areas in which the pebbly part prevails on the fine sand. The soils have a sequence Ap/C are moderately deep soils with rich skeleton from 35% to 40%.

The horizon from 0 to 40 cm light yellowy brown in colour has a structure that tends to be loose, a clayey sandy texture, rich skeleton, chalky at pH 7,9, the horizon from 40cm to 110 cm pale brown in colour, bulky, with texture, rich skeleton, very chalky with pH 8,1 (tab. 15). low organic matter and average C.E.C., on all the pedologic profile.

The apparent density is 1,4 gr/cmc, useful water calculated AWC is 95 mm, belonging to the low water reserve class (50-100 mm).

As for taxonomy the soils belong to the Xerorthents typical skeleton.

Observation: for the soil that hosts the vineyard 'Orto del Prete' the same is valid as for 'Campo la Mora' and for 'Vigna Vecchia' in as much as the two cartographic units intersect to which the soils of these two theses belong.

PHYSICAL AND CHEMICAL ANALYSIS	VALUE	JUDGMENT
Skeletron	Ab.	abundant
Sand	50%	
Silt	32%	
Clay	18%	
pH	8,1	medium alkaline
Electrical conducity	0,118 mS	normal
Total limestone	59,00%	calcareous
Active limestone	7,4	medium
Organic matter	0,14	medium-low
NUTRIENTS ANALYSIS	VALUE	JUDGMENT
Total N	0,02%	medium-low
Assimilable P	4 ppm	medium-low
Assimilable Fe	3 ppm	low
Assimilable Mn	8,2 ppm	medium
Assimilable Cu	0,2 ppm	medium-low
Assimilable Zn	0,3 ppm	medium-low
Soluble Bo	0,26 ppm	medium-low
Exchangeable Ca	1800 ppm	high
Exchangeable Mg	140 ppm	medium
Exchangeable K	80 ppm	low
Exchangeable Na	100 ppm	normal

C.E.C. ANALYSIS	VALUE (meq/100 g)		JUDGMENT
C.E.C.	10,80 meq		medium
Ca	9 meq	83,3%	high
Mg	1,17 meq	10,8%	high
K	0,20 meq	1,9%	low
Na	0,43 meq	4,0%	normal
Basic saturation	100%		high

Table 15. Physical and chemical analysis of the soil of 'Orto del Prete'(profile 0-120 cm).

Figures 46-47. Ground's surface and soil's profile of '*Orto del Prete'*.

3.5.4 'Vigna Vecchia'

The land on which the vineyard is located falls within the cartographic unit called 'Unità Colle Massari' which occupies the very steep slopes, with excessive internal drainage.

Lithology: Messinian sup. Polygenic conglomerates. The substrata is made up of pebbles in sandy soils with areas in which the pebbly part prevails on the fine sand, abundant presence of pebbles right from the surface. Such soils belong to the category that have a sequence Ac/C/Cr, moderately deep with rich skeleton from 35% to 40%.

The horizon from 0 to30/40 cm yellowy brown in color , has a structure that tends to be loose, a sandy texture, rich skeleton, very chalky at pH 7,9, the horizon from 30/40 cm to 70/80 cm pale brown in colour, bulky, with sandy texture, rich skeleton, very chalky with pH 8,1, the strata from 70/80 cm to 110 cm is characterized abundant pebbles with thin layers of chalky sand.

The organic matter and C.E.C. are low, on all the pedologic profile.

The nutrients analyses moreover show a deficit in macro elements, nitrogen, phosphorous and potassium as well as inadequate secondary macro elements and microelements (tab. 16).

The apparent density is 1,4 gr/cmc, useful water calculated AWC is 72 mm, belonging to the low water reserve class (50-100 mm).

As for taxonomy the soils belong to the Xerorthents skeleton.

Figure 48. Ground's surface of '*Vigna Vecchia*'.

Figure 49. Soil's profile of '*Vigna Vecchia'*.

PHYSICAL AND CHEMICAL ANALYSIS	VALUE		JUDGMENT
Skeletron	Ab.		abundant
Sand	67%		
Silt	19%		
Clay	14%		
pH	7,9		sub alkaline
Electrical conducity	0,133 mS		normal
Total limestone	23,50%		calcareous
Active limestone	3,8		medium
Organic matter	0,88		medium-low
NUTRIENTS ANALYSIS	**VALUE**		**JUDGMENT**
Total N	0,06%		low
Assimilable P	5 ppm		medium-low
Assimilable Fe	3,2 ppm		low
Assimilable Mn	15,6 ppm		medium
Assimilable Cu	3,6 ppm		medium
Assimilable Zn	0,4 ppm		medium-low
Soluble Bo	0,42 ppm		low
Exchangeable Ca	1650 ppm		high
Exchangeable Mg	90 ppm		low
Exchangeable K	91 ppm		low
Exchangeable Na	55 ppm		normal
C.E.C. ANALYSIS	**VALUE (meq/100 g)**		**JUDGMENT**
C.E.C.	9,47 meq		low
Ca	5,25 meq	87,2%	high
Mg	0,75 meq	7,9%	medium
K	0,23 meq	2,4%	medium
Na	0,24 meq	2,5%	normal
Basic saturation	100%		high
mg/K ratio (meq/meq)	3,3		medium

Table 16. Physical and chemical analysis of the soil of 'Vigna Vecchia'(profile 0-30/40cm).
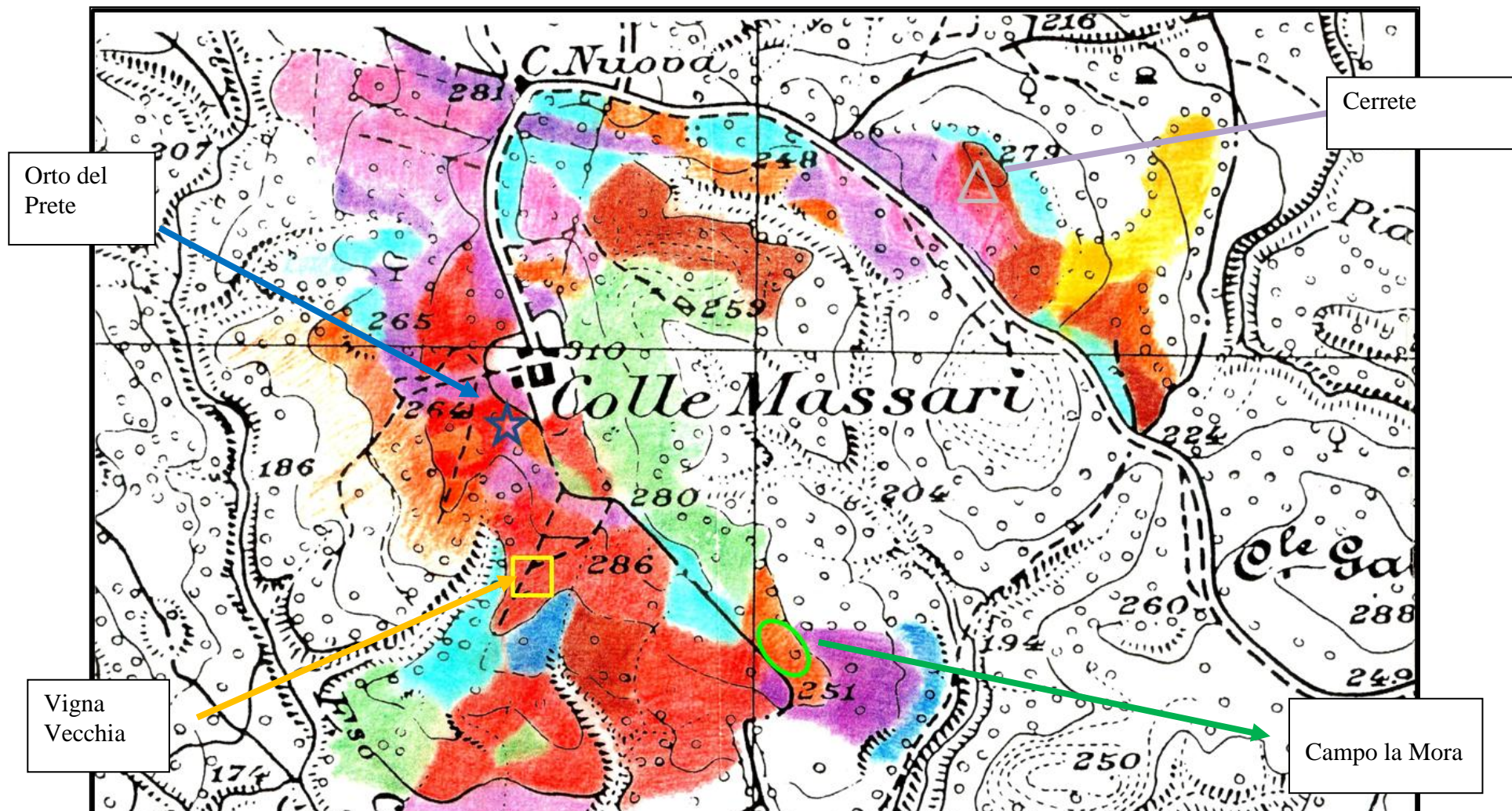
Figure 50. Geopedologic card scale 1:5000; vineyard *Campo la mora* (◯), *Vigna Vecchia* (▢), *Orto del Prete* (☆), *Cerrete* (△)

3.6 Harvest date
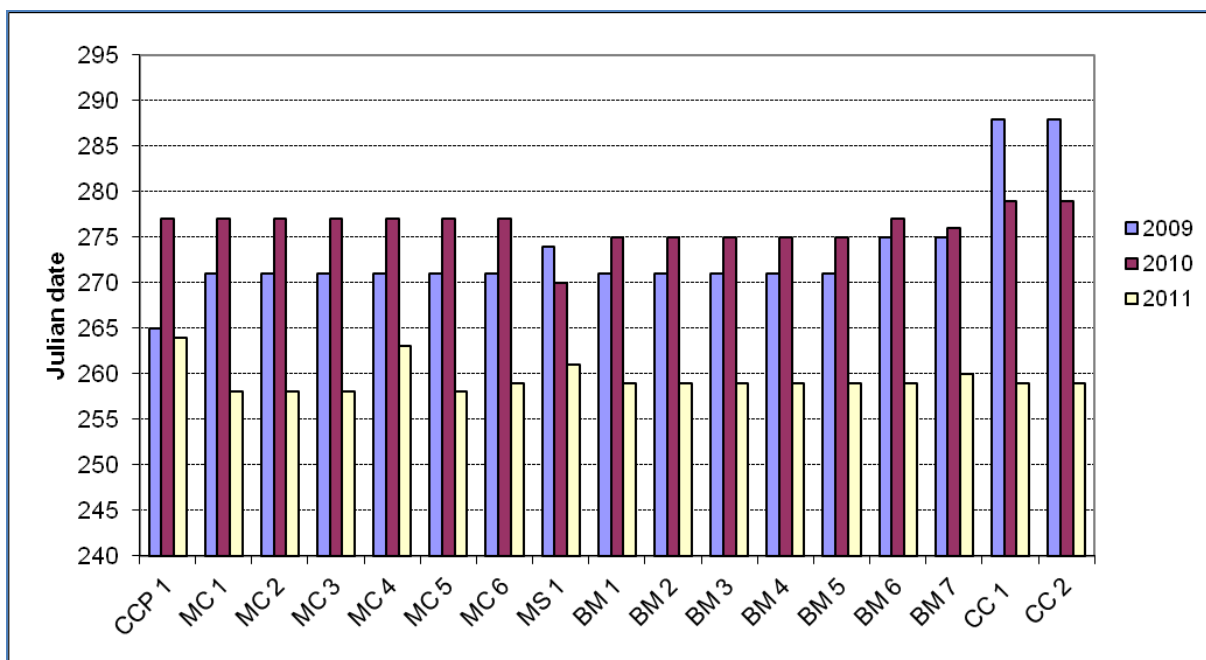
Figure 51. Harvest date: comparison among 2009, 2010 and 2011 seasons.

Harvest time is set between the second half of September and the second half of October. For the year 2009, the first area harvested was the 'Chianti' from the 'Colline Pisane', while the last was the 'Chianti Classico'. Among the theses within the same production areas harvesting time differs only a few days. The year 2010 recorded lower average temperatures compared to the year before and this justifies the delay in harvesting in most of the thesis analysed, exception made for the 'Morellino di Scansano' Denomination and for the two belonging to the 'Chianti Classico', where it was necessary to delay the harvesting even more. Only the bunches from the producer 'Fattoria di Magliano' were picked in September and not in October as in the case of the others. Early harvesting on the other hand, in all the farms in the year 2011 was completed by the 20th September. Such a result was no surprise because the year 2011 was hotter in the period from April to end of October and therefore with a greater cumulus of Growing Degree Days in all the areas. The bunches belonging to the 'Chianti Colline Pisane' denomination were harvested last while two years before they had been the first to be harvested (fig. 51).

3.7 Sensorial characteristics of the grapes at harvest's time

The MANOVA was conducted by examining the parameters linked to the sensorial analysis of the grapes (tab. 17) at harvest's time harvested (using the values of three repeated analysis of 17 theses each year for three years), studying the importance of the variables in function of the chosen factor (tab. 18).

The real numeric values expressed by the panel were convert into percentages values relative to the maximum value of 4.

Variable	Abbreviation	Units
Berry colour	Ber. Col.	s
Skin texture	Skin text.	s
Skin astringency	Skin astr.	s
Skin bitterness	Skin bit.	s
Skin aroma	Skin aro.	s
Skin maturity	Skin mat.	s
Pulp separation	Pulp sep.	s
Pulp acidity	Pulp acid.	s
Pulp swetness	Pulp swe.	s
Pulp aroma	Pulp aro.	s
Pulp maturity	Pulp mat.	s
Seed colour	Seed col.	s
Seed hardness	Seed har.	s
Seed bitterness	Seed bit.	s
Seed astringency	Seed astr.	s
Seed aroma	Seed aro.	s
Seed maturity	Seed mat.	s
Berry aroma	Berry aro.	s
Berry sensorial maturity*	B.S.M.	s

* Berry sensorial maturity was calculated by summing skin's, pulp's and seed's maturity

Table 17. List of abbreviations.

Factor	Dependent variable	F	Sig.
Thesis	Berry colour	25,727	,000
	Pulp separation	16,794	,000
	Pulp sweetness	8,436	,000
	Pulp acidity	4,875	,000
	Pulp aroma	7,100	,000
	Skin texture	11,149	,000
	Skin astringency	17,699	,000
	Skin aroma	7,943	,000
	Skin bitterness	10,120	,000
	Seed colour	9,094	,000
	Seed hardness	3,769	,000
	Seed bitterness	13,893	,000
	Seed astringency	6,431	,000
	Seed aroma	7,427	,000
	Pulp maturity	4,068	,000
	Skin maturity	9,189	,000
	Seed maturity	3,116	,000
	Berry aroma	2,277	,007
	Berry sensorial maturity	1,554	,096

Factor	Dependent variable	F	Sig.
Year	Berry colour	1,577	,212
	Pulp separation	93,822	,000
	Pulp sweetness	10,396	,000
	Pulp acidity	18,280	,000
	Pulp aroma	8,826	,000
	Skin texture	17,695	,000
	Skin astringency	8,107	,001
	Skin aroma	16,785	,000
	Skin bitterness	16,453	,000
	Seed colour	11,740	,000
	Seed hardness	58,463	,000
	Seed bitterness	94,802	,000
	Seed astringency	103,532	,000
	Seed aroma	126,072	,000
	Pulp maturity	14,343	,000
	Skin maturity	13,660	,000
	Seed maturity	62,480	,000
	Berry aroma	26,456	,000
	Berry sensorial maturity	12,986	,000

Factor	Dependent variable	F	Sig.
Thesis * Year	Berry colour	16,377	,000
	Pulp separation	16,247	,000
	Pulp sweetness	3,226	,000
	Pulp acidity	3,333	,000
	Pulp aroma	2,558	,000
	Skin texture	8,494	,000
	Skin astringency	12,496	,000
	Skin aroma	8,793	,000
	Skin bitterness	17,168	,000
	Seed colour	6,305	,000
	Seed hardness	10,468	,000
	Seed bitterness	11,994	,000
	Seed astringency	10,992	,000
	Seed aroma	9,597	,000
	Pulp maturity	2,194	,002
	Skin maturity	9,045	,000
	Seed maturity	6,042	,000
	Berry aroma	3,431	,000
	Berry sensorial maturity	2,315	,001

Table 18 a, b, c. Test of the effects between subjects. (p=<0,05).

All the dependant variables proved to be statistically significant, bar the parameter indicated with berry sensorial maturity linked to the sum of skin's, pulp's and seed's maturity. Such variables do not change their level of significance if, the factor chosen during the statistical analysis, is that of the thesis or the year or interaction between the two. However choosing the year, a non significant statistical variable, the colour of the berry is added (tab. 18).

By using the data previously obtained the level of variability attributable to the different factor was calculated (tab. 19). For most of the parameters the variability is attributable to the year; the thesis, however, shows more variability as concerns berry colour and skin astringency. Skin bitterness shows comparable levels of variability attributable to the different source; most likely this is due to the difficulty in judging the sensation of bitterness.

Variable	% variability due to the thesis	% variability due to the year	% variability due to interaction thesis/year	% variability due to error
Berry colour	57,58	3,53	36,65	2,24
Pulp separation	13,13	73,38	12,71	0,78
Pulp sweetness	36,59	45,09	13,99	4,34
Pulp acidity	17,74	66,50	12,13	3,64
Pulp aroma	36,44	45,30	13,13	5,13
Skin texture	29,08	46,15	22,16	2,61
Skin astringency	45,03	20,63	31,79	2,54
Skin aroma	23,01	48,62	25,47	2,90
Skin bitterness	22,62	36,77	38,37	2,24
Seed colour	32,32	41,72	22,41	3,55
Seed hardness	5,11	79,33	14,20	1,36
Seed bitterness	11,42	77,91	9,86	0,82
Seed astringency	5,27	84,89	9,01	0,82
Seed aroma	5,15	87,49	6,66	0,69
Pulp maturity	18,83	66,39	10,15	4,63
Skin maturity	27,94	41,53	27,50	3,04
Seed maturity	4,29	86,02	8,32	1,38
Berry aroma	6,87	79,77	10,35	3,02
Berry sensorial maturity	8,70	72,73	12,97	5,60

Table 19. Level of variability attributable to the different factor.

From Tukey's statistic test it is possible to note the table with the different subsets and those non differentiated; the most of significant variables creates differentiated homogenous subsets, except for berry's aroma and sensorial maturity (tab. 20-22).

Regarding the sensorial maturity the values shown are the highest in one thesis of the 'Chianti Classico' area and the lowest in the one of 'Morellino di Scansano' that is the thesis with less difference as maturity level among the different parts of the berry (tab. 20). In general, optimal value of sensory maturity are present in Siena's province; this area shows greater variability in its theses if compared to Grosseto (tab. 20).

Grapes coming from 'Chianti Colline Pisane' are characterized by differences among maturation's level of the three parts of the berry; the skin appears more mature than seeds on the contrary, seeds appear more mature than skin in one thesis belongs to the 'Brunello di Montalcino'.

Analysing pulp's maturity, the lowest value belongs to the 'Morellino di Scansano' thesis while the highest to a 'Brunello di Montalcino' thesis (tab. 20).

Regarding skin's maturity the highest value is found in one thesis of the 'Brunello di Montalcino' while the lowest value in 'Morellino di Scansano' thesis already noted (tab. 21). The values obtained from the analysis of seed's maturity indicate the lowest value in one thesis of the 'Chianti Colline Pisane' and the highest in one thesis of the 'Chianti Classico' (tab. 22).

Code	Berry colour	Berry aroma	Berry sensorial maturity	Pulp separation	Pulp sweetness	Pulp acidity	Pulp aroma	Pulp maturity
CCP 1	93,06 bc	81,93 a	81,41 a	83,60 ab	88,9 b-e	84,73 a-d	83,89 a-e	85,15 ab
MC 1	98,61 ef	86,12 a	83,56 a	92,89 ef	93,12 de	84,73 a-d	92,28 ef	90,60 b
MC 2	99,33 f	81,93 a	83,62 a	90,35 c-f	94,79 e	86,40 cde	93,96 f	91,23 b
MC 3	99,33 f	79,13 a	83,28 a	92,04 def	91,4cde	87,24 cde	90,60 b-f	90,18ab
MC 4	96,23 c-f	79,41 a	84,24 a	86,98 a-d	92,2cde	83,89 a-d	88,08 b-f	87,66 ab
MC 5	98,75 ef	84,73 a	83,03 a	93,07 f	93,95 e	88,92 de	92,28 ef	92,07 b
MC 6	99,33 f	84,45 a	85,27 a	93,73 f	89,7cde	86,40 cde	87,24 b-f	89,13 ab
MS 1	86,05 a	78,57 a	85,47 a	90,35 c-f	78,02 a	78,85 ab	77,18 a	80,95 a
BM 1	90,16 b	83,89 a	86,25 a	81,91 a	89,76cde	83,89 a-d	87,24 b-f	85,57 ab
BM 2	96,34 c-f	85,01 a	86,34 a	87,82b-e	93,95 e	91,44 e	90,60 b-f	90,81b
BM 3	96,34 c-f	83,61 a	86,92 a	92,78ef	91,44cde	84,73 a-d	91,44 def	89,97ab
BM 4	95,60 cde	81,37a	87,25 a	86,13 abc	83,05abc	90,60 de	85,57 a-f	86,19 ab
BM 5	99,33 f	81,09 a	87,58 a	93,07 f	83,89 a-d	77,18 a	79,69 ab	83,47 ab
BM 6	98,31 def	85,29 a	88,32 a	93,73 f	93,12 de	88,08 de	93,12 ef	91,86b
BM 7	99,33 f	78,85 a	88,38 a	82,75 ab	88,08 b-e	82,21abc	87,24 b-f	84,93ab
CC 1	95,60 cde	78,29 a	88,81 a	87,82 b-e	79,69 ab	82,21abc	81,37 abc	82,63ab
CC 2	94,75 cd	84,91 a	89,01 a	84,44 ab	79,59 ab	78,76 ab	82,12 a-d	81,06 a

Table 20. Significant parameters with different and non differentiated subsets. Tukey (p=0,05).

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Code	Skin texture	Skin astringency	Skin aroma	Skin bitterness	Skin maturity
CCP 1	91,44 g	91,44 g	72,14 a	88,92 fg	90,18 f
MC 1	88,08efg	83,89 c-g	76,34 ad	87,24 d-g	85,78 def
MC 2	81,37 a-e	75,50 bc	77,18 a-e	79,69 a-e	78,85 a-e
MC 3	72,98 a	65,43 a	73,82abc	72,98 a	71,09 a
MC 4	80,53 a-e	72,14 ab	77,18 a-e	76,34 abc	76,55abc
MC 5	90,60 fg	79,65 b-f	72,98 ab	78,85 a-d	83,05c-f
MC 6	87,24 dg	87,24 fg	77,18 a-e	88,92 fg	87,24 ef
MS 1	84,73 cg	77,18 bcd	78,85 a-e	83,89 c-f	80,74 b-e
BM 1	72,98 a	83,89 c-g	81,37 b-f	84,73 c-g	80,95 b-e
BM 2	78,85 ad	73,82 ab	81,37 b-f	83,05 b-f	78,23 a-d
BM 3	82,21 b-f	78,02 b-e	82,21 c-f	81,37 a-f	79,48 a-e
BM 4	77,18abc	86,40 efg	83,05def	88,08 efg	83,26 c-f
BM 5	90,60 fg	91,44 g	83,89def	93,12 g	90,18f
BM 6	84,73 cg	79,69 b-f	84,63def	83,89 c-f	82,42 b-f
BM 7	74,66 ab	71,30 ab	85,57 ef	74,66 ab	73,61 ab
CC 1	85,57 cg	75,50 bc	85,57 ef	76,34 abc	77,39 a-d
CC 2	84,62 cg	85,46 d-g	88,92 f	87,14 d-g	85,46 def

Table 21. Significant parameters with different and non differentiated subsets. Tukey (p=0,05).

Code	Seed colour	Seed hardness	Seed bitterness	Seed astringency	Seed aroma	Seed maturity
CCP 1	78,85abc	86,40 ab	67,11 a	74,66 ab	72,98 a	76,00 a
MC 1	79,69abc	88,08 ab	80,53 bcd	83,05 bc	82,21 be	82,71abc
MC 2	83,05bcd	84,73 ab	73,82abc	80,53 abc	72,98 a	79,02abc
MC 3	80,53abc	79,69 a	78,02 bcd	72,94 a	73,82ab	77,01ab
MC 4	85,57 be	79,69 a	72,98 abc	72,94 a	72,98 a	76,84 ab
MC 5	83,89bcd	89,76 b	78,86 bcd	79,69 abc	78,85 ad	82,21abc
MC 6	93,12 e	84,73 ab	77,18 bcd	77,18 ab	80,53 a-e	82,55abc
MS 1	85,57 be	86,40 ab	77,18 bcd	75,50 ab	81,37 a-e	81,20abc
BM 1	78,85abc	85,57 ab	80,53 bcd	78,02 ab	82,21 be	81,04abc
BM 2	85,57 be	86,40 ab	90,60 ef	87,24 c	87,24 de	87,41 c
BM 3	93,12 e	86,40 ab	81,37 cd	81,37 abc	83,0cde	85,06 bc
BM 4	89,76 de	88,92 ab	72,98 abc	75,50 ab	77,18abc	80,87abc
BM 5	87,24cde	87,24 ab	72,14 ab	79,69 abc	78,02abc	80,87abc
BM 6	84,73 be	90,60 b	80,53 bcd	78,02 ab	81,37 a-e	83,05abc
BM 7	78,02 ab	79,69 a	78,86 bcd	79,69 abc	75,50abc	78,35 ab
CC 1	79,69abc	79,69 a	83,05 de	82,21 bc	81,37 a-e	81,20abc
CC 2	72,90 a	83,79 ab	93,014 f	87,98 c	87,98 e	85,13 bc

Table 22. Significant parameters with different and non differentiated subsets. Tukey (p=0,05).

From the multivariate analysis factor choice, the year and the statistic test it appears that most of the parameters tested originate differentiated subsets, exception made for the variable berry's colour. The variables linked to seeds are the variables that create well differentiated subsets that indicate a great variability of data in the three years studied.

The year 2011 shows the highest parameters that influence the sensorial maturity of the grapes at harvest's time especially for the variables correlated to the pulp, while the 2010 presents the lowest values that influence seed's level of maturity (tab. 23).

Variable	2009	2010	2011
Berry colour	95,98 a	96,70 a	96,11 a
Pulp separation	86,58 a	86,73 a	93,78 b
Pulp sweetness	86,60 a	87,49 a	91,47 b
Pulp acidity	82,60 a	83,05 a	88,51 b
Pulp aroma	84,68 a	87,93 b	89,25 b
Skin texture	79,35a	83,64 b	85,55 b
Skin astringency	77,72 a	80,07 ab	77,72 b
Skin aroma	76,68 a	81,72 b	81,99 b
Skin bitterness	79,35 a	84,53 b	84,81 b
Seed colour	80,53 a	84,96 b	85,12 b
Seed hardness	78,31 a	88,53 b	88,66 b
Seed bitterness	72,69 a	77,13 b	86,44 c
Seed astringency	74,02 a	75,94 a	87,62 b
Seed aroma	71,50 a	78,90 b	87,77 c
Pulp maturity	84,97 a	86,16 a	90,66 b
Skin maturity	78,27 a	78,27 b	78,27 b
Seed maturity	75,41 a	81,12 b	87,09 c
Berry aroma	78,71 a	81,77 b	86,34 c
Berry sensorial maturity	83,19 a	85,46 a	88,77 b

Table 23. Mean separation by multiple range test (Tukey); the comparison is among data shown in horizontal.

In using the factorial statistic analysis – principal components method - it was possible to put together all the variables noted and calculated in two new complex variables (components) so as to represent 95,38% of the total variability of the sensorial characteristics of the berries at harvest (tab. 24). The descriptors that represent the highest coefficients (tab. 25) operate in a more reliable way in determining the characteristics of sensorial maturity of the berries at harvest.

In particular the first component is mainly linked to the skin and pulp descriptors and the second to the seed as seen in the value of the coefficients in order of increasing importance (tab. 25).

	Weights of rotated factors		
Component	**Total**	**% variability**	**% cumulated**
1	10,72	59,54	59,54
2	6,45	35,84	95,38

Table 24. Results of the factorial analysis: principal components method.

Variable	**Component**	
	1	**2**
Seed hardness	,999	,048
Skin bitterness	,994	
Seed maturity	,993	
Seed astringency	,990	
Seed aroma	,987	
Skin aroma	,987	
Skin maturity	,976	
Seed colour	,971	
Skin astringency	,962	
Skin texture	,918	
Berry aroma	,901	,417
Seed bitterness	,560	,489
Pulp acidity		,989
Pulp maturity		,996
Pulp aroma		,965
Pulp separ		,973
Berry colour		,973
Pulp sweetness		,995

Table 25. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.

The average values of all the thesis per year obtained from the sensorial analysis and the laboratory analysis (tab. 26) of the bunch macro structure at ripening were analyzed together, to verify if there were any correlations among the different parameters noted.

Variable	Abbreviation	Units
pH	pH	n
Sugary content	°Brix	°Brix
Titratable acidity	Titr. Ac.	g/L
Ripening tecnological Index*	Rip. T Index	n
Bunch weight	Bunch wgt	g
Berry weight	Berry wgt	g
Berry seed number	Berry seed num.	n
Berry skin weight	Skin wgt/berry	g/berry
Berry seed weight	Seed wgt/berry	g/berry
Anthocyanins/berry	Anth/berry	mg/berry
Skins percentage	% skin	%
Skin anthocyanins	Anth. skin	mg/Kg
Skin polyphenols	Polyph. skin	mg/Kg
Skin polyphenols percentage	% Skin polyph	%
Seed polyphenols	Polyph seed	mg/Kg
Seeds percentage	Seeds %	%
Polyphenols/berry	Polyph/berry	mg/berry
Total Polyphenols	Tot Polyph	mg/Kg

*Ripening Tecnological Index was so calculated °Brix/Titratable acidity

Table 26. List of abbreviations.

In using the factorial statistic analysis it was possible to put together all the variables noted and calculated in three new complex variables so as to represent 99,84 % of the total variability (tab. 27).

The first component is tied to the variables linked to skin's and seed's description; the third, instead, to pulp's one.

The parameters that influence the technological ripeness and the phenolic richness the grapes characterize the second component, one except for skin's anthocyanins, berry skin weight and seed polyphenols tied to the third component (tab. 28).

The graph (fig. 52) shows how the descriptors that are in the same quadrant are directly correlated while those further away are correlated negatively. The Ripening Index is indeed positively correlated with berry's and skin's aroma, with seed bitterness and skin texture.

The first component is positively correlated with most of the variables examined, while the second is correlated only in part.

The first and the second component are negatively correlated with the titratable acidity, the skin's antochyanins, the mean number of seeds of the berry and the mean weight of the berry.

		Weights of rotated factors	
Component	Total	% variability	% cumulated
1	12,38	39,95	39,95
2	9,45	30,48	70,43
3	9,12	29,41	99,84

Table 27. Results of the factorial analysis: principal components method.

	Component		
	1	2	3
Seed aroma	,977		
Seed maturity	,969		
Seed hardness	,940		
Seed colour	,911		
Berry aroma	,903		
Seed astringency	,898		
Skin aroma	,893	,444	
Skin bitterness	,893	,441	
Skin maturity	,863	,497	
Skin astringency	,840	,525	
Skin texture	,789	,559	
Seed bitterness	,781	-,402	,477
Bunch weight	,619	,500	-,605
Skin polyphenols	,577		-,800
pH	,411	,911	,042
Berry skin weight			-,853
Ripening Index*		,923	
Pulp aroma			,969
Pulp acidity			,977
Pulp maturity			,989
Pulp sweetness			,990
Berry colour			,963
Pulp separation			,963
Skin anthocyanins		-,914	
Berry weight		-,918	
Berry seed num		-,925	
Titratable acidity	-,433	-,902	
Total polyphenols	-,517	-,835	
°Brix	-,580	-,726	
Berry seed weight	-,591	-,691	,416
Seed polyphenols	-,619	-,468	,630

Table 28. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.
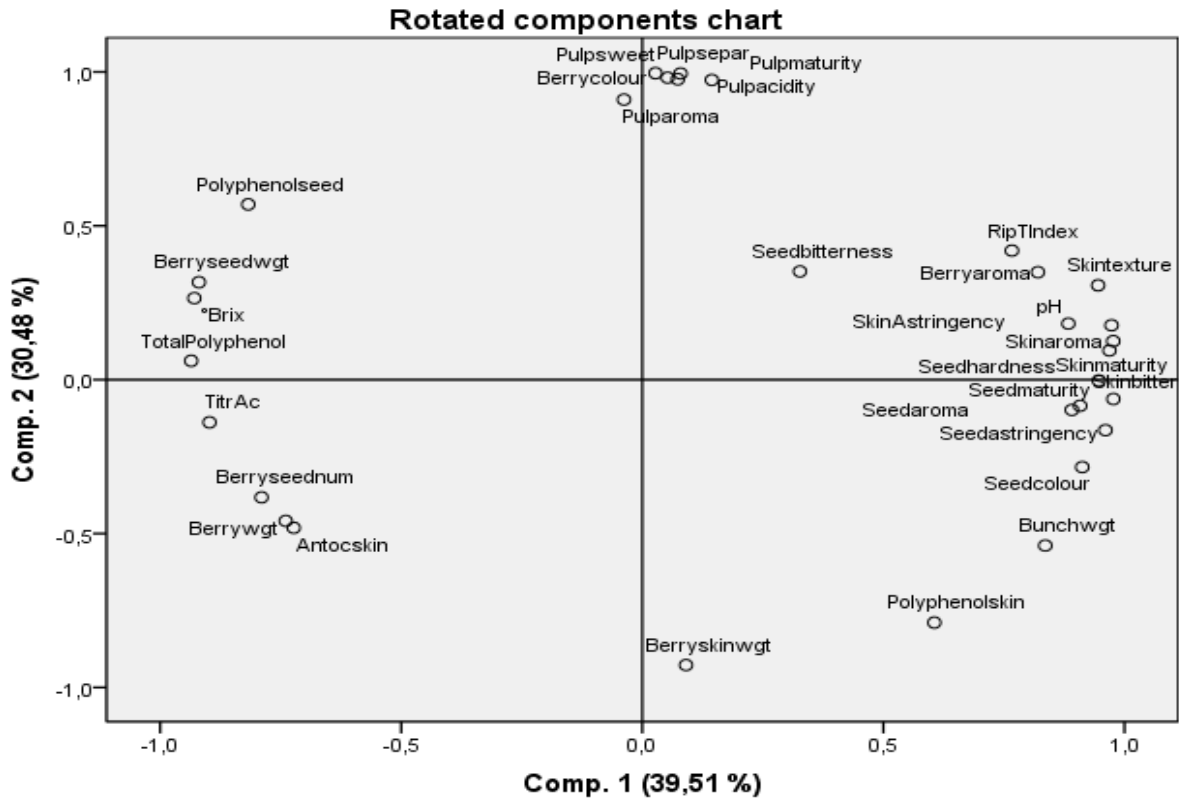
Figure 52. Rotated graph of the first two components obtained from the factorial analysis.

Analysing the multiple linear regression in the three new components and the sensorial maturity of the berry, it is possible to note that there is a significant correlation and that the total ripeness of the berry obtained experimentally is linearly correlated in a significant way (r^2 = 0,980) to that estimated in (tab. 29). Therefore, the berry sensorial maturity can be expressed in the following way (tab. 30).

Berry sensorial maturity $=86,337+F1*4,432+F2*3,923-F3*0,078$

From the table of coefficient values for the estimation of the sensorial maturity of the berry, it can be concluded that the model used is of significant importance and that the Berry sensorial maturity variable, is more relevant with the first two constants rather than with the third one (tab. 30).

Model	R	R-square	R-square correct	Standard deviation Estimate's error
1	,990	,980	,980	,970

Table 29**.** Statistic model of relation between the dependant variable of sensorial maturity of the berry and the three new components obtained from factorial analysis.

Coefficients	B	Standard deviation Error	Sig.
(Costant)	86,337	,131	,000
F 1	4,432	,117	,000
F 2	3,923	,114	,000
F 3	-0,078	,074	,295

Table 30. Coefficient values for the estimation of the sensorial maturity estimated of the berry, standard error and their significance.

Calculating the relation between the berry sensorial maturity expressed and that estimated statistically it can be seen graphically how the ripeness expressed by the panel and that determined statistically are overlapping (fig. 53).
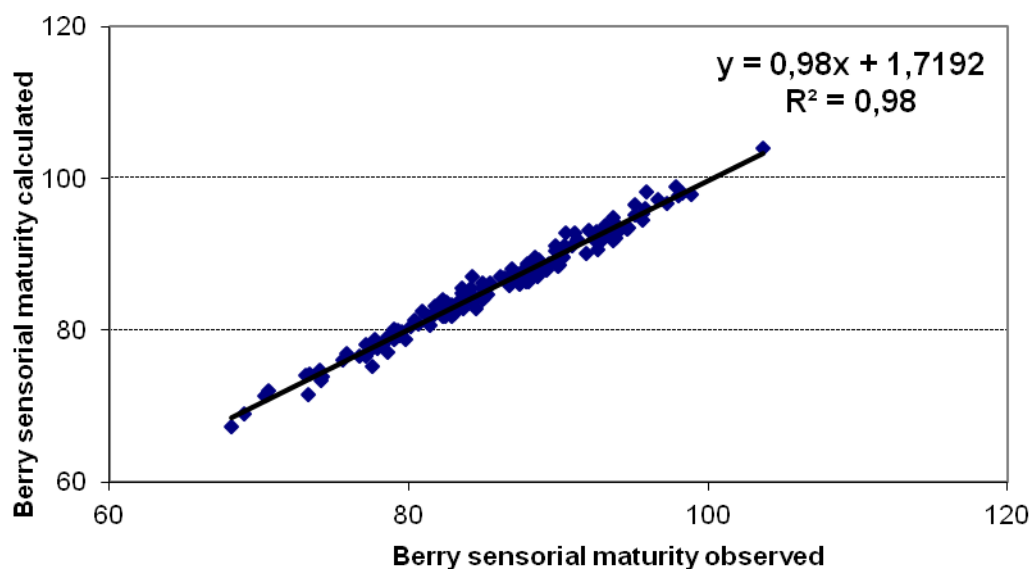
Figure 53. The relation between the ripeness index expressed and that statistically estimated.

In the table of correlations in the parameters examined in the course of our study, only the variables characterized by a probability < 0,00001. Most of the variables show a positive Pearson correlation value. The variable represented by the harvest date is linked negatively to the most parameters analyzed except for titratable acidity.

As foreseen, the variables concerning the ripening of the single berry constituents, global and sensorial ripening are strictly and positively linked to the single parameters that constitute them. There aren't many significant correlation among parameters that influence the technological ripeness and the phenolic richness and sensorial maturity (tab. 31).

Variable	Ber. col.	Pulp sep.	Pulp swe.	Pulp acid.	Pulp aro.	Skin tex.	Skin astr.	Skin aro.	Skin bit.	Seed col.	Seed hard.	Seed bit.	Seed astr.	Seed aro.	Pulp mat.	Skin mat.	Seed mat.	Berry aro.	B. S. M.	Harv. d.
Berry colour		0,38	0,47	0,38	0,48										0,49			0,36	0,53	
Pulp separation	0,38		0,60	0,48	0,55	0,51		0,37		0,46			0,40	0,42	0,75	0,39	0,47	0,58	0,64	-0,50
Pulp sweetness	0,47	0,60		0,69	0,89			0,42		0,46	0,45		0,37		0,93		0,45	0,67	0,72	-0,39
Pulp acidity	0,38	0,48	0,69		0,73					0,48		0,37	0,40	0,39	0,84		0,48	0,61	0,66	-0,42
Pulp aroma	0,48	0,55	0,89	0,73						0,44	0,38		0,39	0,33	0,92		0,45	0,69	0,70	
Skin texture	0,27	0,51					0,62	0,76	0,64	0,41	0,55			0,40	0,40	0,82	0,46	0,63	0,70	
Skin astringency						0,62		0,86	0,85	0,37	0,39					0,93	0,33	0,58	0,63	
Skin aroma		0,37	0,42	0,32		0,76	0,86		0,81	0,47	0,54			0,37	0,44	0,94	0,46	0,76	0,76	
Skin bitter						0,64	0,85	0,81			0,40	0,42				0,92	0,40	0,59	0,63	
Seed colour		0,46	0,46	0,48	0,44	0,41	0,37	0,47	0,40		0,59		0,34	0,43	0,54	0,45	0,60	0,59	0,64	
Seed hardness		0,32	0,45		0,38	0,55	0,39	0,54	0,42	0,59		0,44	0,51	0,64	0,44	0,52	0,77	0,71	0,67	
Seed bitterness				0,37							0,44		0,83	0,89	0,39		0,85	0,66	0,59	
Seed astringency		0,40	0,37	0,40	0,39						0,51	0,83		0,87	0,46	0,38	0,89	0,75	0,71	-0,46
Seed aroma		0,42		0,39	0,33	0,40		0,37		0,43	0,64	0,89	0,87		0,43	0,38	0,95	0,80	0,71	-0,44
Pulp maturity	0,49	0,75	0,93	0,84	0,92	0,40		0,44		0,54	0,44	0,39	0,46	0,43		0,38	0,55	0,75	0,81	-0,42
Skin maturity		0,39	0,34		0,24	0,82	0,93	0,94	0,92	0,45	0,52	0,15	0,38	0,38	0,38		0,45	0,70	0,75	
Seed maturity		0,47	0,45	0,48	0,45	0,46		0,46	0,40	0,60	0,77	0,85	0,89	0,95	0,55	0,45		0,86	0,81	-0,43
Berry aroma	0,36	0,58	0,67	0,61	0,69	0,63	0,58	0,76	0,59	0,59	0,71	0,66	0,75	0,80	0,75	0,70	0,86		0,96	-0,41
Berry Sensorial maturity	0,53	0,64	0,72	0,66	0,70	0,70	0,63	0,76	0,63	0,64	0,67	0,59	0,71	0,71	0,81	0,75	0,81	0,96		-0,37
Harvest date		-0,50	-0,39	-0,42									-0,46	-0,44	-0,42	-0,23	-0,43	-0,41	-0,37	

Table 31. Pearson's correlations. Legend abbreviations is on the previous pages.

The Stepwise discriminant analysis gave the best results compared to the traditional method; analysis of the most relevant variables for statistics purposes were inserted in stepwise.

The 17 theses of our study, before being subjected to discriminant analysis were subdivided by denomination area and company, thus creating a renumbering of the theses analyzed that result be nine regarding this analysis (tab. 32).

Area	Denomination area	Company
1	Chianti Colline Pisane	Beconcini
2	Montecucco	Collemassari
3	Montecucco	Salustri
4	Scansano	Fattoria di Magliano
5	Montalcino	Col D'Orcia
6	Montalcino	Casanova di Neri
7	Montalcino	La Mannella
8	Chianti Classico	Capannelle
9	Chianti Classico	Castello di Albola

Table 32. Area subdivision.

The discriminant analysis highlighted differences between areas examined and some of which may be distinct (fig. 54). The first two canonical functions represent more than 76,0 % of the total variability (tab. 33).

From the centroids graph obtained from the discriminant analysis (fig. 54), it is noted that the points relative to the groups show a enough limited dispersion. Four distinct groups appear in the centroid: the first and the second comprise theses coming from 'Chianti Classico' area that is well detached and the third, 'Chianti Colline Pisane's grapes.

The fourth includes the residual theses: the numbers four and five are the more distinguishable while many points linked to numbers two and seven are superimposed.

The two Montecucco theses do not appear very close differently from those of the 'Brunello and Montalcino'. In the 'Chianti Classico' the two theses are very different.

The 95,1% of the original grouping data were classified correctly, while 85,2% of the cases grouped cross-validated are reclassified correctly (tab. 34).

Function	Eingenvalue	% of variance	% cumulated	Canonical correlation
1	41,626	73,8	73,8	,988
2	7,396	13,1	86,9	,939
3	4,006	7,1	94,0	,895
4	1,923	3,4	97,4	,811
5	,603	1,1	98,5	,613
6	,440	,8	99,3	,553
7	,360	,6	99,9	,515
8	,043	,1	100,0	,203

Table 33. Eigenvalues of discriminant analysis.
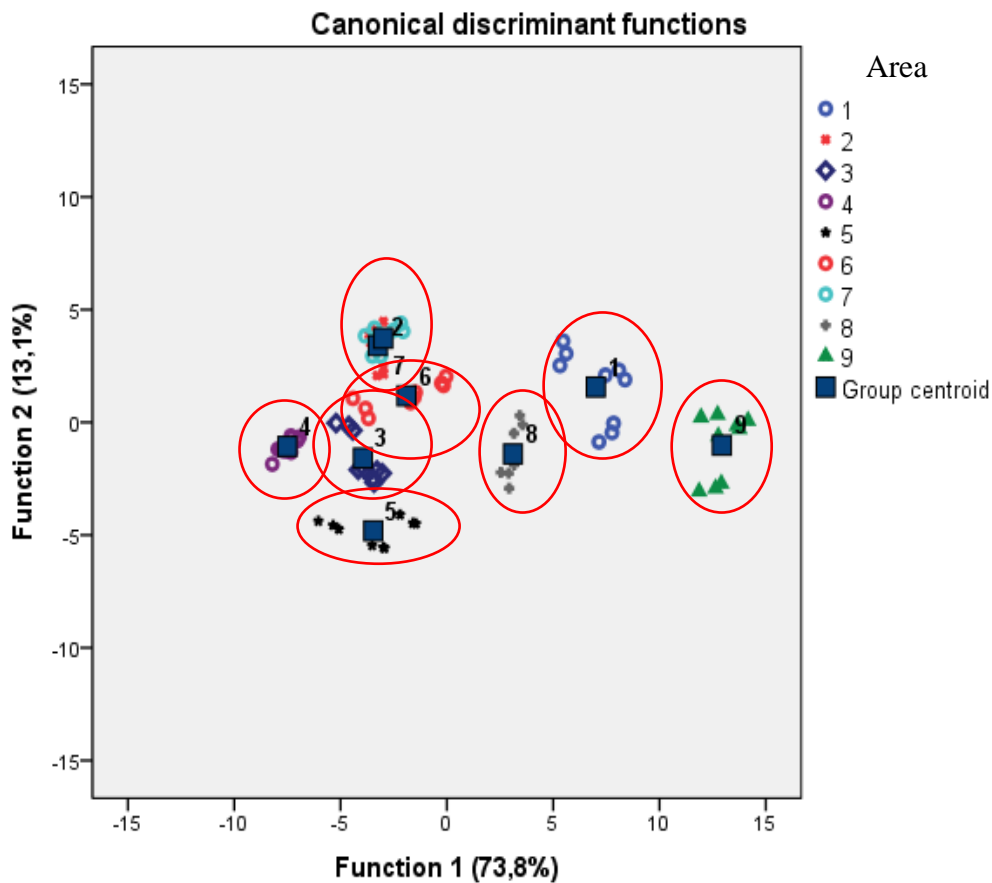
Figure 54. Centroids obtained from the cluster analysis of the sensorial characteristics of the grapes at harvest's time.

		Area	Group expected									Totals
			1	2	3	4	5	6	7	8	9	
Cross-Validation a	%	1	100,0	,0	,0	,0	,0	,0	,0	,0	,0	100,0
		2	,0	100,0	,0	,0	,0	,0	,0	,0	,0	100,0
		3	,0	,0	66,7	11,1	,0	22,2	,0	,0	,0	100,0
		4	,0	,0	,0	100,0	,0	,0	,0	,0	,0	100,0
		5	,0	,0	,0	,0	100,0	,0	,0	,0	,0	100,0
		6	,0	,0	33,3	,0	,0	66,7	,0	,0	,0	100,0
		7	,0	33,3	,0	,0	,0	33,3	33,3	,0	,0	100,0
		8	,0	,0	,0	,0	,0	,0	,0	100,0	,0	100,0
		9	,0	,0	,0	,0	,0	,0	,0	,0	100,0	100,0

Table 34. Classification results.
a. Cross validation is done only for those cases in the analysis in cross validation, each case is classified by the functions derived from all cases other than that case.
b.95,1% of original grouped cases correctly classified.
c.85,2% of cross-validated grouped cases correctly classified.

Statistical analysis was also used to investigate the features and possible statistically significant differences of the grapes coming from the theses as part of the same Denomination of Origin. The theses belonging to 'Montecucco' area, were then subjected to multivariate analysis, factorial, discriminating, linear regression and correlation. Among the theses coming from the area of 'Montalcino' was also studied the case of 'Col D'Orcia' estate in order to study in detail the clone effect grown in the same site of cultivation.

3.7.1 'Montecucco' area

As results from the multivariate analysis of variance, statistically significant parameters do not remain the same if the factor chosen during the statistical analysis is changed. The parameters related to pulp, except for acidity and separation, remain no significant when the source is represented by year or year interaction for thesis. If the year is chosen as the factor, all the variables become significant (tab. 35).

Factor	Dependent variable	F	Sig.	Factor	Dependent variable	F	Sig.
Thesis	Berry colour	8,304	,000	Year	Berry colour	5,839	,006
	Pulp separation	5,941	,000		Pulp separation	89,148	,000
	Pulp sweetness	,824	,541		Pulp sweetness	7,533	,002
	Pulp acidity	,927	,475		Pulp acidity	5,918	,006
	Pulp aroma	1,794	,139		Pulp aroma	4,072	,025
	Skin texture	12,788	,000		Skin texture	18,160	,000
	Skin astringency	22,447	,000		Skin astringency	27,924	,000
	Skin aroma	7,510	,000		Skin aroma	18,660	,000
	Skin bitterness	12,439	,000		Skin bitterness	25,609	,000
	Seed colour	6,988	,000		Seed colour	9,816	,000
	Seed hardness	5,164	,001		Seed hardness	39,187	,000
	Seed bitterness	3,103	,020		Seed bitterness	41,147	,000
	Seed astringency	5,958	,000		Seed astringency	90,515	,000
	Seed aroma	6,086	,000		Seed aroma	92,088	,000
	Pulp maturity	,649	,664		Pulp maturity	8,056	,001
	Skin maturity	12,232	,000		Skin maturity	21,507	,000
	Seed maturity	2,565	,044		Seed maturity	44,420	,000
	Berry aroma	2,694	,036		Berry aroma	22,884	,000
	Berry sensorial maturity	1,834	,131		Berry sensorial maturity	12,991	,000

Factor	Dependent variable	F	Sig.
Thesis * Year	Berry colour	2,569	,019
	Pulp separation	1,652	,131
	Pulp sweetness	1,212	,316
	Pulp acidity	3,686	,002
	Pulp aroma	1,427	,208
	Skin texture	5,996	,000
	Skin astringency	12,607	,000
	Skin aroma	7,022	,000
	Skin bitterness	25,654	,000
	Seed colour	7,874	,000
	Seed hardness	9,205	,000
	Seed bitterness	7,555	,000
	Seed astringency	6,596	,000
	Seed aroma	6,713	,000
	Pulp maturity	,563	,833
	Skin maturity	9,770	,000
	Seed maturity	4,447	,000
	Berry aroma	2,390	,027
	Berry sensorial maturity	1,396	,222

Table 35 a, b, c. Test of the effects between subjects (p=<0,05).

By using the data previously obtained, the level of variability attributable to the different factor was calculated (tab. 36). For most of the parameters the variability is attributable to the year; the thesis, however, shows more variability as concerns berry colour. Skin bitterness shows comparable levels of variability attributable to the different factor.

It is noted a high percentage value of error in pulp aroma variable.

Variable	% variability due to the thesis	% variability due to the year	% variability due to interaction thesis/year	% variability due to error
Berry colour	46,88	32,97	14,50	5,65
Pulp separation	6,08	91,21	1,69	1,02
Pulp sweetness	7,80	71,27	11,47	9,46
Pulp acidity	8,04	51,32	31,97	8,67
Pulp aroma	21,63	49,10	17,20	12,06
Skin texture	33,70	47,86	15,80	2,64
Skin astringency	35,09	43,65	19,71	1,56
Skin aroma	21,97	54,57	20,54	2,92
Skin bitterness	19,22	39,58	39,65	1,55
Seed colour	27,21	38,23	30,67	3,89
Seed hardness	9,47	71,83	16,87	1,83
Seed bitterness	5,88	77,92	14,31	1,89
Seed astringency	5,72	86,98	6,34	,96
Seed aroma	5,75	86,97	6,34	,94
Pulp maturity	6,32	78,46	5,48	9,74
Skin maturity	27,48	48,32	21,95	2,25
Seed maturity	4,89	84,72	8,48	1,91
Berry aroma	9,30	79,00	8,25	3,45
Berry sensorial maturity	10,65	75,44	8,11	5,81

Table 36. Level of variability attributable to the different factor.

From Tukey test it is possible to note the table with the different subsets and those non differentiated (tab 37-39). The significant variable that creates the most differentiated homogenous subsets is skin astringency. The values obtained from the analysis of the pulp, instead, create no differentiated homogenous subsets.

'Montecucco' area shows optimal value of sensory maturity and small variability in its theses (tab. 37-38). Regarding the sensorial maturity the values shown are higher in one thesis of 'ColleMassari' estate and in the thesis of 'Salustri' estate (tab. 37).

 The MC3 thesis is characterized by differences among maturation's level of the three berry parts; the skin appears less matured than seeds and pulp; on the contrary, MC6 is characterized by similar maturation's level of the berry at harvest's time (tab. 37-39).

Analysing pulp's maturity, the lowest value belongs to MC4 thesis while the highest to MC5 thesis (tab. 37).

Regarding skin's maturity the highest values are found in the grapes belonging to MC6, thesis already highlighted as having similar maturation's level of the berry (tab. 38).

The values obtained from the analysis of seed's maturity indicate the lowest value in MC4 and the highest in MC1 (tab. 39).

The highest values are found in the pulp rather skin and seeds (tab. 37-39).

Code	Berry colour	Berry aroma	Berry sensorial maturity	Pulp separation	Pulp sweetness	Pulp acidity	Pulp aroma	Pulp maturity
MC 1	98,61 b	86,12 a	89,00 a	92,89 b	92,27 a	84,72 a	92,27 a	90,60 a
MC 2	99,33 b	81,93 a	86,34 a	90,35 ab	93,11 a	86,40 a	93,95 a	91,23 a
MC 3	99,33 b	79,13 a	83,61 a	92,04 b	91,43 a	87,24 a	90,60 a	90,18 a
MC 4	96,23 a	79,41 a	83,55 a	86,97 a	93,95 a	83,89 a	88,08 a	87,66 a
MC 5	98,75 b	84,72 a	88,37 a	93,06 b	89,76 a	88,92 a	92,27 a	92,06 a
MC 6	99,33 b	84,44 a	88,80 a	93,73 b	94,79 a	86,40 a	87,24 a	89,13 a

Table 37. Significant parameters with different and non differentiated subsets. Tukey (p=0,05).

Code	Skin texture	Skin astringency	Skin aroma	Skin bitterness	Skin maturity
MC 1	88,08 bc	83,89 de	83,89 bc	87,24 b	85,77 cd
MC 2	81,37 b	75,50 bc	78,85 abc	79,69 a	78,85 bc
MC 3	72,98 a	65,43 a	72,98 a	72,98 a	71,09 a
MC 4	80,53 ab	72,14 ab	77,17 ab	76,33 a	76,54 ab
MC 5	90,60 c	79,69 cd	83,05 bc	78,85 a	83,05 bcd
MC 6	87,24 bc	87,24 e	85,56 c	88,92 b	87,24 d

Table 38. Significant parameters with different and non differentiated subsets. Tukey (p=0,05).

Code	Seed colour	Seed hardness	Seed bitterness	Seed astringency	Seed aroma	Seed maturity
MC 1	79,69 a	88,08 b	80,53 b	83,05 b	82,21 c	82,71 a
MC 2	83,05 a	84,72 ab	73,82 ab	80,53 b	72,98 a	79,02 a
MC 3	80,53 a	79,69 a	78,01 ab	72,98 a	73,82 ab	77,01 a
MC 4	85,56 ab	79,69 a	72,98 a	72,98 a	72,98 a	76,84 a
MC 5	83,89 a	89,76 b	78,85 ab	79,69 ab	78,85 abc	82,21 a
MC 6	93,11 b	84,72 ab	77,17 ab	77,17 ab	80,53 bc	82,54 a

Table 39. Significant parameters with different and non differentiated subsets. Tukey (p=0,05).

From the multivariance analysis it appears that all of the parameters tested originate differentiated homogenous subsets. The variables linked to skin and seeds are the variables that create well differentiated subsets that indicate a great variability of data in the three years studied.

The year 2011 shows the highest parameters that influence the sensorial maturity of the grapes at harvest's time especially for the variables correlated to the pulp; the 2009, instead, presents the highest values that influence skin's level of maturity.

In all three years variables related to seed's maturity were those with the lowest values (tab. 40).

Variable	2009	2010	2011
Berry colour	99,33 b	97,90 a	98,55 ab
Pulp separation	95,00 b	83,60 a	95,93 b
Pulp sweetness	94,79 b	88,08 a	94,79 b
Pulp acidity	85,56 ab	83,46 a	89,76 b
Pulp aroma	89,34 ab	88,92 a	93,95 b
Skin texture	86,40 b	77,17 a	86,82 b
Skin astringency	83,47 c	70,88 a	77,59 b
Skin aroma	84,30 b	74,24 a	82,21 b
Skin bitterness	84,72 b	73,40 a	83,89 b
Seed colour	87,24 b	79,69 a	85,98 b
Seed hardness	88,92 b	75,08 a	89,34 b
Seed bitterness	76,33 b	69,62 a	84,72 c
Seed astringency	76,33 b	67,11 a	89,76 c
Seed aroma	78,01 b	65,01 a	87,66 c
Pulp maturity	91,01 b	85,88 a	93,53 b
Skin maturity	84,72 b	73,92 a	82,63 b
Seed maturity	81,37 b	71,30 a	87,49 c
Berry aroma	83,88 b	76,06 a	87,94 b
Berry sensorial maturity	88,33 b	81,23 a	90,28 b

Table 40. Mean separation by multiple range test (Tukey); the comparison is among data shown in horizontal.

In using the factorial statistic analysis it was possible to put together all the variables noted and calculated in three new complex variables (components) so as to represent 98,95 % of the total variability of the sensorial characteristics of the berries at harvest (tab. 41). The descriptors that represent the highest coefficients (tab. 42) operate in a more reliable way in determining the characteristics of sensorial maturity of the berries at harvest.

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The first component is tied to the most of the parameters correlated to the pulp except for the value of separation, to the berry's characteristics, to berry sensorial maturity and to the most of the parameters correlated to the skin. Variables linked to the description of the seeds are associated with the second component. The last component is characterized, however, by skin's texture and bitterness (tab. 42).

| Component | Weights of rotated factors | | |
	Total	% variability	% cumulated
1	8,21	43,22	43,22
2	6,82	35,88	79,10
3	3,77	19,85	98,95

Table 41. Results of the factorial analysis: principal components method.

| Variable | Component | | |
	1	2	3
Pulp aroma	,998		
Skin aroma	,970		
Pulp sweetness	,943		
Pulp acidity	,924		
Pulp maturity	,881	,472	
Skin Astringency	,842	-,528	
Berry aroma	,836	,427	
Berry colour	,767		
Berry Sensorial maturity	,750	,498	,434
Seed colour	,697	-,421	,579
Skin maturity	,679		,730
Seed hardness		,927	
Seed maturity		,890	
Pulp separation		,954	
Skin texture		,503	,846
Seed astringency		,985	
Seed aroma		,870	,493
Skin bitterness			,989
Seed bitterness		,876	,466

Table 42. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.

Extracting only two components from all the data collected it is possible to explain 85,02% of the total variability (tab. 43). In particular the first component is greatly linked to the variables already mentioned for the description of the first component; the second is composed of the sum of the second and the third component of the previous analysis (tab. 44).

| Component | Weights of rotated factors | | |
	Total	% variance	% cumulated
1	8,41	44,26	44,26
2	7,74	40,76	85,02

Table 43. Results of the factorial analysis extracting only the first 2 components: method of the principal components.

| Variable | Component | |
	1	2
Skin aroma	,986	
Pulp aroma	,973	
Pulp acidity	,897	
Pulp sweetness	,875	
Skin astringency	,849	-,513
Berry aroma	,843	,536
Seed colour	,840	
Skin maturity	,819	
Pulp maturity	,811	,467
Berry colour	,792	,435
Berry Sesorial maturity	,772	,631
Skin texture		,757
Seed hardness		,833
Seed maturity		,979
Skin bitterness		,460
Pulp separation		,835
Seed aroma		,984
Seed astringency		,987
Seed bitterness		,978

Table 44. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.

The average values of all the thesis per year obtained from the sensorial analysis and the laboratory analysis of the bunch macro structure at ripening were analyzed together, to verify if there were any correlations among the different parameters noted.

In using the factorial statistic analysis it was possible to put together all the variables noted and calculated in three new complex variables so as to represent 99,34 % of the total variability (tab. 45).

The first component is tied to some sensorial variables related to seeds and skin and some technological and phenolic richness like sugary and anthocyanins content, the pH and the mean weight of the berry. Variables linked to berry sensorial maturity, to skin astringency and to the description of the pulp are associated with the second component.

The parameters that influence the seeds and titratable acidity characterize the third component (tab. 46).

| Component | Weights of rotated factors | | |
	Total	% variability	% cumulated
1	12,07	37,73	37,73
2	10,01	31,29	69,02
3	9,70	30,32	99,34

Table 45. Results of the factorial analysis: principal components method.

Variable	Component		
	1	2	3
°Brix	,991		
Berry seed number	,989		
Seed polyphenols	,988		
Ripening Tecnological Index	,987		
pH	,885		-,438
Total polyphenols	,867		,495
Berry weight	,625		-,763
Skin astringency	,566	,622	-,540
Titratable acidity	,564		-,809
Berry skin weight	,484		,874
Pulp aroma		,903	
Skin aroma		,876	
Pulp sweetness		,920	
Skin polyphenols			,966
Pulp maturity		,913	
Pulp acidity		,976	
Berry seed weight			,991
Seed hardness		,469	,883
Pulp separation			,942
Berry aroma		,975	
Berry colour		,893	
Seed colour		,738	-,663
Berry Sensorial maturity		,941	
Skin maturity		,851	
Seed astringency	-,422		,856
Seed maturity	-,531	,520	,669
Seed aroma	-,678		,639
Seed bitterness	-,706		,667
Skin texture	-,817	,553	
Skin anthocyanins	-,859		
Skin bitterness	-,909		
Bunch weight	-,992		

Table 46. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.

Extracting only two components from all the data collected it is possible to explain 74,26% of the total variability (tab 47).

In particular the first component is greatly linked to the variables already mentioned for the description of the first component; the second is composed of the sum of the second and the third component of the previous analysis (tab. 48).

The graph (fig. 55) shows how the descriptors that are in the same quadrant and that are close to the ripening of the berry are directly correlated to it while those further away are correlated negatively. The Ripening Technological Index is indeed positively correlated with the sugary content, the pH, the seed's and skin's weight, with the grade of polyphenols in the berry and in the skins and, regarding sensorial parameters, with some characteristics of the pulp.

Berry sensorial maturity, on the contrary, is positively correlated, obviously with the level of maturity of the three different part of the berry, berry's aroma and colour. It is negatively correlated with the variables linked to technological and phenolic richness of the grapes at harvest's time.

The first and the second component are negatively correlated with the mean weight of the bunch.

| Component | Total | Weights of rotated factors | |
		% variance	% cumulated
1	13,25	41,39	41,39
2	10,52	32,87	74,26

Table 47. Results of the factorial analysis extracting only the first 2 components: method of the principal components.

Variable	Component	
	1	2
pH	1,000	
Seed polyphenols	,930	
Berry weight	,912	
°Brix	,912	
Titratable acidity	,878	
Berry seed number	,852	
Ripening Tecnological Index	,842	
Skin astringency	,838	
Skin aroma	,596	,668
Pulp aroma	,567	,777
Total Polyphenols	,561	
Pulp sweetness		,942
Seed colour		
Pulp acidity		,965
Pulp maturity		,983
Berry skin weight		,350
Berry colour		,846
Berry aroma		,963
Skin maturity		,602
Berry Sensorial maturity		,946
Skin polyphenols		,344
Seed hardness		,795
Pulp separation		,693
Berry seed weight		
Skin bitter	-,654	
Seed maturity	-,675	,732
Seed astringency	-,697	,613
Skin texture	-,701	,538
Seed aroma	-,818	,572
Seed bitterness	-,876	,468
Bunch weight	-,903	
Skin anthocyans	-,998	

Table 48. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.
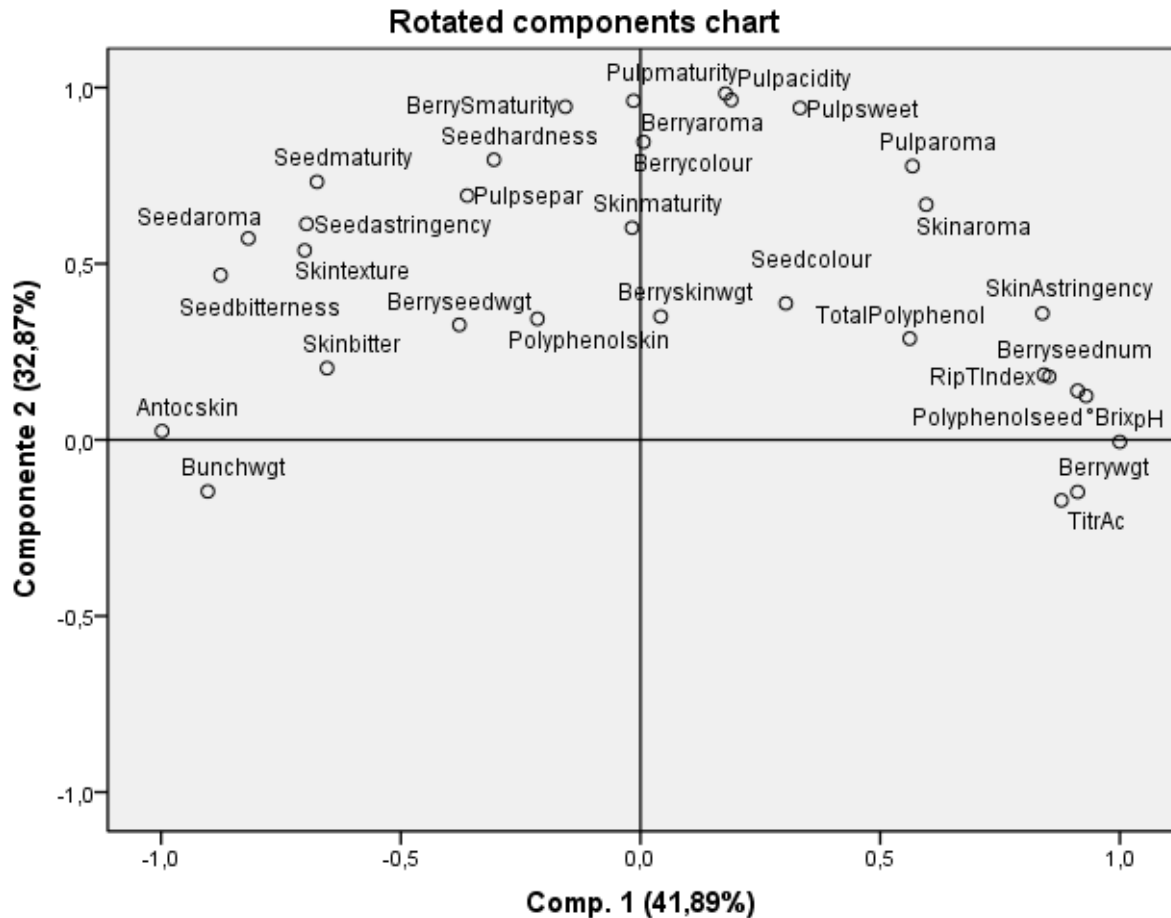
Figure 55. Rotated graph of the first two components obtained from the factorial analysis.

Analysing the multiple linear regression in the three new components and the berry sensorial maturity, it is possible to note that there is a significant correlation and that the total ripeness of the berry obtained experimentally is linearly correlated in a significant way ($r^2 = 0,993$) to that estimated (tab. 49). Therefore, the berry sensorial maturity can be expressed in the following way (tab. 50).

Berry sensorial maturity $=88,884+F1*3,571+F2*2,335+F3*2,066$

From the table of coefficient values for the estimation of the sensorial maturity of the berry, it can be concluded that the model used is of significant importance, that the Berry sensorial maturity variable, is relevant with all three constants (tab. 50).

Model	R	R-square	R-square correct	Standard deviation Estimate's error
1	,996	,993	,993	,614

Table 49. Statistic model of relation between the dependant variable of sensorial maturity of the berry and the three new components obtained from factorial analysis.

Coefficients	B	Standard deviation Error	Sig.
(Costant)	88,884	,114	,000
F 1	3,571	,115	,000
F 2	2,335	,122	,000
F 3	2,066	,086	,000

Table 50. Coefficient values for the estimation of the sensorial maturity estimated of the berry, standard error and their significance.

Calculating the relation between berry sensorial maturity expressed and that estimated statistically it can be seen graphically how the ripeness expressed by the panel and that determined statistically are overlapping (fig. 56).
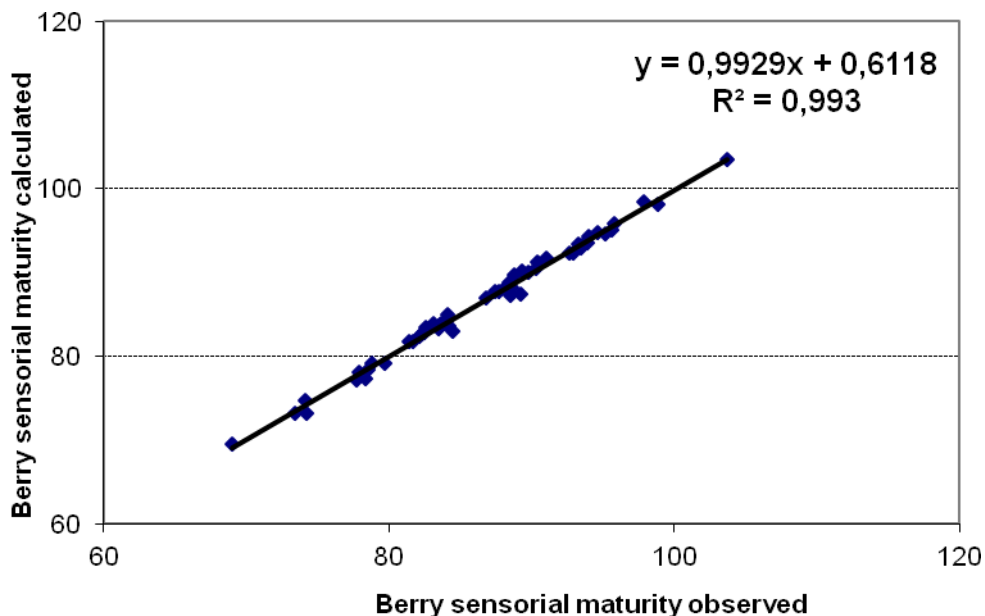
Figure 56. The relation between the ripeness index expressed and that statistically estimated.

Examining the correlation between the parameters analyzed, in the table only the variables with a probability <0,00001 are reported. The mean weight of the bunch and the skin's anthocyanins, are the parameters that don't present significant Pearson's correlations (tab. 51). In most cases there are values of Pearson's correlation positive, however the parameters connected with the technological maturity of the grapes are negatively correlated. The variable represented by the harvest date is linked negatively to the most parameters analyzed. As foreseen, the variables concerning the ripening of the single berry constituents, global and sensorial ripening are strictly and positively linked to the single parameters that constitute them. Positive Pearson correlation values were found in mean weight of the skins and separation of the pulp. There aren't many significant correlation among parameters that influence the technological ripeness and the phenolic richness and sensorial maturity. Nevertheless positive Pearson correlation values were found in mean weight of the skins and separation of the pulp and in skin's polyphenols and seed's astringency (tab. 51).

	Ber. col.	Pulp sep.	Pulp swe.	Pulp acid.	Pulp aro.	Skin tex.	Skin astr.	Skin aro.	Skin bit.	Seed col.	Seed hard.	Seed bit.	Seed astr.	Seed aro.	Pulp mat.	Skin mat.	Seed mat.	Berry aro.	B. S. M.	Harv.d
Berry colour																			0,60	
Pulp separation			0,65	0,51		0,58					0,65	0,69	0,68	0,78	0,75		0,76	0,75	0,75	-0,66
Pulp sweetness		0,65			0,79						0,73		0,64	0,63	0,89		0,70	0,75	0,78	
Pulp acidity					0,71										0,83				0,58	
Pulp aroma			0,79	0,71											0,89			0,67	0,64	
Skin texture		0,58					0,83	0,86	0,81		0,66	0,64	0,66	0,76		0,92	0,74	0,84	0,85	
Skin Astringency						0,83		0,91	0,80		0,61			0,67	0,44	0,94	0,67	0,79	0,80	
Skin aroma						0,86	0,91		0,84	0,60				0,70	0,58	0,96	0,69	0,88	0,87	
Skin bitterness						0,81	0,80	0,84			0,59	0,62	0,59	0,72		0,93	0,71	0,74	0,77	
Seed colour								0,60									0,58		0,62	
Seed hardness		0,65	0,73			0,66	0,61		0,59			0,72	0,82	0,83	0,58	0,65	0,90	0,76	0,79	
Seed bitterness		0,69				0,64			0,62		0,72		0,87	0,88	0,63	0,61	0,88	0,77	0,79	-0,65
Seed astringency		0,68	0,64			0,66			0,59		0,82	0,87		0,92	0,66	0,63	0,94	0,84	0,82	-0,79
Seed aroma		0,78	0,63			0,76	0,67	0,70	0,72		0,83	0,88	0,92		0,64	0,76	0,97	0,91	0,88	-0,76
Pulp maturity		0,75	0,89	0,83	0,89			0,58			0,58	0,63	0,66	0,64			0,69	0,80	0,82	
Skin maturity						0,92	0,94	0,96	0,93		0,65	0,61	0,63	0,76	0,48		0,75	0,86	0,87	
Seed maturity		0,76				0,74	0,67	0,69	0,71	0,58	0,90	0,88	0,94	0,97	0,69	0,75		0,90	0,91	-0,69
Berry aroma		0,75	0,75		0,67	0,84	0,79	0,88	0,74		0,76	0,77	0,84	0,91	0,80	0,86	0,90		0,98	-0,61
Berry S.maturity	0,60	0,75	0,78	0,58	0,64	0,85	0,80	0,87	0,77	0,62	0,79	0,79	0,82	0,88	0,82	0,87	0,91	0,98		
Harvest date		-0,66									-0,65	-0,79	-0,76				-0,69	-0,61		

Table 51. Pearson's correlations. Legend abbreviations is on the previous pages.

The Stepwise discriminant analysis gave the best results compared to the traditional method; analysis of the most relevant variables for statistics purposes were inserted in stepwise.

The discriminant analysis highlighted differences between areas examined and some of which may be distinct (fig. 57). The first two canonical functions represent more than 91,6 % of the total variability (tab. 52).

Function	Eingenvalue	% of variance	% cumulated	Canonical correlation
1	42,273	82,6	82,6	,988
2	4,788	9,4	91,9	,910
3	2,602	5,1	97,0	,850
4	1,103	2,2	99,2	,724
5	,430	,8	100,0	,549

Table 52. Eigenvalues of discriminant analysis.

From the centroids graph obtained from the discriminant analysis (fig. 57), it is noted that the points relative to the groups show a enough limited dispersion. Four distinct groups appear in the centroid: the fifth includes the thesis coming from a different estate and one of 'ColleMassari' winery indeed some points are superimposed.

The 95,1% of the original data grouping were classified correctly, while 92,6% of the cases grouped cross-validated are reclassified correctly (tab. 53).
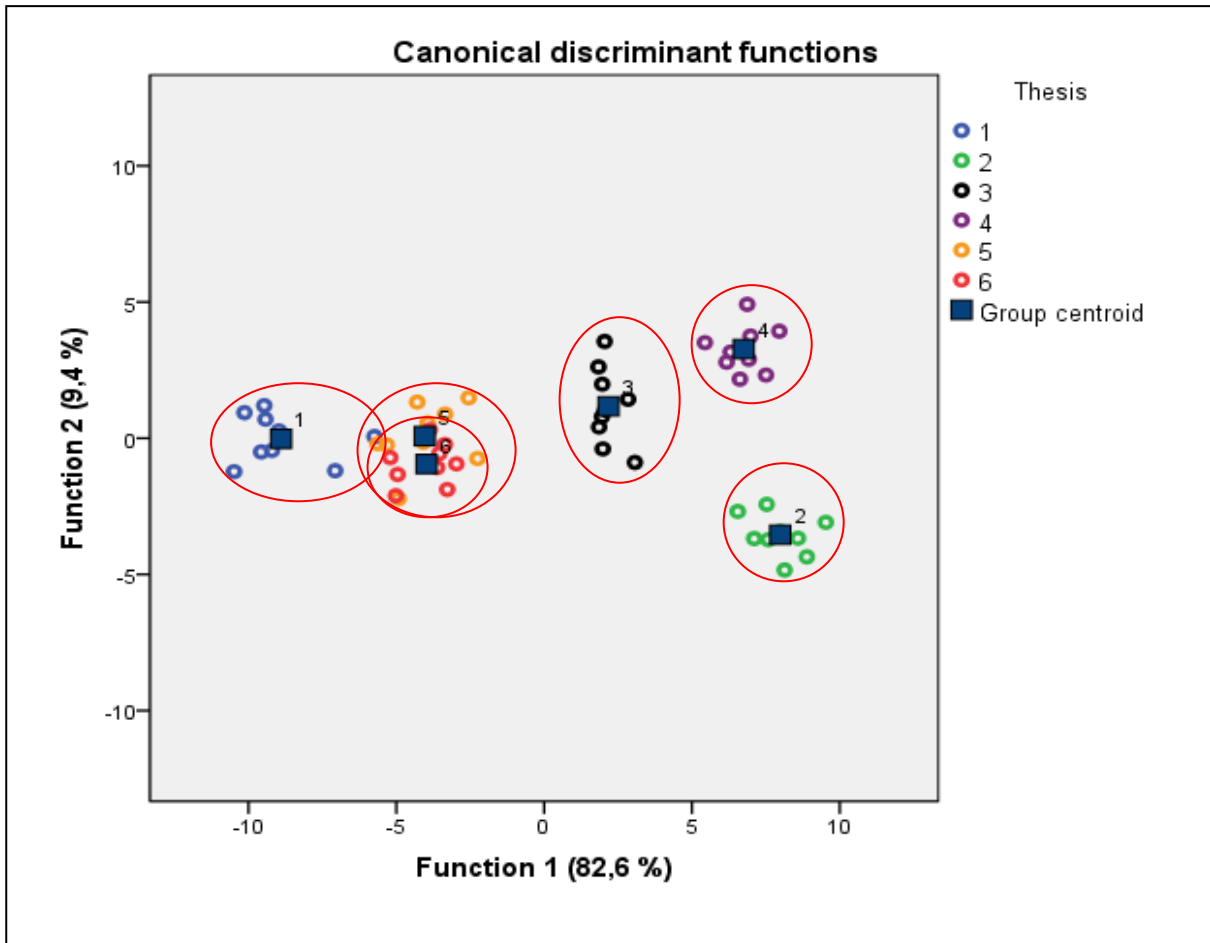
Figure 57. Centroids obtained from the cluster analysis of the sensorial characteristics of the grapes at harvest's time.

		Thesis	**1**	**2**	**3**	**4**	**5**	**6**	**Totals**
Cross-validation a	%	1	88,9	,0	,0	,0	,0	11,1	100,0
		2	,0	100,0	,0	,0	,0	,0	100,0
		3	,0	,0	100,0	,0	,0	,0	100,0
		4	,0	,0	,0	100,0	,0	,0	100,0
		5	,0	,0	,0	,0	66,7	33,3	100,0
		6	,0	,0	,0	,0	,0	100,0	100,0

(Header row spanning columns 1–6: "Group expected")

Table 53. Classification results.
a. Cross validation is done only for those cases in the analysis in cross validation, each case is classified by the functions derived from all cases other than that case.
b.95,1% of original grouped cases correctly classified.
c.92,6% of cross-validated grouped cases correctly classified.

3.7.2 'Col d'Orcia' estate

From the multivariate analysis, with the thesis as factor, what emerges is that among the dependent variables the no significant ones for the sensorial variables are seed's hardness, berry's aroma and berry's sensorial aroma.

The variables analyzed change their level of significance if, the factor chosen during the statistical analysis changes; indeed choosing the year, many non significant statistical variable are added. In this case, separation, sweetness, aroma and maturity of the pulp and skin texture become the only significant variables.

Pulp maturity and berry sensorial aroma are the two parameters that become non significant when the factor is represented by year interaction by thesis (tab. 54).

Factor	Dependent variable	F	Sig.
Thesis	Berry colour	14,408	,000
	Pulp separation	22,603	,000
	Pulp sweetness	6,226	,001
	Pulp acidity	9,764	,000
	Pulp aroma	6,241	,001
	Skin texture	14,425	,000
	Skin astringency	14,951	,000
	Skin aroma	4,767	,004
	Skin bitterness	6,244	,001
	Seed colour	8,037	,000
	Seed hardness	,459	,765
	Seed bitterness	18,729	,000
	Seed astringency	6,413	,001
	Seed aroma	5,344	,002
	Pulp maturity	2,702	,049
	Skin maturity	7,034	,000
	Seed maturity	2,842	,041
	Berry aroma	,895	,479
	Berry sensorial maturity	,569	,687

Factor	Dependent variable	F	Sig.
Year	Berry colour	41,532	,000
	Pulp separation	122,865	,000
	Pulp sweetness	8,134	,002
	Pulp acidity	2,343	,113
	Pulp aroma	12,004	,000
	Skin texture	5,056	,013
	Skin astringency	1,226	,308
	Skin aroma	2,651	,087
	Skin bitterness	1,946	,160
	Seed colour	2,553	,095
	Seed hardness	2,913	,070
	Seed bitterness	,423	,659
	Seed astringency	2,408	,107
	Seed aroma	1,218	,310
	Pulp maturity	9,404	,001
	Skin maturity	,699	,505
	Seed maturity	,257	,775
	Berry aroma	2,288	,119
	Berry sensorial maturity	1,478	,244

Factor	Dependent variable	F	Sig.
Thesis * Year	Berry colour	11,504	,000
	Pulp separation	4,473	,001
	Pulp sweetness	3,074	,012
	Pulp acidity	4,399	,001
	Pulp aroma	2,831	,018
	Skin texture	7,781	,000
	Skin astringency	8,614	,000
	Skin aroma	3,930	,003
	Skin bitterness	9,193	,000
	Seed colour	3,999	,003
	Seed hardness	7,103	,000
	Seed bitterness	17,108	,000
	Seed astringency	14,679	,000
	Seed aroma	12,041	,000
	Pulp maturity	1,825	,111
	Skin maturity	4,926	,001
	Seed maturity	8,146	,000
	Berry aroma	2,538	,031
	Berry sensorial maturity	1,946	,089

Table 54 a, b, c. Test of the effects between subjects (p=<0,05).

The variability quota attributed to the different factor was calculated using the data previously obtained (tab. 55).

For most of the parameters the variability is attributable to the year; nevertheless most variables show comparable levels of variability attributable to the different factor.

It is noted a high percentage value of error in berry sensorial aroma variable.

Variable	% variability due to the thesis	% variability due to the year	% variability due to interaction thesis/year	% variability due to error
Berry colour	21,05	60,68	16,81	1,46
Pulp separation	14,98	81,40	2,96	,66
Pulp sweetness	33,77	44,12	16,68	5,42
Pulp acidity	55,77	13,39	25,13	5,71
Pulp aroma	28,27	54,37	12,83	4,53
Skin texture	51,04	17,89	27,53	3,54
Skin astringency	57,97	4,75	33,40	3,88
Skin aroma	38,61	21,47	31,83	8,10
Skin bitterness	33,96	10,59	50,01	5,44
Seed colour	51,56	16,38	25,65	6,41
Seed hardness	4,00	25,39	61,90	8,71
Seed bitterness	50,27	1,14	45,91	2,68
Seed astringency	26,18	9,83	59,91	4,08
Seed aroma	27,26	6,21	61,43	5,10
Pulp maturity	18,09	62,99	12,22	6,70
Skin maturity	51,50	5,11	36,06	7,32
Seed maturity	23,21	2,10	66,53	8,17
Berry aroma	13,32	34,04	37,76	14,88
Berry sensorial maturity	11,40	29,60	38,97	20,03

Table 55. Level of variability attributable to the different factor.

From Tukey's test it is possible to note the table with the different subsets and those non differentiated (tab. 56-58).

The significant variables create differentiated homogenous subsets except for seed's hardness and its maturity, pulp's maturity, berry aroma and berry sensorial maturity.

Skin astringency is the variable that creates well differentiated subsets that give rise to a wide range of data variability (tab. 56).

'Col d'Orcia' grapes in general shows optimal values of sensory maturity; the highest values are found in the pulp rather than in seeds and in skin; the latter is characterized by greater variability (tab. 56-58).

BM2 thesis is characterized by the highest maturity of the pulp and seeds, on the contrary in BM5 is skin to be more mature than the other two parts of the berry and it shows the lowest values of pulp's and seed's maturity.

Code	Berry colour	Berry aroma	Berry sensorial maturity	Pulp separation	Pulp sweetness	Pulp acidity	Pulp aroma	Pulp maturity
BM 1	90,16 a	83,89 a	84,24 a	81,91 a	89,76 abc	83,89 ab	87,24 ab	85,56 a
BM 2	96,34 bc	85,00 a	87,58 a	87,82 b	93,95 c	91,43 b	90,60 b	90,81 a
BM 3	96,34 bc	83,61 a	86,92 a	92,77 c	91,43 bc	84,72 ab	91,43 b	89,97 a
BM 4	95,60 b	81,37 a	85,46 a	86,13 b	83,05 a	90,60 b	85,56 ab	86,19 a
BM 5	99,33 c	81,09 a	87,25 a	93,06 c	83,89 ab	77,17 a	79,69 a	83,47 a

Table 56. Significant parameters with different and non differentiated subsets. Tukey (p=0,05).

Code	Skin texture	Skin astringency	Skin aroma	Skin bitterness	Skin maturity
BM 1	72,98 a	83,89 bc	82,21 ab	84,72 a	80,95 a
BM 2	78,85 ab	73,82 a	77,17 a	83,05 a	78,22 a
BM 3	82,21 b	78,01 ab	76,33 a	81,37 a	79,48 a
BM 4	77,17 ab	86,40 cd	81,37 ab	88,08 ab	83,26 ab
BM 5	90,60 c	91,43 d	85,56 b	93,11 b	90,18 b

Table 57. Significant parameters with different subsets. Tukey (p=0,05).

Code	Seed colour	Seed hardness	Seed bitterness	Seed astringency	Seed aroma	Seed maturity
BM 1	78,85 a	85,56 a	80,53 b	78,01 a	82,21 ab	81,03 a
BM 2	85,56 ab	86,40 a	90,60 c	87,24 b	87,24 b	87,41 a
BM 3	93,11 b	86,40 a	81,37 b	81,37 ab	83,05 ab	85,06 a
BM 4	89,76 b	88,92 a	72,98 a	75,50 a	77,17 a	80,86 a
BM 5	87,24 b	87,24 a	72,14 a	79,69 a	78,01 a	80,86 a

Table 58. Significant parameters with different and non differentiated subsets. Tukey (p=0,05).

From the MANOVA analysis, it appears that most of the parameters examined originate non differentiated subsets.

The variables linked to pulp are the variables that create well differentiated subsets that indicate a great variability of data in the three years studied (tab. 59).

In 2010 the highest values were recorded concerning sensorial analysis, that show, at harvest, a high maturity level of the berry in most of its components, compared to the other years except for seed's variables and separation and acidity of the pulp (tab. 59).

The year 2011 stands out for the highest parameters that influence the description of seeds and the 2009 just for seed hardness (tab. 59).

Variable	2009	2010	2011
Berry colour	96,98 b	99,05 b	90,62 a
Pulp separation	78,53 a	93,22 b	93,26 b
Pulp sweetness	83,55 a	91,10 b	90,60 b
Pulp acidity	84,56 a	84,05 a	88,08 a
Pulp aroma	82,04 a	92,11 b	86,57 a
Skin texture	77,51 a	83,55 b	80,03 ab
Skin astringency	83,05 a	84,05 a	81,03 a
Skin aroma	79,02 a	83,05 a	79,52 a
Skin bitterness	86,07 a	84,05 a	88,08 a
Seed colour	85,56 a	89,59 a	85,56 a
Seed hardness	88,58 a	84,05 a	88,08 a
Seed bitterness	79,02 a	79,02 a	80,53 a
Seed astringency	78,01 a	81,03 a	82,04 a
Seed aroma	81,54 a	80,03 a	83,05 a
Pulp maturity	82,04 a	89,97 b	89,59 b
Skin maturity	81,41 a	83,67 a	82,16 a
Seed maturity	82,54 a	82,74 a	83,85 a
Berry aroma	80,86 a	85,06 a	83,05 a
Berry sensorial maturity	84,80 a	88,22 a	85,85 a

Table 59. Mean separation by multiple range test (Tukey); the comparison is among data shown in horizontal.

By factorial analysis it was possible to reduce the number of variables to three main components able to represent 98,88% of the total variability of the sensorial characteristics of the berries at harvest (tab. 60).

In particular the first component is mainly linked to the skin and pulp descriptors and the second to the seeds. Pulp acidity and seed astringency are associated with the third component (tab. 61).

	Weights of rotated factors		
Component	Total	% variability	% cumulated
1	9,79	51,51	51,51
2	6,42	33,77	85,28
3	2,58	13,60	98,88

Table 60. Results of the factorial analysis: principal components method.

	Component		
Variable	1	2	3
Seed hardness		,989	
Seed colour		,989	
Seed maturity		,949	
Seed aroma		,887	,430
Seed bitterness		,853	
Pulp acidity		,480	,874
Seed astringency		,675	,701
Skin aroma	,997		
Skin maturity	,986		
Pulp maturity	,970		
Skin texture	,961		
Pulp sweetness	,948		
Skin bitterness	,928		
Pulp aroma	,919		
Skin astringency	,918		
Berry aroma	,822	,565	
Berry Sensorial maturity	,821	,494	
Berry colour	,687	,427	,410
Pulp separation	,643	-,704	

Table 61. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.

Extracting only two components from all the data collected it is possible to explain 89,84% of the total variability (tab. 62). In particular the first component is greatly linked to the variables that describe pulp's and skin's level of maturation; the second is connected to the seed's characteristics and to the pulp acidity (tab. 63).

	Weights of rotated factors		
Component	Total	% variance	% cumulated
1	9,72	51,18	51,18
2	7,35	38,66	89,84

Table 62. Results of the factorial analysis extracting only the first 2 components: method of the principal components.

Variable	Component	
	1	2
Seed maturity		,993
Seed aroma		,978
Seed bitterness		,938
Seed hardness		,934
Seed colour		,934
Seed astringency		,886
Pulp acidity		,762
Skin aroma	,998	
Skin maturity	,992	
Pulp maturity	,981	
Skin bitterness	,955	
Skin astringency	,938	
Skin texture	,937	
Pulp sweetness	,918	
Pulp aroma	,884	
Berry Sensorial maturity	,811	,583
Berry aroma	,794	,573
Pulp separation	,697	-,543
Berry colour	,689	,563

Table 63. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.

The average values of all the thesis per year obtained from the sensorial analysis and the laboratory analysis of the bunch (macro structure) at ripening were analyzed together, to verify if there were any correlations among the different parameters noted.

In using the factorial statistic analysis it was possible to put together all the variables noted and calculated in three new complex variables so as to represent 99,32 % of the total variability (tab. 64).

The first component is tied to some sensorial variables related to seeds and pulp and to some technological and phenolic richness like polyphenols total content, mean weight and mean number of seeds. Variables linked to only sensorial variables are associated with the second component.

The parameters that influence technological and phenolic characteristics, pulp acidity, seed's aroma and astringency characterize the third component (tab. 65).

| | **Weights of rotated factors** | | |
Component	Total	**%** variability	**%** cumulated
1	11,60	35,15	35,15
2	11,51	34,88	70,03
3	9,67	29,29	99,32

Table 64. Results of the factorial analysis: principal components method.

| Variable | Component | | |
	1	2	3
Skin polyphenols	-,988		
Berry seed number	,979		
Berry seed weight	,974		
°Brix	-,970		
Berry weight	,912		
Pulp separation	-,887		
Total polyphenols	-,848		-,502
Seed hardness	,836	,494	
Seed colour	,836	,494	
Berry skin weight	,785		,592
Seed maturity	,702	,532	,472
Berry sensorial maturity		,989	
Berry aroma		,953	
Skin astringency		,945	
Pulp maturity		,938	
Skin maturity		,931	
Skin texture		,908	-,416
Skin bitter	-,458	,883	
Berry colour		,882	
Skin aroma		,865	
Pulp sweetness		,820	-,572
Seed bitterness	,526	,742	,414
Pulp aroma		,736	-,676
pH			,936
Bunch weight			,923
Ripening tecnological Index			-,903
Skin anthocyanins	-,405		-,887
Pulp acidity		,473	,877
Titratable acidity	,482		,848
Seed polyphenols	-,529		-,821
Harvest date	,695		-,712
Seed astringency		,648	,710
Seed aroma	,660		,687

Table 65. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.

Extracting only two components from all the data collected it is possible to explain 84,70% of the total variability (tab. 66).

In particular the first component is greatly linked to the variables that describe technological, phenolic, sensorial characteristics especially regarding seeds except the sensation of bitterness. The second is composed of only sensorial variables (tab. 67).

The graph (fig. 58) shows how the descriptors that are in the same quadrant and that are close to the ripening of the berry are directly correlated to it while those further away are correlated negatively. Berry sensorial maturity is positively correlated with aroma and colour of the berry, maturity and sweetness of the pulp and with texture of the skin. It is negatively correlated, on the contrary, with the variables linked to technological and phenolic richness of the grapes at harvest's time especially regarding pH and mean weight of the berry and of the bunch.

Ripening Technological Index is positively correlated with variables linked to technological and phenolic characteristics and to separation of the pulp.

The first and the second component aren't negatively correlated with any variables.

	Weights of rotated factors		
Component	**Total**	**% variance**	**% cumulated**
1	16,19	49,06	49,06
2	11,76	35,65	84,70

Table 66. Results of the factorial analysis extracting only the first 2 components: method of the principal components.

Variable	Component 1	Component 2
Berry sensorial maturity		,979
Berry aroma		,977
Skin texture		,956
Skin maturity		,933
Pulp maturity		,928
Skin astringency		,912
Pulp sweetness		,889
Skin bitterness		,852
Berry colour		,850
Pulp aroma		,820
Harvest date		
Berry skin weight	,977	
Seed aroma	,952	
Berry weight	,947	
Titratable acidity	,900	
Berry seed weight	,881	
Berry seed number	,869	
Seed maturity	,858	,513
Bunch weight	,815	
Seed hardness	,814	,517
Seed colour	,814	,517
pH	,790	
Seed bitterness	,690	,715
Seed astringency	,673	,564
Pulp acidity	,616	
Skin aroma	-,461	,887
Pulp separation	-,813	
Skin polyphenols	-,842	
Ripening tecnological index	-,844	
Skin Anthocyanins	-,864	
°Brix	-,887	
Seed polyphenol	-,919	
Total polyphenols	-,971	

Table 67. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.
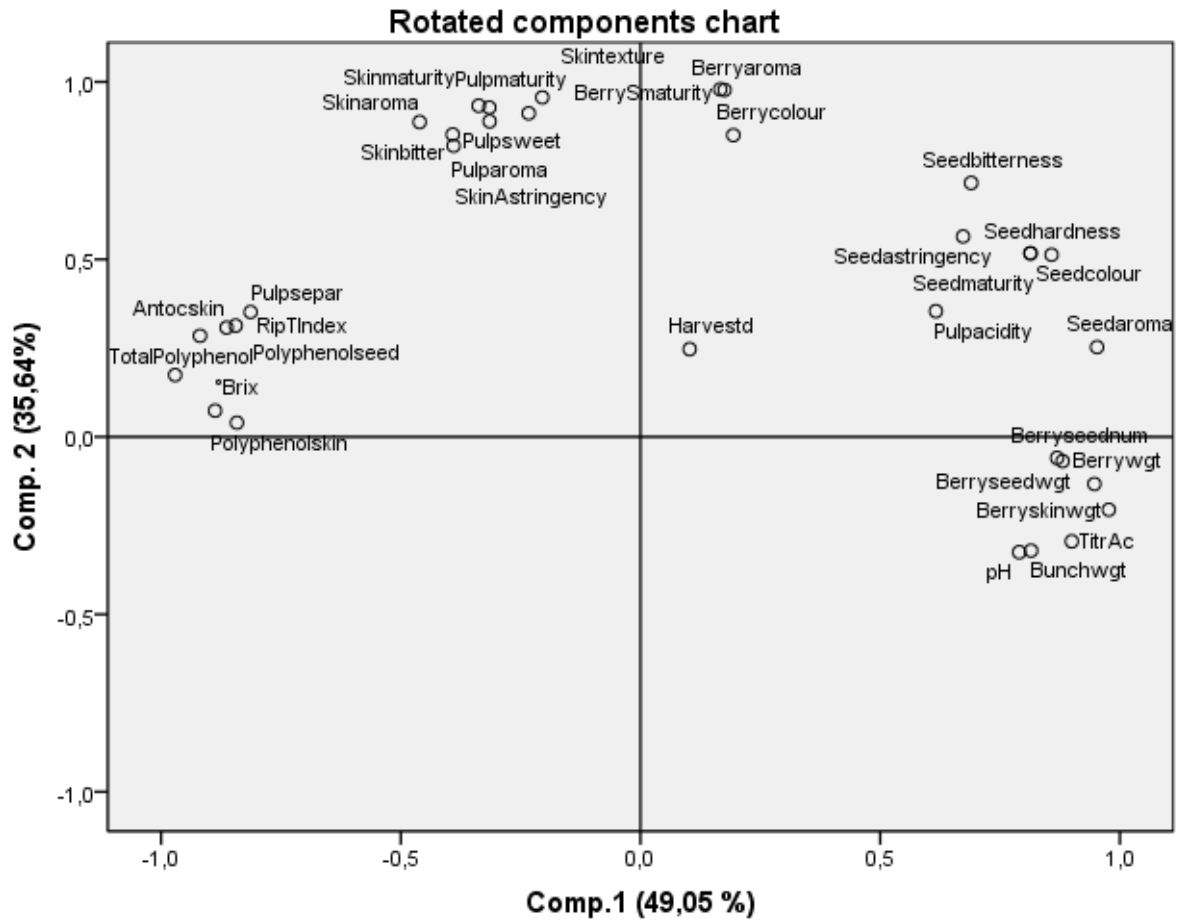
Figure 58. Rotated graph of the first two components obtained from the factorial analysis.

Analyzing the multiple linear regression between the three new components and the berry sensorial maturity it was clear that an important correlation existed and that the berry sensorial maturity experimentally determined is linearly correlated in an important way ($r^2 = 0,967$) to that estimated (tab. 68). Thus the total ripening index of the berry can be expressed as follows (tab. 69).

Berry sensorial maturity = 87,575+F1*1,182+F2*3,910-F3*0,012

From the table of coefficient values for the estimation of the sensorial maturity of the berry, it can be concluded that the model used is of significant importance, however it is more relevant with the component 1 and 2 rather than with 3 one (tab. 69).

Model	R	R-square	R-square correct	Standard deviation Estimate's error
1	,984	,969	,967	1,092

Table 68. Statistic model of relation between the dependant variable of sensorial maturity of the berry and the three new components obtained from factorial analysis.

Coefficients	B	Standard deviation Error	Sig.
(Costant)	87,575	,278	,000
F 1	1,182	,257	,000
F 2	3,910	,116	,000
F 3	-,012	,223	,956

Table 69. Coefficient values for the estimation of the sensorial maturity estimated of the berry, standard error and their significance.

Calculating the relation between berry sensorial maturity expressed and that estimated statistically it can be noted graphically how the ripeness expressed by the panel and that determined statistically are overlapping (fig. 59).
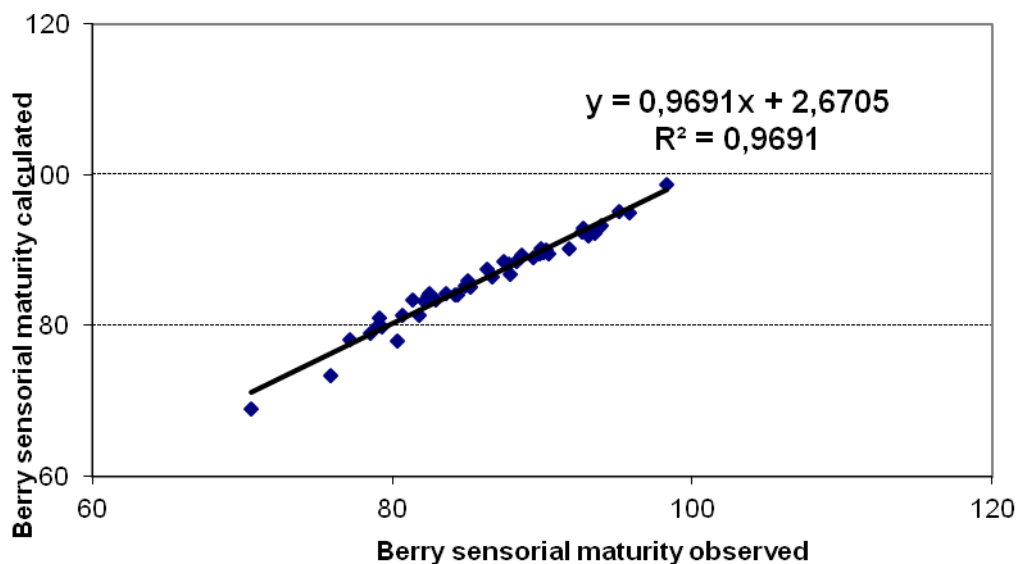
Figure 59. The relation between the ripeness index expressed and that statistically estimated.

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In the table of correlations in the parameters examined in the course of our study, only the variables characterized by a probability < 0,00001 are found on the table (tab. 70). The pH and harvest date are the parameters that don't present significant Pearson's correlations .Most of the variables show a positive Pearson's correlation value. Negative Pearson's correlation values were found in many parameters linked to the weight and among technological and phenolic characteristics.

As foreseen, the variables concerning the ripening of the single berry constituents, global and sensorial ripening are strictly and positively linked to the single parameters that constitute them. There aren't many significant correlation among parameters that influence the technological ripeness, and the phenolic richness and sensorial maturity. Nevertheless, positive Pearson's correlation values were found between °Brix and skin's texture and its maturity and negative between berry colour and berry seeds weight and pulp separation.

Variable	Ber. col.	Pulp sep.	Pulp swe.	Pulp acid.	Pulp aro.	Skin tex.	Skin astr.	Skin aro.	Skin bit.	Seed col.	Seed hard.	Seed bit.	Seed astr.	Seed aro.	Pulp mat.	Skin mat.	Seed mat.	Berry aro.	B. S. M.
Berry colour																			0,65
Pulp separation															0,67				
Pulp sweetness					0,88							0,69	0,64	0,66	0,91		0,69	0,85	0,72
Pulp acidity														0,66	0,72		0,66		
Pulp aroma			0,88									0,68	0,64		0,92		0,68	0,83	0,70
Skin texture																0,71			
Skin astringency								0,89	0,84							0,89			
Skin aroma							0,89		0,84							0,95			
Skin bitterness							0,84	0,84								0,92			
Seed colour														0,65			0,69		0,70
Seed hardness																	0,72		0,65
Seed bitterness			0,69		0,68								0,92	0,89	0,67		0,90	0,77	0,66
Seed astringency			0,64		0,64							0,92		0,91	0,71		0,94	0,80	0,78
Seed aroma			0,66	0,66								0,89	0,91		0,67		0,95	0,81	0,73
Pulp maturity		0,67	0,91	0,72	0,92					0,65		0,67	0,71	0,67			0,75	0,86	0,79
Skin maturity						0,71	0,89	0,95	0,92										
Seed maturity			0,69	0,66	0,68					0,69	0,72	0,90	0,94	0,95	0,75			0,85	0,82
Berry aroma			0,85		0,83							0,77	0,80	0,81	0,86		0,85		0,93
Berry S maturity	0,65		0,72		0,70					0,70	0,65	0,66	0,78	0,73	0,79	0,58	0,82	0,93	

Table 70. Pearson's correlations. Legend abbreviations is on the previous pages.

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Discriminant analysis on the sensorial characteristics of the grapes at harvest's time highlighted differences between clones examined and all may be well distinct (fig. 60).

The first two canonical functions represent more than 98,9 % of the total variability (tab. 71).

Function	Eingenvalue	% of variance	% cumulated	Canonical correlation
1	388,562	80,8	80,8	,999
2	87,138	18,1	98,9	,994
3	3,686	,8	99,7	,887
4	1,596	,3	100,0	,784

Table 71. Eigenvalues of discriminant analysis.

From the centroids graph obtained from the discriminant analysis (fig. 55), it is noted that the points relative to the groups show a very limited dispersion. Five distinct groups appear in the centroid; above all, the number one, is well detached from the other four.

100,0% of the original grouping are classified correctly, and 100,0% of the cases grouped cross-validated are reclassified correctly (tab. 72).
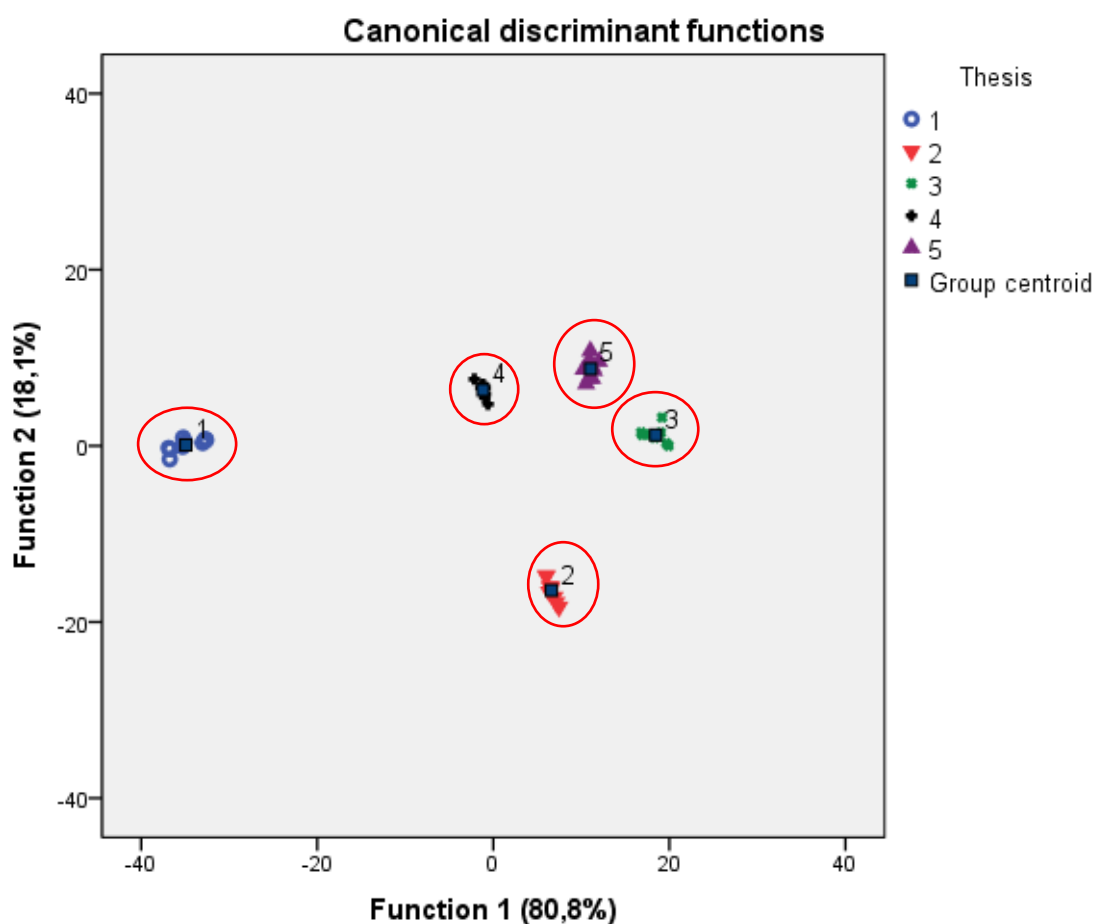
Figure 60. Centroids obtained from the cluster analysis of the sensorial characteristics of the grapes at harvest's time.

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			Group expected					
		Thesis	**1**	**2**	**3**	**4**	**5**	**Totals**
Crtoss- validation a	%	1	100,0	,0	,0	,0	,0	100,0
		2	,0	100,0	,0	,0	,0	100,0
		3	,0	,0	100,0	,0	,0	100,0
		4	,0	,0	,0	100,0	,0	100,0
		5	,0	,0	,0	,0	100,0	100,0

Table 72. Classification results.

a.Cross validation is done only for those cases in the analysis in cross validation, each case is classified by the functions derived from all cases other than that case.

b.100,0% of original grouped cases correctly classified.

c.100,0% of cross-validated grouped cases correctly classified.

3.8 Tecnological and phenolic characteristics of the grapes at harvest's time

Variable	Abbreviation	Units
pH	pH	n
Sugary content	°Brix	°Brix
Titratable acidity	Titr Ac	g/L
Ripening Index*	Rip Index	n
Bunch weight	Bunch wgt	g
Berry weight	Berry wgt	g
Berry seed number	Berry seed num	n
Berry skin weight	Skin wgt/berry	g/berry
Berry seed weight	Seed wgt/berry	g/berry
Anthocyanins/berry	Anth/berry	mg/berry
Skins	% skin	%
Skin Anthocyanins	Anth skin	mg/Kg
Skin Polyphenols	Polyph skin	mg/Kg
Skin polyphenols percentage	% Skin polyph	%
Seed polyphenols percentage	Polyph seed	mg/Kg
Seed percentage	Seeds %	%
Polyphenols/berry (mg/Kg)	Polyph/berry	mg/berry
Total Polyphenols	Tot Polyph	mg/Kg

*Ripening Tecnological Index was so calculated °Brix/Titratable acidity

Table 73. List of abbreviations.

MANOVA was also conducted by examining the parameters (tab. 73) linked to the laboratory analysis of the grapes (tab. 73) (using the values of three repeated analysis of 17 theses each year for three years), studying the importance of the variables in function of the chosen source (tab. 74).

Factor	Dependent variable	F	Sig.
Thesis	Bunch weight	28579,211	,000
	Berry weight	14,811	,000
	pH	70,538	,000
	°Brix	68,658	,000
	Titratable acidity	28,239	,000
	Ripening index*	30,587	,000
	Berry skin weight	14,126	,000
	Skins %	9,625	,000
	Berry seed number	9,422	,000
	Seed weight/berry	1,302	,211
	Seeds %	1,246	,247
	Anthocyanins skin	5,571	,000
	Polyphenols skin	4,916	,000
	Polyphenols seed	5,540	,000
	Total polyphenols	6,253	,000
	% Skinpolyphenols	3,611	,000
	Anthocyanins/berry	4,118	,000
	Polyphenols/berry	4,635	,000

Factor	Dependent variable	F	Sig.
Year	Bunch weight	7483,430	,000
	Berry weight	87,936	,000
	pH	407,945	,000
	°Brix	5,791	,004
	Titratable Acidity	80,129	,000
	Ripening Index*	21,621	,000
	Berry skin weight	145,787	,000
	Skins %	33,965	,000
	Berry seed number	10,181	,000
	Seed weight/berry	,213	,808
	Seeds %	1,499	,228
	Anthocyanins skin	9,777	,000
	Polyphenols skin	31,049	,000
	Polyphenols seed	39,459	,000
	Total polyphenols	21,332	,000
	% Skinpolyphenols	46,425	,000
	Anthocyanins/berry	1,365	,260
	Polyphenols/berry	12,226	,000

Factor	Dependent variable	F	Sig.
Thesis * Year	Bunch weight	8920,264	,000
	Berry weight	11,484	,000
	pH	26,873	,000
	°Brix	17,680	,000
	Titratable acidity	10,196	,000
	Ripening Index*	12,356	,000
	Berry skin weight	6,359	,000
	Skins %	3,276	,000
	Berry seed number	4,643	,000
	Seed weight/berry	1,141	,304
	Seeds %	,948	,554
	Anthocyanins skin	3,878	,000
	Polyphenols skin	3,226	,000
	Polyphenols seed	3,868	,000
	Total polyphenols	4,511	,000
	% Skinpolyphenols	2,451	,000
	Anthocyanins/berry	3,962	,000
	Polyphenols/berry	5,211	,000

Table 74 a, b, c. Test of the effects between subjects (p=<0,05).

All the dependant variables proved to be statistically significant, except two parameters linked to seeds mean weight/berry and the seed weight percentage compared to the other components of the berry. Such variables do not change their level of significance if, the factor chosen during the statistical analysis, is that of the thesis or the year or interaction between the two. However choosing the year, a non significant statistical variable, anthocyanins /berry is added.

By using the data previously obtained the level of variability attributable to the different factor was calculated (tab. 75).

For most of the parameters the greater variability is attributable to the year as shown in the values for the berry weight, pH, titratable acidity, berry skin weight, skins %, skin polyphenols, seed polyphenols, total polyphenols and % skin polyphenols. The thesis, however, shows more variability as concerns bunch weight and °Brix, while the other parameters show comparable levels of variability attributable to the different source.

High percentage value of error in the two variables linked to the seeds was found.

Variable	% variability due to the thesis	% variability due to the year	% variability due to interaction thesis/year	% variability due to error
Bunch weight	63,53	16,64	19,83	0,00
Berry weight	12,85	76,31	9,97	0,87
pH	13,93	80,56	5,31	0,20
°Brix	73,72	6,22	18,98	1,07
Titratable acidity	23,62	67,02	8,53	0,84
Ripening Index	46,65	32,98	18,85	1,53
Berry skin weight	8,45	87,16	3,80	0,60
Skins %	20,11	70,96	6,84	2,09
Berry seed number	37,32	40,33	18,39	3,96
Seed weight/berry	35,61	5,83	31,20	27,35
Seeds %	26,56	31,94	20,20	21,31
Skin anthocyanins	27,55	48,34	19,17	4,94
Skin polyphenols	12,23	77,25	8,03	2,49
Seed polyphenols	11,11	79,13	7,76	2,01
Total polyphenols	18,89	64,45	13,63	3,02
% Skin polyphenols	6,75	86,80	4,58	1,87
Anthocyanins/berry	39,42	13,07	37,94	9,57

Table 75. Level of variability attributable to the different factor.

From Tukey's statistic test it is possible to note the table with the different subsets and those non differentiated (tab. 76-78). The significant variables that create the most differentiated homogenous subsets are those linked to the weight of the berry and the weight of the bunch. The values obtained from the analysis of the latter form a number of subsets equal to the number of theses that indicate great variability in the samples tested, the mean weight of the bunch lies between the minimum value of 167 grams and a maximum of 356 grams, both belonging to the two thesis of the 'Brunello di Montalcino' denomination. Moreover the two thesis mentioned above also differ in the mean weight of the berry, but a lower number of varied homogenous subsets are formed.

Regarding the pH the values shown are lower in one thesis of the 'Chianti Classico' and higher in one of 'Montecucco', the °Brix grade showing the highest value from one thesis from the 'Brunello di Montalcino' production area, and the lowest from the 'Chianti Classico' area (tab. 76).

The other grapes from the three remaining theses, exception made for those from the 'Morellino di Scansano', show medium to high sugar levels, reaching over 28 °Brix. Moreover the 'Brunello di Montalcino' denomination shows greater variability in their theses if compared to 'Montecucco' (tab. 76).

Regarding titratable acidity, the highest values are found in one thesis in the grapes of the 'Chianti Classico' and in one of 'Montecucco', while the lowest value in the vineyard of the 'Chianti Classico' in the 'Chianti Colline Pisane' (tab. 76), with average values in the remaining vineyards. Excluding extreme values, within the denominations there is no notable variability of data.

As for the standard of polyphenols, the mean value is average to low, the overall total is less present in the 'Chianti Classico' thesis already highlighted as having the lowest pH values and sugar levels. The 'Brunello di Montalcino' thesis, that stands out for its mean value of 3700 mg/Kg of polyphenols expressed as catechin, is that already noted for the highest °Brix value and for having the lightest berry and bunch (tab. 76). Analysing the total anthocyanins content two theses emerged as not being notable for the other variables. The lowest value belongs to a 'Brunello di Montalcino' thesis while the highest to that of the 'Montecucco' thesis. Among the variables that are not statistically different seed, weight/berry and anthocyanins /berry gave to different subsets unlike seeds % (tab. 78).

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Thesis	Bunch weight (g)	Berry weight (g)	pH	°Brix	Titratable Acidity (g/L)	Ripen. Index	Berry skin weight (g)	Skins %
CCP 1	191,85 b	1,99 bcd	3,60 l	24,61 c	5,01 a	5,04 g	0,39 abc	0,19 ab
MC 1	257,04 i	1,81 b	3,43 gh	25,07 cd	6,96 f	3,66 cd	0,38 ab	0,20 ab
MC 2	239,37 f	2,07cde	3,44 gh	24,82 cd	8,07 h	3,12 bc	0,39 abc	0,19 a
MC 3	335,51 r	2,24 de	3,50 i	23,27 b	6,45 c-f	3,64 cd	0,42 a-d	0,18 a
MC 4	200,37 d	2,00 bcd	3,51 i	25,60 cd	6,33b-f	4,078 def	0,37 a	0,18 a
MC 5	249,52 h	1,87bc	3,67 l	25,05 cd	6,09 b-e	4,11 def	0,37 a	0,19 ab
MC 6	328,79 q	1,97 bcd	3,47 hi	25,89 d	6,40 b-f	4,04 def	0,40 a-d	0,20 ab
MS 1	318,47o	2,09 de	3,30 cd	20,75 a	5,86 bc	3,71 cd	0,39 abc	0,18 a
BM 1	267,11 l	2,33 fg	3,29 cd	25,46 cd	5,82 bc	4,43 ef	0,61 g	0,26 cd
BM 2	242,82 g	1,95bcd	3,34 def	25,31 cd	5,74 abc	4,58 fg	0,46 c-f	0,24 bc
BM 3	195,162 c	1,99 bcd	3,37 ef	25,62 cd	5,88 bc	4,48 ef	0,47 c-f	0,23 bc
BM 4	274,47 n	2,25 efg	3,31 cde	24,97 cd	6,04 bcd	4,16 def	0,48 def	0,21 ab
BM 5	166,08 a	1,607 a	3,38 fg	28,62 e	5,55 ab	5,75 h	0,40 a-d	0,26 cd
BM 6	270,36 m	2,43 g	3,26 bc	23,57 b	6,73 def	3,59 cd	0,52 ef	0,23 abc
BM 7	355,55 s	1,97bcd	3,23 b	25,53 cd	6,78 def	3,89 de	0,55 fg	0,283 d
CC 1	230,09 e	2,09 de	3,28 bcd	20,37 a	6,92 ef	2,97 ab	0,43 a-d	0,20 ab
CC 2	327,45 p	2,14de	3,2 0 a	20,98 a	9,04 i	2,44 a	0,45 a-d	0,21 ab

Table 76. Significant parameters with different and non differentiated subsets. Tukey Test (p=0,05).

Thesis	Berry seed number	Anthocya-nins Skin (mg/Kg)	Polyphe-nols Skin (mg/kg)	Polyphe-nols Seed (mg/kg)	Total Polyphe-nols (mg/kg)	% Skin Polyphe-nols	Polyphe-nols /berry (mg/berry)
CCP 1	2,01 b-e	522abc	1587 a-d	1607 cde	3195 b-e	50 b	6 abcd
MC 1	2,38 def	728d	1703 bcd	1740 e	3443 de	50 b	6 abcd
MC 2	2,48 f	630 bcd	1786 cd	1373 a-e	3160 b-e	43 ab	6 bcd
MC 3	2,56 f	661bcd	1292 a	1351 a-e	2644 ab	49 b	5 abc
MC 4	2,31 b-f	615 bcd	1547 abc	1465 b-e	3013 a-d	48 b	6 abc
MC 5	2,42 ef	594 bcd	1734 bcd	1440 a-e	3174 b-e	44 ab	5 abc
MC 6	2,20 b-f	580 bcd	1596 a-d	168 de	3282 cde	51 b	6 bcd
MS 1	2,32 def	513 abc	1493 abc	1360 a-e	2853 a-d	47 b	6 abc
BM 1	2,60 f	359 a	1432 abc	1408 a-e	2841 a-d	49 b	6 bcd
BM 2	2,16 b-f	569 bcd	1581 a-d	1260 a-d	2842 a-d	44 ab	5 ab
BM 3	1,56 a	473 ab	1518 abc	1289 a-d	2807 abc	45 b	6 abc
BM 4	1,87 abc	521 abc	1382 ab	1193 abc	2575 ab	46 b	5 abc
BM 5	1,93 a-d	671 cd	1949 d	1780 e	3729 e	47 b	5 abc
BM 6	2,19 b-f	487 abc	1504 abc	1482 -e	2987 a-d	47 b	7 d
BM 7	1,78 ab	653 bcd	1781 cd	1028 a	2810 abc	35 a	5 a
CC 1	2,15 bcdef	624 bcd	1753 bcd	1440 a-e	3194 b-e	45 b	6 bcd
CC 2	2,37 def	508 bc	1430 abc	1092 ab	2522 a	42 ab	5 ab

Table 77. Significant parameters with non differentiated subsets. Tukey Test (p=0,05).

Thesis	Seed weight/berry (g/berry)	Seeds %	Anthocyanins /berry (mg/berry)
CCP 1	0,09 ab	0,05 a	1,01 a-d
MC 1	0,10 ab	0,05 a	1,31 cd
MC 2	0,10 ab	0,05 a	1,36 d
MC 3	0,10 ab	0,04 a	1,33 d
MC 4	0,12 ab	0,06 a	1,23 bcd
MC 5	0,08 ab	0,04 a	1,10 a-d
MC 6	0,11 ab	0,06 a	1,13 a-d
MS 1	0,09 ab	0,04 a	1,06 a-d
BM 1	0,11 ab	0,05 a	0,87 a
BM 2	0,09 ab	0,04 a	1,09 a-d
BM 3	0,06 a	0,03 a	0,93 ab
BM 4	0,08 ab	0,03 a	1,15 a-d
BM 5	0,07 ab	0,05 a	0,97 abc
BM 6	0,10 ab	0,04 a	1,20 a-d
BM 7	0,07 ab	0,03 a	1,26 bcd
CC 1	0,08 ab	0,04 a	1,26 bcd
CC 2	0,22 b	0,10 a	1,08 a-d

Table 78. Non significant parameters with non differentiated subsets. Tukey Test (p=0,05).

From the multivariate analysis factor choice, the year and the Tukey statistic test it appears that most of the parameters tested originate differentiated subsets, exception made for the variables seed weight/berry, anthocyanins/berry and seed%. In bunch weight, berry weight, pH, berry skin weight, skins% and seed polyphenols, instead, it is the variables that create well differentiated subsets that indicate a great variability of data in the three year period studied. The year 2009 shows the highest parameters that influence the technological ripeness of the grapes while in the following two years higher quantities of polyphenols are registered (tab.79).

Variable	2009	2010	2011
Bunch weight (g)	274,97 c	251,167 a	259,16 b
Berry weight (g)	2,26 c	1,85 a	2,03 b
pH	3,53c	3,28 a	3,35 b
°Brix	24,60 b	24,58 b	24,15 a
Titratable acidity (g/L)	6,08 a	7,24 b	6,04 a
Ripening Index	4,21 b	3,68 a	4,06 b
Berry skin weight (g)	0,54 c	0,35 a	0,44 b
Skins %	0,24 c	0,19 a	0,22 b
Berry seed number	2,34 b	2,16 a	2,07 a

Variable	2009	2010	2011
Seed weight/berry (g/berry)	0,10 a	0,11 a	0,10 a
Seeds %	0,04 a	0,06 a	0,05 a
Skin anthocyanins (mg/Kg)	513 a	609 b	591 b
Skin polyphenols (mg/Kg)	1528 a	1452 a	1797 b
Seed polyphenols (mg/Kg)	1193 a	1662 c	1380 b
Total polyphenols (mg/Kg)	2721 a	3115 b	3177 b
% Skin polyphenols	43,08 a	52,86 b	43,37 a
Anthocyanins/berry(mg/Kg)	1,15 a	1,10 a	1,17 a
Polyphenols/berry (mg/Kg)	6,08 b	5,64 a	6,32 b

Table 79. Mean separation by multiple range test (Tukey); the comparison is among data shown in horizontal.

In using the factorial statistic analysis it was possible to put together all the variables noted and calculated in four new complex variables (components) so as to represent 92,53% of the total variability of the macro structural characteristics of the berries at harvest (tab. 80). The descriptors that represent the highest coefficients (tab. 81) operate in a more reliable way in determining the characteristics of technological ripeness and phenol ripeness of the berries at harvest. The first component is tied to the weight of the bunch, to the number and grade of the polyphenols in the seeds, to the percentage and weight of the skins, the second, instead, to the weight of the berry and to the polyphenols per berry. The total polyphenols, of the skins and the polyphenols per berry, anthocyanins of the skins and per berry are the variables that characterize the third component calculated by factorial analysis while the fourth by the seed as a percentage value compared to the other components of the berry and as weight expressed in grams (tab. 81).

	Weights of rotated factors		
Component	Total	% variability	% cumulated
1	5,62	31,23	31,23
2	4,53	25,15	56,39
3	4,20	23,34	79,73
4	2,30	12,80	92,53

Table 80. Results of the factorial analysis: principal components method.

Variable	Component			
	1	2	3	4
Seed Polyphenols	,955			
Bunch weight	,768	-,605		
% Skin polyphenols	,754		-,625	
Berry seed number	,735			,459
Total polyphenols			,767	
Skin anthocyanins		-,442	,779	
Seeds %		-,493		,762
Anthocyanins/berry			,957	
Titratable acidity		-,927		
Seed weight/berry				,976
Skin polyphenols			,927	
Polyphenols /berry		,790	,507	
°Brix		,501	,582	
pH	-,649	,441		-,490
Berry weight	-,662	,729		
Berry skin weight	-,848	,420		
Skins %	-,863			

Table 81. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.

Extracting only two components from all the data collected it is possible to explain 69,85% of the total variability (tab. 82).

In particular the first component is greatly linked to the polyphenol content of the skin, to the total polyphenols, to the mean weight of the berry and to that of the seed in terms of the total weight of the berry, to the total of pH and acidity. The second on the other hand, to the polyphenols of the seeds and to the grade of polyphenols per berry (tab. 83).

The graph (fig. 61) shows how the descriptors that are in the same quadrant and that are close to the ripening of the berry are directly correlated to it while those further away are correlated negatively. The Ripening Index is indeed positively correlated with the sugar level and with the grade of polyphenols in the berry and skins and negatively with the parameters tied to the characteristics of the seed. Moreover the first component is positively correlated with all the variables examined, while the second is correlated only in part, in fact it is tied negatively to the acidity measure worthy of note, to the polyphenols present in the skins and seeds and to the average weight of the seeds and of the bunch.

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	Weights of rotated factors		
Component	Total	% variance	% cumulated
1	6,50	36,13	36,13
2	6,07	33,72	69,85

Table 82. Results of the factorial analysis extracting only the first 2 components: method of the principal components.

Variable	Component	
	1	2
Skin polyphenols	,829	
Total polyphenols	,765	
Berry weight	,760	-,577
Seed weight/berry	,667	,043
% Skin polyphenols	,645	,712
Polyphenols /berry	,542	,715
Skin anthocyanins	,541	-,630
Anthocyanins/berry		-,606
Ripening Index		-,548
Seed Polyphenols		,888
Seeds %		-,317
Titratable acidity		,850
Berry skin weight		,789
Polyphenols/berry		,929
pH	-,762	,542
°Brix	-,834	
Berry seed number	-,895	
Skins %	-,913	

Table 83. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance .
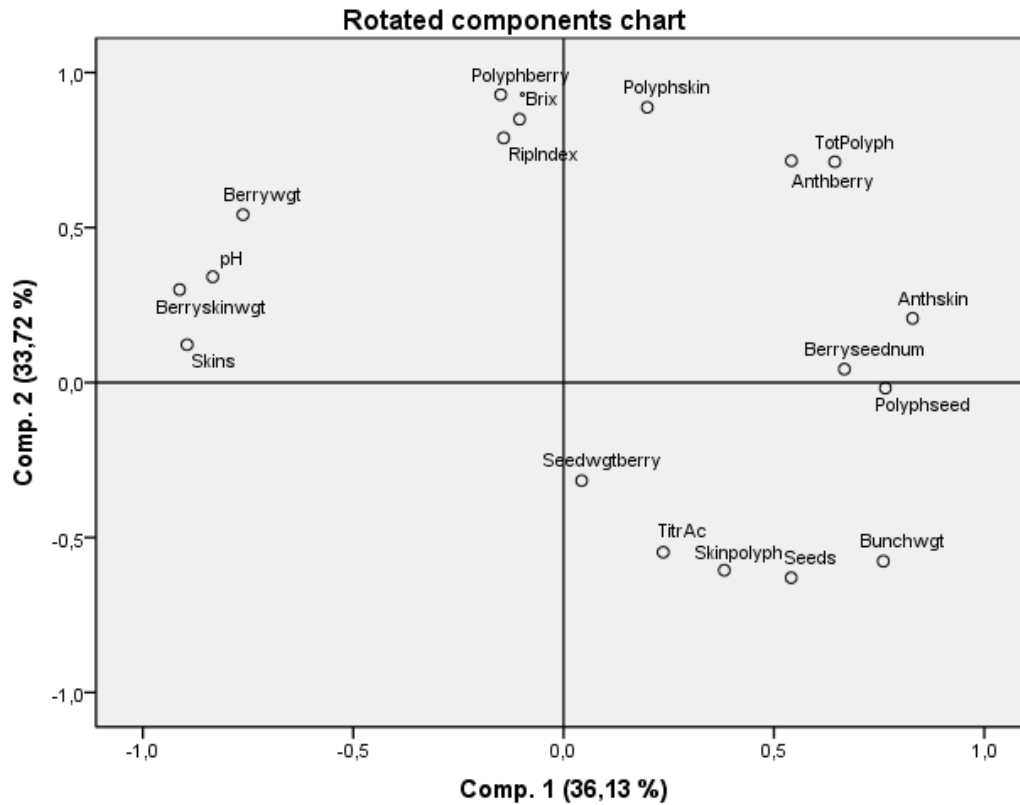
Figure 61. Rotated graph of the first two components obtained from the factorial analysis.

Analysing the multiple linear regression in the four new components and the ripeness index of the berry, it is possible to note that there is a significant correlation and that the total ripeness of the berry obtained experimentally is linearly correlated in a significant way ($r^2 = 0,822$) to that estimated in (tab. 84). Therefore, the total ripeness index of the berry can be expressed in the following way (tab. 85).

Ripening Index $=3,241-F1*0,124+F2*0,729+F3*0,236-F4*0,078$

From the table of coefficient values for the estimation of the total ripeness of the berry, it can be concluded that the model used is of significant importance, that the Ripening Index variable, is more relevant with the last three constants rather than with the first (tab. 84).

Model	R	R-square	R-square correct	Standard deviation Estimate's error
1	,907	,822	,818	,470

Table 84**.** Statistic model of relation between the dependant variable of total ripeness of the berry and the four new components obtained from factorial analysis.

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Coefficients	B	Standard deviation Error	Sig.
(Costant)	3,241	,048	,000
F 1	-,124	,052	,018
F 2	,729	,031	,000
F 3	,236	,048	,000
F 4	-,078	,013	,000

Table 85. Coefficient values for the estimation of the total maturity estimated of the berry, standard error and their significance.

Calculating the relation between the index ripeness expressed and that estimated statistically it can be seen graphically how the ripeness expressed by the panel and that determined statistically are overlapping (fig. 62).
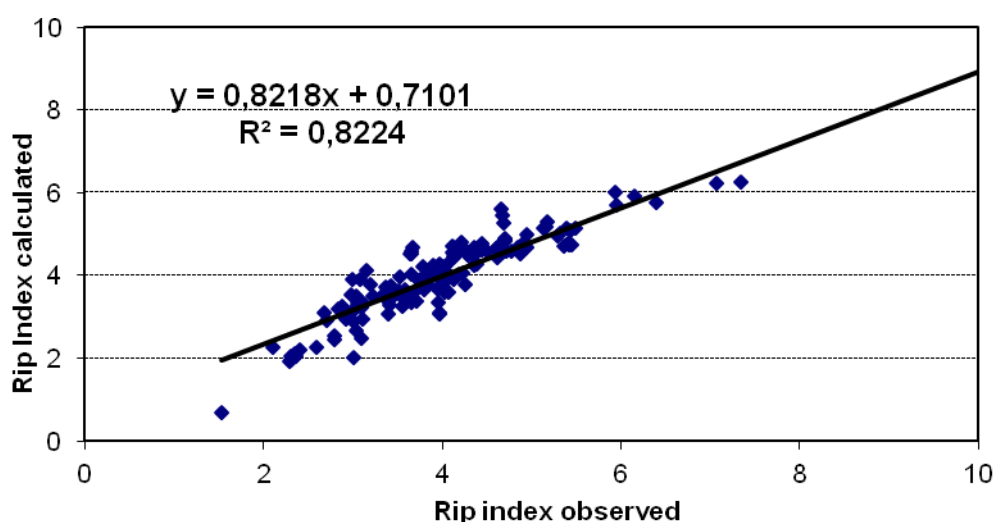
Figure 62. The relation between the ripeness index expressed and that statistically estimated.

Examining the correlation between the parameters analyzed, in the table only the variables with a probability <0,00001 are reported. and the characters in bold indicate the negativity of the value indicated.

In most cases there are values of Pearson's correlation positive. However the parameters connected with the weight of the bunch, and grape skins, are negatively correlated with levels of total polyphenols, and polyphenols found in the skins and seeds (tab. 86).

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	Bunch wgt	Berry wgt	pH	°Brix	Titr ac	Rip Index	Berry skin wgt	Skins %	Berry seed num	Seed wgt/ berry	Seeds %	Skin anth	Skin polyph	Seed polyph	Tot polyph	% Skin polyph	Anth/ berry	Polyph/ berry	F 1	F 2	F 3	F 4
Bunch weight				**0,42**										**0,36**	**0,37**					**0,40**		
Berry weight				**0,33**		**0,29**	0,70		0,43			**0,46**	**0,46**	**0,50**	**0,62**			**0,41**	0,47		**0,36**	
pH					**0,39**																0,44	
°Brix	**0,42**	0,33				0,57															0,51	0,34
Titr Acidity			**0,39**			**0,82**													**0,34**	**0,81**		
Rip Index				0,57	**0,82**														0,37	0,87		
Berry skin weight		0,70						0,70				**0,33**		0,50	0,46	**0,34**			**0,53**			
Skins %							0,70									0,33						
Berry seed number		0,43																				
Seed weight/berry											0,98								**0,58**			0,99
Seeds %										0,98									**0,49**		0,27	0,96
Anthocyanins skin		**0,46**					**0,33**						0,42		0,38		0,75				0,72	
Polyphenols skin		**0,46**										0,42			0,72	**0,41**					0,72	
Polyphenols seed	**0,36**	**0,50**					**0,50**								0,83	0,78		0,39	0,74			
Total Polyphenols	**0,37**	**0,62**					**0,46**					0,38	0,72	0,83				0,44	0,60		0,47	
% Skin polyphenols							**0,34**	**0,33**					**0,41**	0,78					0,59		**0,38**	
Anthocyanins berry												0,75									0,54	
Polyphenols/ berry		0,41												0,39	0,44							
F 1		0,47			**0,34**	0,37	**0,53**			**0,58**	**0,49**			0,74	0,60	0,59				0,37		**0,62**
F 2	**0,40**		0,44	0,51	**0,81**	0,87													0,37			
F 3		**0,36**		0,34								0,72	0,72		0,47	**0,38**	0,54					
F 4										0,99	0,96								**0,62**			

Table 86. Pearson's correlations. Bold numbers are preceded by the minus sign. Legend abbreviations is on the previous pages.

The statistical analysis was also used to investigate the features and possible statistically significant differences of the grapes coming from the theses as part of the same Denomination of Origin. The theses, divided in 'Montecucco', were then subjected to MANOVA, factorial, discriminating, linear regression and correlation analysis.

Among the theses coming from the area of 'Montalcino' was also studied the case of 'Col D'Orcia' estate in order to study in detail the clone effect grown in the same site of cultivation.

3.8.1 'Montecucco' area

As results from the MANOVA, statistically significant parameters do not remain the same if the factor chosen during the statistical analysis is changed. Berry's and bunch's weight, pH, titratable acidity, ripening index, the percentage of polyphenols of skins and polyphenols per berry represent the dependent variables that remain no statistically different. The parameters related to polyphenols become no significant when the factor is represented by year or interaction year by thesis (tab. 87).

Factor	Dependent variable	F	Sig.	Factor	Dependent variable	F	Sig.
Thesis	Bunch weight	13303,90	,000	Year	Bunch weight	11899,079	,000
	Berry weight	14,306	,000		Berry weight	33,938	,000
	pH	10,549	,000		pH	74,902	,000
	°Brix	16,301	,000		°Brix	2,184	,131
	Titratable acidity	17,630	,000		Titratable acidity	21,076	,000
	Ripening Index	19,012	,000		Ripening Index	12,819	,000
	Berry skin weight	,864	,517		Berry skin weight	52,663	,000
	Skins %	1,009	,430		Skins %	30,503	,000
	Berry seed number	,598	,702		Berry seed number	4,494	,020
	Seed weight/berry	1,650	,179		Seed weight/berry	,591	,560
	Seeds %	1,253	,311		Seeds %	,577	,568
	Skin anthocyanins	2,920	,030		Skin anthocyanins	2,207	,128
	Skin polyphenols	2,260	,075		Skin polyphenols	17,000	,000
	Seed polyphenols	2,791	,035		Seed polyphenols	9,198	,001
	Total polyphenols	1,546	,207		Total polyphenols	,395	,677
	% Skin polyphenols	5,330	,001		% Skin polyphenols	41,904	,000
	Anthocyans / berry	3,166	,021		Anthocyans /berry	,690	,509
	Polyphenols/berry	2,766	,037		Polyphenols/berry	10,682	,000

Factor	Dependent variable	F	Sig.
Thesis * Year	Bunch weight	3622,812	,000
	Berry weight	13,204	,000
	pH	11,079	,000
	°Brix	17,868	,000
	Titratable acidity	4,188	,003
	Ripening Index	4,018	,003
	Berry skin weight	3,594	,007
	Skins %	2,991	,017
	Berry seed number	3,536	,007
	Seed weight/berry	1,178	,346
	Seeds %	1,610	,172
	Skin anthocyanins	3,775	,005
	Skin polyphenols	1,264	,302
	Seedpolyphenols	3,796	,005
	Total polyphenols	3,192	,012
	% Skin polyphenols	1,727	,142
	Anthocyans /berry	3,447	,008
	Polyphenols/berry	2,587	,033

Table 87 a, b, c. Test of effects between subjects (p=<0,05).

By using the data previously obtained the level of variability attributable to the different factor was calculated (tab. 88). For most of the parameters the variability is attributable to the year; the thesis, however, shows more variability as concerns ripening index, the other parameters show comparable levels of variability attributable to the different factor.

Variable	% variability due to the thesis	% variability due to the year	% variability due to interaction thesis/year	% variability due to error
Bunch weight	46,15	41,28	12,57	0,00
Berry weight	22,91	54,35	21,14	1,60
pH	10,82	76,80	11,36	1,03
°Brix	43,64	5,85	47,83	2,68
Titratable acidity	40,16	48,02	9,54	2,28
Ripening Index	51,60	34,79	10,90	2,71
Berry skin weight	1,49	90,61	6,18	1,72
Skins %	2,84	85,92	8,42	2,82
Berry seed number	6,21	46,68	36,73	10,39
Seed weight/berry	37,33	13,38	26,65	22,63
Seeds %	28,23	12,99	36,25	22,52
Skin anthocyanins	29,49	22,29	38,12	10,10
Skin polyphenols	10,50	78,98	5,87	4,65
Seedpolyphenols	16,63	54,80	22,62	5,96
Total polyphenols	25,20	6,45	52,05	16,30
% Skin polyphenols	10,67	83,87	3,46	2,00
Anthocyans /berry	38,13	8,31	41,51	12,04
Polyphenols/berry	16,24	62,71	15,18	5,87

Table 88. Level of variability attributable to the different factor.

From Tukey's statistic test it is possible to note the table with the different subsets and those non differentiated (tab 89-91). The significant variables that create the most differentiated homogenous subsets are those linked to the mean weight of the bunch, to the sugary and acids content, to the ripening index, and to the percentage of polyphenols contained in the skin.

The values obtained from the analysis of the mean weight of the bunch form a number of subsets equal to the number of thesis that indicate great variability in the samples tested, indeed this variable lies between the minimum value of 200 grams and a maximum of 300 grams. The sugar concentration is medium high; the thesis with the lowest value shows about 24° Brix and the one with the highest value is reaching over 28 °Brix: this latter thesis is the same already mentioned for the heaviest bunch which also differs from the others for the greatest total polyphenols content and the lowest in anthocyanins.

The berries of the theses show good values of total acidity, this variable in one case has reached 8 g/L (tab. 90-91).

Between not statistically different variables, only the variable seed weight/berry originates different subsets (tab. 91).

Thesis	Bunch weight (g)	Berry weight (g)	pH	°Brix	Titratable Acidity (g/L)	Ripen. Index	Skin Anthocya-nins (mg/kg)	Seed Polyphe-nols (mg/Kg)
MC 1	255,47 d	1,75a	3,42 ab	25,07 b	6,92 a	3,68 bc	737b	1817 ab
MC 2	239,37 c	2,07 b	3,43 ab	24,82 ab	8,07 b	3,12 a	661 ab	1374 a
MC 3	290,30 e	2,09 b	3,41 a	23,97 a	6,98 a	3,45 ab	694 ab	1685 ab
MC 4	200,37 a	2,00 b	3,51 bc	25,6 bc	6,33 a	4,07 cd	615ab	1465 ab
MC 5	219,37 b	1,67 a	3,55 c	26,25 c	6,32 a	4,16 d	602 ab	1698 ab
MC 6	305,71 f	2,02 b	3,56 c	27,6 d	6,50 a	4,25 d	498 a	1906 b

Table 89. Significant parameters with differentiated subsets. Tukey Test (p=0,05).

Thesis	Polyphenols/ berry (mg/berry)	% Skin Polyphenols	Anthocyanins/ berry (mg/berry)
MC 1	6,14 ab	50,86 bc	1,29 a
MC 2	6,50 ab	43,19 a	1,36 a
MC 3	6,47 ab	53,04 bc	1,36 a
MC 4	5,99 ab	48,27 ab	1,23 a
MC 5	5,75 a	48,94 ab	1,00 a
MC 6	6,86 b	56,21 c	1,00 a

Table 90. Significant parameters with different and non differentiated subsets. Tukey Test (p=0,05).

Thesis	Berry skin weight	Skins %	Berry seed number	Seeds %	% Skin Polyphenols	Total Polyphenols (mg/kg)	Seed weight/ berry
MC 1	0,36 a	0,20 a	2,42 a	0,06 a	1735,10 a	3552 a	0,10 ab
MC 2	0,39 a	0,19 a	2,49 a	0,05 a	1786,98 a	3161 a	0,10 ab
MC 3	0,36 a	0,17 a	2,42 a	0,04 a	1464,91 a	3149 a	0,09 ab
MC 4	0,37 a	0,18 a	2,31 a	0,06 a	1547,87 a	3013 a	0,12 b
MC 5	0,30 a	0,18 a	2,23 a	0,04 a	1769,04 a	3467 a	0,07 a
MC 6	0,38 a	0,19 a	2,42 a	0,05 a	1489,25 a	3395 a	0,10 ab

Table 91. Non significant parameters with different and non differentiated subsets. Tukey Test (p=0,05).

The year appears the most of the parameters tested originate differentiated subsets, exception made for total polyphenols and for variables related to anthocyanins and to seeds. The year 2009 shows the highest parameters that influence the technological ripeness of the grapes at the harvest while in the following two years higher quantities of polyphenols are registered (tab. 92).

Variable	2009	2010	2011
Bunch weight	229,96 a	237,31 b	272,84 c
Berry weight	2,12 c	1,78 a	1,99 b
pH	3,67 c	3,44 b	3,38 a
°Brix	26,20 b	25,51 a	24,92 a
Titratable acidity	6,86 b	7,36 c	6,38 a
Ripening Index	3,88 b	3,53 a	3,94b
Berry skin weight	0,47 c	0,28 a	0,38 b
Skins %	0,22 c	0,15 a	0,19 b
Berry seed number	2,65 b	2,26 a	2,34 a
Seed weight/berry	0,11 a	0,09 a	0,09 a
Seeds %	0,05 a	0,05 a	0,05 a
Skin anthocyanins	590,39 a	684,46 a	622,34 a
Skin polyphenols	1719,39 b	1399,44 a	1875,36 b
Seed polyphenols	1494,45 a	1873,56 b	1443,98 a
Total polyphenols	3213,84 a	3272,00 a	3319,34 a
% Skin polyphenols	45,49 a	57,14 b	43,35 a
Anthocyans /berry	1,26 a	1,20 a	1,20 a
Polyphenols/berry	6,79 b	5,74 a	6,52 b

Table 92. Mean separation by multiple range test (Tukey); the comparison is among data shown in horizontal.

By using the factorial statistic analysis it was possible to put together all the variables noted and calculated in four new complex variables (components) so as to represent 95,49% of the total variability of the technological characteristics of the berries at harvest (tab. 93). The descriptors that represent the highest coefficients (tab. 94) operate in a more reliable way in determining the characteristics of technological ripeness and phenol resources of the berries at harvest.

There are only three values of the coefficients less than 0.4, including two linked to the titratable acidity, and then all remaining variables have influence for the purpose of analysis.

The first component is tied to the most of the parameters studied except for the value of total acidity, mean weight of berry and of anthocyanins present in the skins; these values are associated with the second component. The last component is characterized, however, to pH and polyphenols content of skins (tab. 94).

	Weights of rotated factors		
Component	Total	% variability	% cumulated
1	8,91	49,51	49,51
2	5,28	29,35	78,87
3	2,99	16,63	95,49

Table 93. Results of the factorial analysis: principal components method.

Variable	Component		
	1	2	3
Polyphenols/berry	,986		,094
Total polyphenols	,980		
Seed polyphenols	,952		
°Brix	,816	,483	
Skin polyphenols	,811	,553	
Skins %	,788	,580	
Berry skin weight	,721	,496	,463
Seeds %	,706	,599	
Seed weight/berry	,693	,657	
Berry seed number	,644	,472	,601
pH			-,896
Titratable acidity		-,951	
% Skin polyphenols			-,699
Berry weight		-,807	-,457
Skin anthocyanins		-,740	-,548
Anthocyans /berry	-,867	-,463	
Bunch weight	-,867	-,463	

Table 94. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included because unimportant.

Extracting only two components from all the data collected it is possible to explain 88,33% of the total variability (tab. 95).

In particular the first component is greatly linked to the variables already mentioned for the description of the first component; the second is composed of the sum of the second and third component of the previous analysis (tab. 96).

The graph (fig. 63) shows how the descriptors that are in the same quadrant and that are close to the ripening of the berry are directly correlated to it while those further away are correlated negatively. The Ripening Index is indeed positively correlated with the sugary content, the pH, the seeds's and skins's weight, and with the grade of polyphenols in the berry and skins.

On the contrary, it is negatively correlated with the mean weight of the berry and of the bunch and the titratable acidity.

The first and the second component are negatively correlated with the antochyanins and the mean weight of the berry and of the bunch.

| Component | Weights of rotated factors | | |
	Total	% variance	% cumulated
1	9,55	53,04	53,04
2	6,35	35,29	88,33

Table 95. Results of the factorial analysis extracting only the first 2 components: method of the principal components.

| Variable | Component | |
	1	2
Polyphenols/berry	,993	
Total polyphenols	,990	
Seed polyphenols	,954	
°Brix	,847	,524
Skin polyphenols	,830	,476
Skins %	,821	,556
Berry skin weight	,814	,555
Seeds %	,749	,651
Seed weight/berry	,743	,651
Berry seed number	,727	,669
pH	,695	,674
% Skin polyphenols		-,803
Titratable acidity		-,697
Berry weight		
Skin anthocyanins		-,906
Anthocyans /berry	-,424	-,893
Bunch weight	-,889	-,437

Table 96. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.
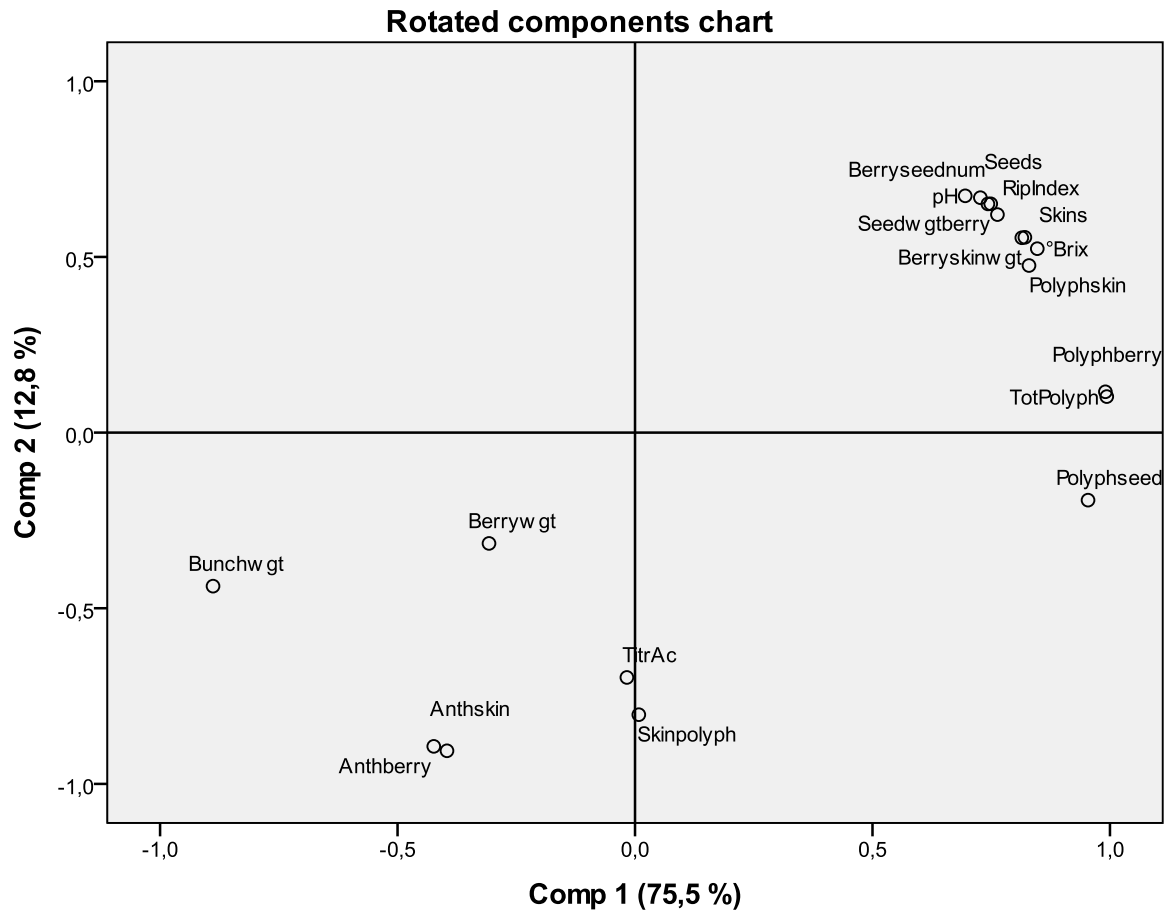
Figure 63. Rotated graph of the first two components obtained from the factorial analysis.

Analysing the multiple linear regression in the three new components and the ripeness index of the berry, it is possible to note that there is a significant correlation and that the total ripeness of the berry obtained experimentally is linearly correlated in a significant way ($r^2 = 0,665$) to that estimated in (tab. 97). Therefore, the total ripeness index of the berry can be expressed in the following way (tab. 98).

Ripening Index = 4,006+F1*0,99+F2*0,160+F3*0,152

From the table of coefficient values for the estimation of the total ripeness of the berry, it can be concluded that the model used is of significant importance, though the Ripening Index variable, is more relevant with the last constant rather than with the first two (tab. 98).

Model	R	R-square	R-square correct	Standard deviation Estimate's error
1	,815	,665	,640	,351

Table 97. Statistic model of relation between the dependant variable of total ripeness of the berry and the three new components obtained from factorial analysis.

Coefficients	B	Standard deviation Error	Sig.
(Costant)	4,006	,062	,000
F1	,099	,103	,340
F2	,160	,055	,006
F3	,152	,031	,000

Table 98. Coefficient values for the estimation of the total ripeness estimated of the berry, standard error and their significance.

Examining the correlation between the parameters analyzed, in the table only the variables with a probability <0,00001 are reported and the characters in bold indicate the negativity of the value indicated.

There are a few significant Pearson's correlations and they are expressed in like way from positive and negative values.

Bunch weight, pH, berry seed number, polyphenols/berry, are the parameters that don't present significant Pearson's correlations (tab. 99).

Variable	Berry weight (g)	°Brix	Titr. Ac. (g/L)	Rip Index	Berry skin weight (g)	Seed weight/ berry (g)	Seeds %	Skin anthocy. (mg/Kg)	Skin polyph. (mg/Kg)	Seed polyph. (mg/Kg)	Total polyph. (mg/Kg)	% Skin polyph.	Anthocy./ berry (mg/berry)
Berry weight (g)					0,68					**0,66**			
Titratable acidity (g/L)				**0,88**									
Ripening Index		0,57	**0,88**										
Berry skin weight (g)	0,68												
Skins %					0,88								
Seed weight /berry (g/berry)							0,88						
Seeds %						0,88							
Skin anthocyanins (mg/Kg)													0,86
Skin polyphenols (mg/Kg)												**0,64**	
Seed polyphenols (mg/Kg)	**0,66**										0,78	0,79	
Total polyphenols (mg/Kg)										0,78			
% Skin polyphenols									**0,64**	0,79			
Anthocyanins/berry (mg/berry)								0,86					

Table 99. Pearson's correlations. Bold numbers are preceded by the minus sign. Legend abbreviations is on the previous pages.

Discriminant analysis on the technological and phenolic characteristics of the grapes at harvest's time highlighted differences between areas examined and some of which may be distinct (fig. 64).

The first two canonical functions represent more than 77,0 % of the total variability (tab. 100).

Function	Eingenvalue	% of variance	% cumulated	Canonical correlation
1	12,212	57,8	57,8	,961
2	4,083	19,3	77,1	,896
3	3,029	14,3	91,5	,867
4	1,457	6,9	98,4	,770
5	,346	1,6	100,0	,507

Table 100. Eigenvalues of discriminant analysis.

From the centroids graph obtained from the discriminant analysis (fig. 64), it is noted that the points relative to the groups show a limited dispersion. Two distinct groups appear in the centroid: the first includes the thesis coming from a different a vineyard of a different farm from the other five theses and that is the only one that well differs from the other, because well detached. The second the residual theses: the number two is the most distinguishable while some points linked to number four and five are superimposed.

The 95,5% of the original grouping are classified correctly, while 68,2% of the cases grouped cross-validated are reclassified correctly (tab. 101).
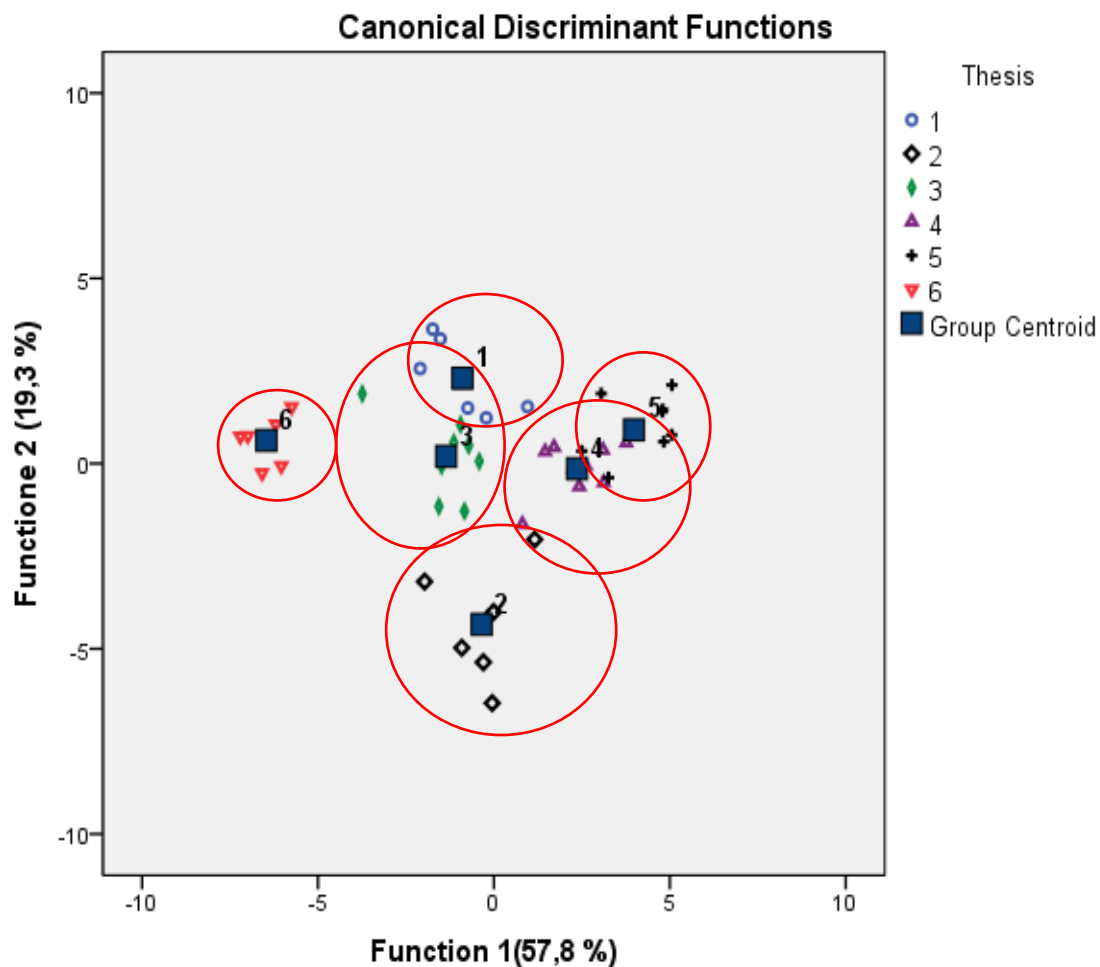
Figure 64. Centroids obtained from the cluster analysis of the characteristics of the grapes at harvest's time.

		Thesis	Group expected						Totals
			1	**2**	**3**	**4**	**5**	**6**	
Cross-validation a	%	1	33,3	,0	50,0	16,7	,0	,0	100,0
		2	,0	66,7	16,7	,0	,0	16,7	100,0
		3	37,5	12,5	50,0	,0	,0	,0	100,0
		4	11,1	,0	11,1	66,7	11,1	,0	100,0
		5	,0	,0	,0	11,1	88,9	,0	100,0
		6	,0	,0	,0	,0	,0	100,0	100,0

Table 101. Classification results.

a. Cross validation is done only for those cases in the analysis in cross validation, each case is classified by the functions derived from all cases other than that case.

b. 95,5% of original grouped cases correctly classified.

c. 68,2% of cross-validated grouped cases correctly classified.

3.8.2 'Col d'Orcia' estate

As results from the multivariance analysis the dependant variables proved to be statistically significant.

If the thesis is chosen as factor, titratable acidity and percentage of seed's polyphenols become non significant statistical variables; instead choosing the year ripening index, the percentage of skins and the anthocyanins's content, become non significant statistical variables.

Seed's percentage, polyphenols level and skin's percentage polyphenols are the parameters that become non significant when the factor is represented by year by thesis (tab. 102).

Factor	Dependent variable	F	Sig.	Factor	Dependent variable	F	Sig.
Thesis	Bunch weight	19832,816	,000	Year	Bunch weight	10903,491	,000
	Berry weight	62,925	,000		Berry weight	77,761	,000
	pH	11,196	,000		pH	466,432	,000
	°Brix	22,696	,000		°Brix	7,985	,002
	Titratable acidity	1,904	,136		Titratable acidity	19,359	,000
	Ripening Index	8,226	,000		Ripening Index	,040	,961
	Berry skin weight	29,807	,000		Berry skin weight	42,400	,000
	Skins %	2,925	,037		Skins %	1,374	,269
	Berry seed number	21,754	,000		Berry seed number	6,252	,005
	Seed weight/ berry	11,557	,000		Seed weight/ berry	5,403	,010
	Seeds %	4,249	,008		Seeds %	5,840	,007
	Skin anthocyanins	42,798	,000		Skin anthocyanins	14,454	,000
	Skin polyphenols	13,246	,000		Skin polyphenols	6,225	,005
	Seed polyphenols	7,521	,000		Seed polyphenols	3,669	,038
	Total polyphenols	20,314	,000		Total polyphenols	4,967	,014
	% Skin polyphenols	,941	,454		%Skin polyphenols	4,243	,024
	Anthocyans /berry	14,924	,000		Anthocyans / berry	1,807	,182
	Polyphenols/ berry	4,892	,004		Polyphenols/ berry	9,494	,001

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Factor	Dipendent variable	F	Sig.
Thesis * Year	Bunch weight	3184,300	,000
	Berry weight	45,261	,000
	pH	11,801	,000
	°Brix	6,298	,000
	Titratable acidity	35,852	,000
	Ripening Index	13,840	,000
	Berry skin weight	21,948	,000
	Skins %	3,073	,012
	Berry seed number	6,416	,000
	Seed weight/berry	5,539	,000
	Seeds %	,675	,709
	Skin anthocyanins	26,345	,000
	Skin polyphenols	4,834	,001
	Seed polyphenols	1,217	,323
	Total polyphenols	4,816	,001
	% Skin polyphenols	,607	,765
	Anthocyans /berry	25,144	,000
	Polyphenols/berry	9,050	,000

Table 102 a, b, c. Test of the effects between subjects (p=<0,05).

By using the data previously obtained the level of variability attributable to the different factor was calculated (tab. 103).

For most of the parameters the variability is attributable to the thesis; the year, however, shows more variability as concerns berry's and seed's weight, pH, seed's and polyphenols's percentage and polyphenolic content per berry.

Titratable acidity, ripening index and anthocyanins content per berry are the parameters that show more variability when the factor is represented by year interaction by thesis (tab. 103).

The variability quota attributed to the different factor was calculated using the data previously obtained.

Variable	% variability due to the thesis	% variability due to the year	% variability due to interaction thesis/year	% variability due to error
Bunch weight	58,47	32,14	9,39	0,00
Berry weight	33,66	41,60	24,21	0,53
pH	2,28	95,11	2,41	0,20
°Brix	59,76	21,02	16,58	2,63
Titratable acidity	3,28	33,31	61,69	1,72
Ripening Index	35,60	0,17	59,90	4,33
Berry skin weight	31,33	44,56	23,07	1,05
Skins %	34,94	16,41	36,71	11,94
Berry seed number	61,41	17,65	18,11	2,82
Seed weight/berry	49,18	22,99	23,57	4,26
Seeds %	36,11	49,64	5,74	8,50
Skin anthocyanins	50,59	17,09	31,14	1,18
Skin polyphenols	52,35	24,60	19,10	3,95
Seed polyphenols	56,10	27,37	9,08	7,46
Total polyphenols	65,32	15,97	15,49	3,22
% Skin polyphenols	13,86	62,48	8,94	14,72
Anthocyans /berry	34,81	4,21	58,64	2,33
Polyphenols/berry	20,02	38,85	37,03	4,09

Table 103. Level of variability attributable to the different factor.

From Tukey's statistic test it is possible to note the table with the different subsets and those non differentiated (tab. 104-106).

The significant variables create differentiated homogenous subsets except for titratable acidity and seed's polyphenols expressed by percentage (tab. 104-105).

The values obtained from the analysis of bunch's weight form a number of subsets equal to the number of theses that indicate great variability in the samples tested, the mean weight of the bunch lies between a minimum value of 167 grams and a maximum of 274 grams. Berry's weight, instead, creates less homogenous subsets.

The thesis BM5, stands out from others ones, for the highest value of bunch's weight, of sugary content, and of polyphenols's supply; besides, this thesis shows the lowest value of pH (tab. 104-106).

Thesis	Bunch weight (g)	Berry weight (g)	pH	°Brix	Ripening Index	Berry skin weight (g)	Skins %	Berry seed number	Seed weight/ berry (g/berry)
BM 1	267,11 d	2,33 c	3,29 a	25,46 a	4,43 a	0,61 c	0,26 b	2,60 c	0,11 c
BM 2	242,82 c	1,95 b	3,33 ab	25,31 a	4,58 a	0,46 b	0,24 ab	2,16 b	0,09 b
BM 3	195,16 b	1,99 b	3,36 bc	25,62 a	4,48 a	0,47 b	0,23 ab	1,56 a	0,06 a
BM 4	274,46 e	2,25 c	3,30 a	24,97 a	4,16 a	0,48 b	0,21 a	1,87 b	0,08 ab
BM 5	166,08 a	1,60 a	3,38 c	28,62 b	5,74 b	0,40 a	0,26 b	1,93 b	0,07 ab

Table 104. Significant parameters with differentiated subsets. Tukey Test (p=0,05).

Thesis	Seeds %	Skin anthocyanins (mg/kg)	Seed polyphenols (mg/kg)	Total polyphenols (mg/kg)	Anthocyans / berry (mg/berry)	Polyphenols/ berry (mg/berry)	Skin polyphenols (mg/kg)
BM 1	0,05 b	359 a	1409 a	2841 a	0,87 a	6,51 b	1433 a
BM 2	0,04 b	570 c	1261 a	2842 a	1,09 b	5,48a	1581 a
BM 3	0,03 a	473 b	1289 a	2808 a	0,93 a	5,58 a	1519 a
BM 4	0,03 ab	521 bc	1193 a	2575 a	1,15 b	5,76 a	1382 a
BM 5	0,04 b	671d	1780 b	3729 b	0,97 a	5,70 a	1949 a

Table 105. Significant parameters with different and non differentiated subsets. Tukey Test (p=0,05).

Thesis	Titratable acidity (g/L)	%Skin polyphenols
BM 1	5,81 a	49,52 a
BM 2	5,74 a	44,53 a
BM 3	5,88 a	45,94 a
BM 4	6,04 a	46,02 a
BM 5	5,55 a	47,58 a

Table 106. Non significant parameters with different and non differentiated subsets. Tukey Test (p=0,05).

From the multivariance analysis where factor choice is the year and the Tukey statistic test, it appears that most of the parameters tested originate differentiated subsets, exception made for the variables ripening index, anthocyanins's content per berry and percentage of skins.

The years 2009 and 2010 show the highest parameters that influence the technological ripeness of the grapes; the highest quantities of polyphenols, instead are registered in 2011 (tab. 107).

In the year 2009 are highlighted the parameters that influence the technological ripeness of the grapes while in the following two years higher quantities of polyphenols are registered; in 2010 stood out the parameters that influence the phenolic richness (tab. 107).

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Variable	2009	2010	2011
Bunch weight	260,24 c	214,36 b	212,773a
Berry weight	2,29 c	1,81 a	1,97 b
pH	3,45 c	3,12 a	3,42 b
°Brix	25,44 a	26,76 b	25,80 a
Titratable acidity	5,58 a	6,31 b	5,52 a
Ripening Index	4,65 a	4,67 a	4,72 a
Berry skin weight	0,56 c	0,42 a	0,48 b
Skins %	0,24 a	0,23 a	0,25 a
Berry seed number	2,18 b	2,03 ab	1,86 a
Seed weight/berry	0,08 ab	0,07 a	0,10 b
Seeds %	0,03 a	0,04 ab	0,05 b
Skin anthocyanins	466 a	570 c	519 b
Skin polyphenols	1474 a	1538 a	1705 b
Seed polyphenols	1288 a	1529 b	1341 ab
Total polyphenols	2763 a	3068 b	3047b
% Skin polyphenols	46,91 ab	49,74 b	43,50 a
Anthocyans /berry	1,04 a	0,98 a	0,98 a
Polyphenols/berry	6,26 b	5,39 a	5,76 a

Table 107. Mean separation by multiple range test (Tukey) the comparison is among data shown in horizontal.

In using the factorial statistic analysis it was possible to put together all the variables noted and calculated in four new complex variables (components) so as to represent 96,19% of the total variability of the technological characteristics of the berries at harvest (tab. 108). The descriptors that represent the highest coefficients (tab. 109) operate in a more reliable way in determining the characteristics of technological ripeness and phenol richness of the berries at harvest's time.

Only three values present coefficients of less than 0,4 and two of them are linked to the titratable acidity and so all the remaining operate in a more reliable way in determining the characteristics of technological ripeness and phenol richness of the theses.

The first component is tied to the sugar content and to the seeds (expressed in mean number per berry and in berry's total weight); the second, instead to the pH, to the titratable acidity, to the bunch's weight and to the anthocyanins's content.

The seed's and skin's percentage are the variables that characterize the third component calculated by factorial analysis while the fourth is marked by the polyphenols located in the seeds and in the skins (tab. 109).

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| Component | Weights of rotated factors | | |
	Total	% variability	% cumulated
1	6,61	36,74	36,74
2	6,19	34,43	71,17
3	2,29	12,75	83,92
4	2,21	12,27	96,19

Table 108. Results of the factorial analysis: principal components method.

| | Component | | | |
	1	2	3	4
Seed weight/berry	,912			
Berry seed number	,901			
Polyphenols/berry	,843	,419		
Berry weight	,827	,467		
Berry skin weight	,746	,650		
Anthocyans /berry	,738	-,492		
Titratable acidity		,893		
% Skin polyphenols				,894
Bunch weight		,938	-,048	
pH		,906		
Seeds %		-,442	,852	
Skins %			,834	
Seed polyphenols				,858
Skin anthocyanins		-,928		
Total polyphenols	-,614			,516
Skin polyphenols	-,785		,462	
°Brix	-,895			

Table 109. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.

Extracting only two components from all the data collected it is possible to explain 78,42 % of the total variability (tab. 110).

In particular the first component is greatly linked to the most of the variables analysed in the study; the second, on the other hand, to only seed's anthocyanins and poliphenols content. (tab. 111).

The graph (fig. 65) shows how the descriptors that are in the same quadrant and that are close to the ripening of the berry are directly correlated to it while those further away are correlated negatively. The Ripening Index is indeed positively correlated with the seed's polyphenols,

and with skin's anthocyanins and negatively with the pH, the titratable acidity and bunch's mean weight.

The first and the second component are negatively correlated with the sugar and the total polyphenols content and with the percentage of skins and seeds.

Moreover the first component is negatively correlated with seed's anthocyanins and polyphenols, while the second is negatively correlated with the acidity and the bunch's weight.

	Weights of rotated factors		
Component	Totale	% variance	% cumulated
1	10,380	57,665	57,665
2	3,737	20,762	78,427

Table 110. Results of the factorial analysis extracting only the first two components: method of the main components.

	Component	
	1	2
Berry weight	,971	
Berry skin weight	,941	
Polyphenols/berry	,921	
Titratable acidity	,895	
Berry seed number	,883	,419
Bunch weight	,826	-,547
pH	,789	-,567
Seed weight/berry	,775	
Anthocyans /berry		,878
% Skin polyphenols		,669
Skins %		-,643
Seeds %	-,545	
Seed polyphenols	-,616	
Skin polyphenols	-,783	-,517
°Brix	-,839	
Total polyphenols	-,862	
Skin anthocyanins	-,868	,450

Table 111. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance .
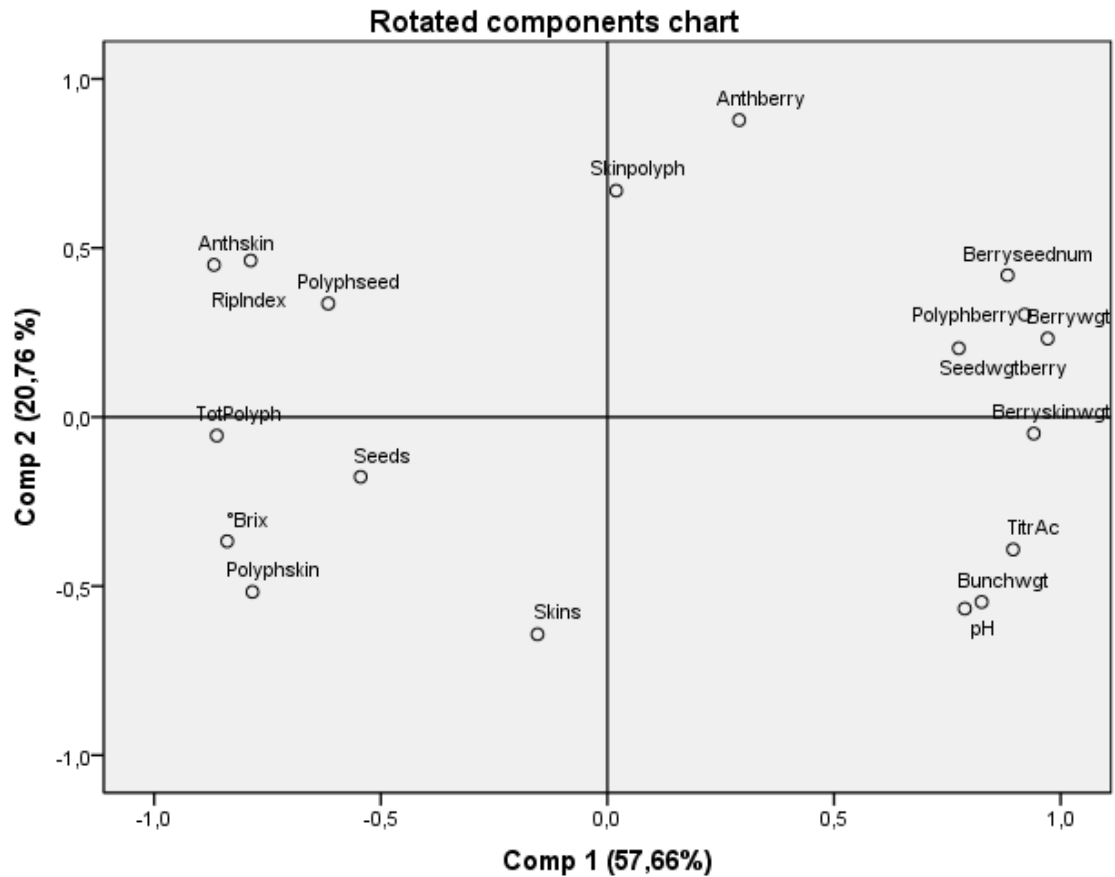
Figure 65. Rotated graph of the first two components obtained from the factorial analysis.

Analysing the multiple linear regression in the four new components and the ripeness index of the berry, it is possible to note that there is a non significant correlation and that the total ripeness of the berry obtained experimentally is slightly linearly correlated ($r^2 = 0,344$) to that estimated in (tab. 112).

Model	R	R-square	R-square correct	Standard Deviation Estimate's error
1	,586	,344	,278	1,09

Table 112. Statistic model of relation between the dependant variable of total ripeness of the berry and the four new components obtained from factorial analysis.

Therefore, the total ripeness index of the berry can be expressed in the following way (tab.113).

Ripening Index = 5,583-F1*0,528-F2*0,565+F3*0,136-F4*0,063

From the table of coefficient values for the estimation of the total ripeness of the berry, it can be concluded that the model used is of significant importance, that the Ripening Index variable, is more relevant with the first and second constant rather than with the third and fourth one (tab. 113).

	B	Standard deviation Error	Sig.
(Costant)	5,583	,273	,000
F1	-,528	,221	,022
F2	-,565	,159	,001
F3	,136	,215	,530
F4	-,063	,171	,714

Table 113. Coefficient values for the estimation of the total ripeness estimated of the berry, standard error and their significance.

Calculating the relation between the index ripeness expressed and that estimated statistically it can be seen graphically how the ripeness expressed by the panel and that determined statistically are overlapping (fig. 66).
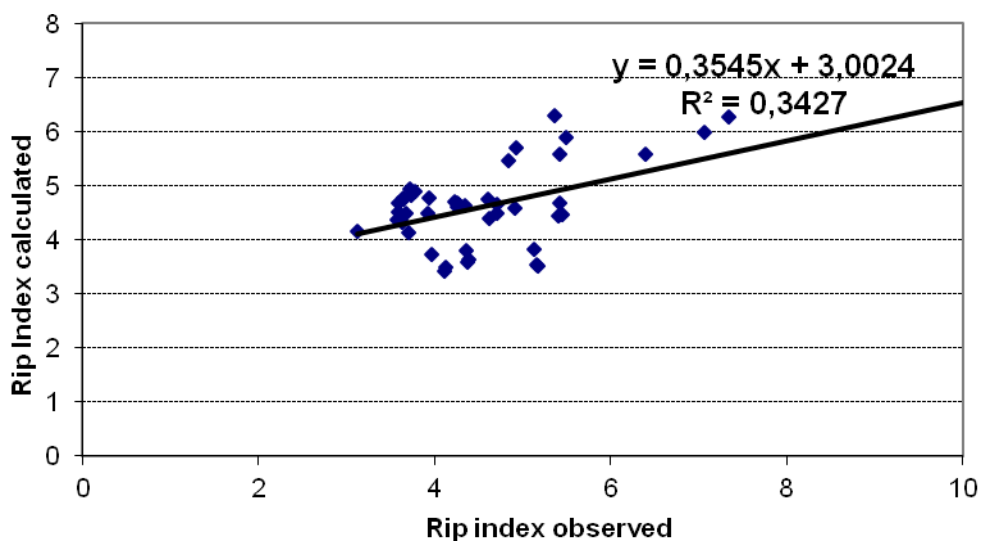
Figure 66. The relation between the ripeness index expressed and that statistically estimated.

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Examining the correlation between the parameters analyzed, in the table only the variables with a probability <0,00001 are reported and the characters in bold indicate the negativity of the value indicated.

In most cases there are values of Pearson's correlation positive, however the parameters connected with the technological maturity of the grapes are negatively correlated.

The pH and anthocyanins's level per berry, are the parameters that don't present significant Pearson's correlations (tab. 114).

Variable	Bun. wght	Ber. wght	°Brix	Titr. Ac.	Rip Ind.	Ber. skin wght	Ski. %	Ber. seed num.	Seed wght /ber.	See. %	Skin anth.	Skin poly.	Sees. poly.	Tot. polyp.	% Skin polyp.	Polyph /berry	F1	F2	F3	F4
Bunch weight														**0,60**				0,88		
Berry weight			**0,65**			0,84		0,57	0,61		**0,63**	**0,77**		**0,76**		0,70	0,67			
°Brix		**0,65**				0,60												**0,58**		
Titratable acidity					0,86															
Ripening index				0,86							0,63									
Berry skin weight		0,84	**0,60**					0,59	0,70			**0,61**				0,62	0,71			
Skins %																			0,63	
Berry seed number		0,57				0,59			0,61								0,66			
Seed weight/berry		0,61				0,70		0,61		0,63						0,57	0,87		0,68	
Seeds %						0,06			0,63										0,91	
Skin anthocyanins		**0,63**			0,63													**0,60**		
Skin polyphenols		**0,77**				**0,61**								0,85						
Seed polyphenols														0,86	0,60					0,82
Total polyphenols	**0,60**	0,76										0,85	0,86					**0,59**		
% Skin polyphenols													0,60							0,87
Polyphenols/ berry		0,70				0,62			0,57								0,64			

Table 114. Pearson's correlations. Bold numbers are preceded by the minus sign. Legend abbreviations is on the previous pages.

Discriminant analysis on the technological and phenolic characteristics of the grapes at harvest's time highlighted differences among clones examined and some of which may be distinct (fig. 67).

The first two canonical functions represent more than 90,0 % of the total variability (tab. 115).

Function	Eingenvalue	% of variance	% cumulated	Canonical correlation
1	21,472	68,5	68,5	0,977
2	6,831	21,8	90,3	0,934
3	2,121	6,8	97	0,824
4	,937	3	100	0,696

Table 115. Eigenvalues of discriminant analysis.

From the centroids graph obtained from the discriminant analysis (fig. 67), it is noted that the points relative to the groups show a limited dispersion. Three distinct groups appear in the centroids: the first comprises the thesis BM2, BM3 e BM4 that intersect each others. The second BM1 and the third BM5 which well differs from the other, because well detached from the other theses.

The 100,0% of the original grouping are classified correctly, while 84,4% of the cases grouped cross-validated are reclassified correctly (tab. 116).
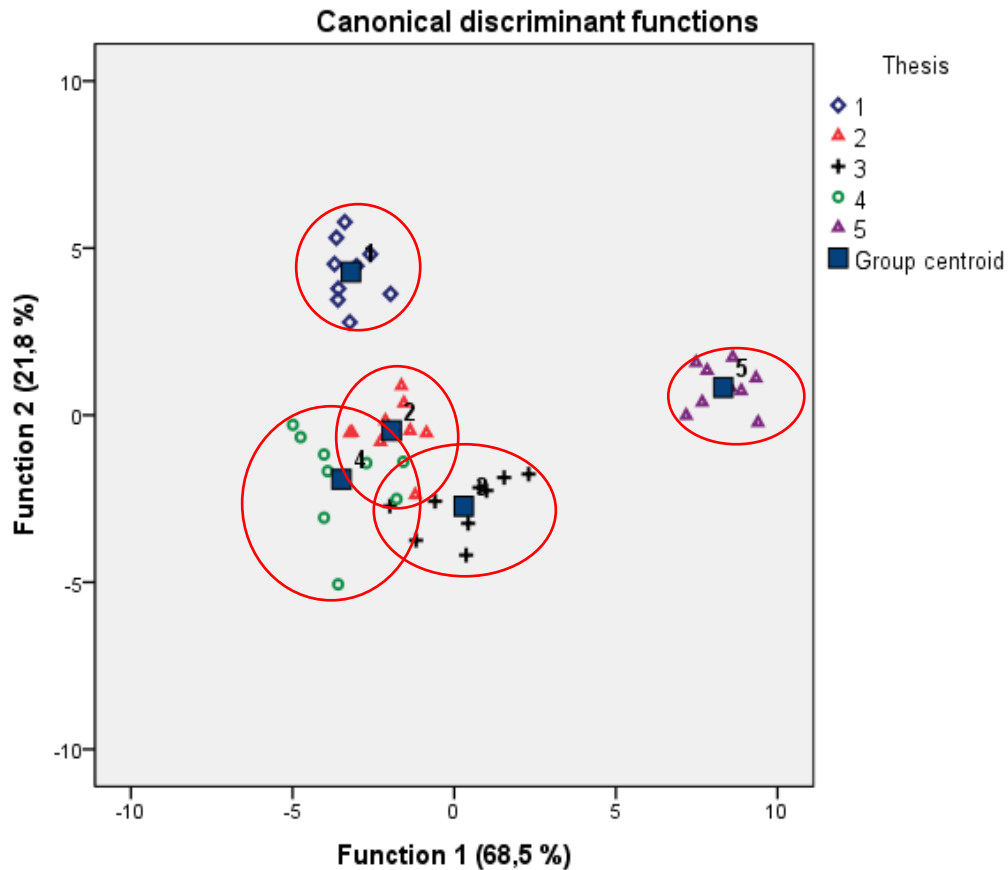
Figure 67. Centroids obtained from the cluster analysis of the characteristics of the grapes at harvest's time.

		Thesis	**Group expected**					**Totals**
			1	2	3	4	5	
Cross-validation a	%	1	100,0	,0	,0	,0	,0	100,0
		2	,0	77,8	11,1	11,1	,0	100,0
		3	,0	11,1	88,9	,0	,0	100,0
		4	,0	11,1	11,1	77,8	,0	100,0
		5	11,1	,0	11,1	,0	77,8	100,0

Table 116. Classification results.
a. Cross validation is done only for those cases in the analysis In cross validation, each case is classified by the functions derived from all cases other than that case.
 b. 100,0% of original grouped cases correctly classified.
 c. 84,4% of cross-validated grouped cases correctly classified.

3.9 Aroma characteristics of the grapes at harvest's time

The analysis performed by GC-MS allowed the identification of 220 aromatic compounds; subdivided into 147 generated by enzymatic hydrolysis and 73 by acid hydrolysis.

Among these, only compounds present in significant quantities underwent statistical analysis and they were divided into their belonging classes (tab. 117-118).

Ratios between compounds which are reported in literature as varietal ratios of the 'Sangiovese' cultivar were also studied (tab. 119).

Acids	Aldehydes	Benzene derivates
isocrotonic acid	nonanal	benzaldehyde
hexanoic acid	citral	methyl benzoate
hexanoic acid, 2-ethyl	**Aliphatic alcohols**	acetophenone
2-hexenoic acid	isoamyl alcohol	ethyl benzoate
sorbic acid	1-pentanol	methyl salicylate
nonanoic acid	2-buten-1-ol, 3-methyl	benzaldehyde, 2,5-dimethyl
n-decanoic acid	1-hexanol	1-phenylethanol
myristic acid	3-hexen-1-ol	benzyl alcohol
pentadecanoic acid	trans-2-Hexenol	2-phenylethanol
2,6 dimetil 6-hydroxy-2,7 octadienoic-acid	1-octen-3-ol	benzenepropanol
hexadecanoic acid	octanol	β-phenoxyethyl alcohol
stearic acid	4-octen-2,7-diol	2-(4-methoxyphenyl)ethanol
oleic acid		6-methoxy-3-methylbenzofuran
linoleic acid		benzoic acid
abscisic acid		3',5'-dimethoxyacetophenone
		3,4-dimethoxybenzyl alcohol
		cinnamic acid
		2,3,4-trimethoxybenzyl alcohol

Table117a.Compounds released by enzymatic hydrolysis (heterosides, ET1).

Esters	Norisoprenoids
dimethyl succinate	actinidol A
palmitic acid, methyl ester	actinidol B
methyl palmitoleate	3,4-diidro-3-oxo-α-ionol I
methyl stearate	3,4-diidro-3-oxo-α-ionol II
methyl linoleate	3,4-diidro-3-oxo-α-ionol III
methyl linolenate	3-hydroxy- β-damascone
methyl n-pentadecanoate	3-oxo- α -ionol
fumaric acid, ethyl 2-methyl allyl ester	2,3-dehydro-4-oxo-7,8-dihydro- β-ionone
Monoterpenols	methyl- β-ionone
linalool oxide A	blumenol C
linalool oxide B	3-hydroxy-7,8-dihydro- β-ionol
linalool	vomifoliol
α-terpineol	7,8 dihydrovomifoliol
linalool oxide C (epoxylinalol)	**Phenols**
linalool oxide D (epoxylinalol)	guaiacol
citronellol	phenol
myrtenol	4-vinylguaiacol
nerol	eugenol
isogeraniol	methoxyeugenol
geraniol	phenol, 3,4,5-trimethoxy
exo-2-hydroxycineole	coniferol 1
p-mentha-1,8-dien-6-ol	coniferol 2
diol 1	**Vanillins**
p-cymen-7-ol	vanillin
diol 2	methyl vanillate
2,3-pinanediol	acetovanillone
trans-8-hydroxy-linalool	homosyringic acid
p-menth-8-en-3-ol (isopulegol)	zingerone
cis-8- hydroxy-linalool	homovanillic alcohol
geranic acid	3,4,5-trimethoxybenzyl alcohol
p-menth-1-ene-7,8-diolo	homovanillic acid
	acetosyringone

Table117b.Compounds released by enzymatic hydrolysis (heterosides 1, ET1).

Alcohols monoterpenols	Norisoprenoids
linalool	trimethyl-dihydro-naphtalene (TDN)
1-terpinenol	calamenene
4-terpineol	α-calacorene
hotrienol	TDN 2
myrcenol	1,1,6,8-tetramethyl-1,2-dihydro-naphthal
cis-β-terpineol	naphthalene, 1,4,6-trimethyl-
ocimenol 1	biphenyl, 4-isopropyl-
α-terpineol	cadalene
γ-terpineol	**Alcohols + ethers norisoprenoids**
ocimenol 2	vitispiran 1
2-cyclohexene-1-methanol, 2,6,6-trimethyl-	vitispiran 2
citronellol	riesling acetale
nerol	lanceol, cis
geraniol	actinidol A
exo-2-hydroxycineole	actinidol B
p-menth-1-en-9-ol	OH-TDN
p-mentha-1,8-dien-6-ol	γ-eudesmol
p-mentha-1,4-dien-7-ol	α-cadinol
Hydrocarbon monoterpenols	α-ionol
α-terpin	1,2-naphthalenediol, 1,2,3,4-tetrahydro
γ-terpin	1-naphthalenol, 1,2,3,4-tetrahydro
terpinolene	**Ketones norisoprenoids**
spiro[4.4]nona-1,6-diene	4-(2,4,4-trimethyl-cyclohexa-1,5-dienyl)
Oxides monoterpenols	β-damascenone
2H-pyran, 2-ethenyltetrahydro-2,6,6-trimethyl	ethanone, 1-(2,3-dihydro-1,1-dimethyl-1H
1,4-cineol	4-(2,6,6-trimethylcyclohexa-1,3-dienyl)but-3-en-2-one
furan, tetrahydro-2,2-dimethyl	mansonone C
trans-rose oxide	1.4,4,5,8-tetramethyl-4H-chromene
cis -rose oxide	4-(2,3,6-trimethylphenyl)-2-butanone
limonene oxide	megastigmatrienone
linalool oxide A	1,4-hexadien-3-one, 5-methyl-1-[2,6,6-trimethyl-2,4-cyclohexadien-1-yl]-
linalool oxide B	3,3,5,6-tetramethyl-1-indanone
2H-pyran, 3,6-dihydro-4-methyl-2-(2-methyl-1-propenyl)-(nerol oxide 1)	
2H-pyran, 3,6-dihydro-4-methyl-2-(2-methyl-1-propenyl)-(nerol oxide 2)	
3,6-dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran	

Table 118.Compounds released by acid hydrolysis (heterosides 2, ET2).

Linalool oxA/linalool oxB >1 (enzymatic hydrolysis)	
Linalool oxC/linalool oxD >1 (enzymatic hydrolysis)	
Linalool/geraniol < 1 (enzymatic hydrolysis)	
Trans 8-OH Linalool/cis 8-OH linalool >1 (enzymatic hydrolysis)	
Trans 8-OH Linalool + cis 8-OH linalool/p-menth-1en-7,8-diol >1 (enzymatic hydrolysis)	
3-hydroxy β-damascenone/3-oxyde α-ionol <1 (enzymatic hydrolysis)	
Linalool oxA/linalool oxB >1 (acid hydrolysis)	

Table 119. Ratios between compounds.

The aromatic compounds, underwent MANOVA, factorial, discriminating and correlating statistical analysis (tab. 120).

Abbreviation	Variable	M.U.
Aliph. Alc. ET1	Aliphatic alcohols (enzymatic hydrolysis)	ng/g
Der. Benzene ET1	Benzene derivates (enzymatic hydrolysis)	"
Phenols ET1	Phenols (enzymatic hydrolysis)	"
Vanillins ET1	Vanillins (enzymatic hydrolysis)	"
Monoterp. ET 1	Monoterpenols (enzymatic hydrolysis)	"
Norisopren. ET1	Norisoprenoids (enzymatic hydrolysis)	"
Aldehydes ET1	Aldehydes (enzymatic hydrolysis)	"
Acids ET1	Acids (enzymatic hydrolysis)	"
Esters ET1	Esters (enzymatic hydrolysis)	"
Hydro. monot. ET2	Hydrocarbon monoterpenols (acid hydrolysis)	"
Oxi. monot. ET2	Oxides monoterpenols (acid hydrolysis)	"
Alc. monot. ET2	Alcohols monoterpenols (acid hydrolysis)	"
Hydr. norisopr. ET2	Hydrocarbon norisoprenoids (acid hydrolysis)	"
Ket. norisopr. ET2	Ketones norisoprenoids (acid hydrolysis)	"
Alc. norisopr. + Ether ET2	Alcohols + ethers norisporenoids (acid hydrolysis)	"
Heterosides 1	Compounds released by enzymatic hydrolysis	"
Heterosides 2	Compounds released by acid hydrolysis	"
Total	Compounds released by enzymatic and acid hydrolysis	"
V158	Linalool oxA /linalool oxB (enzymatic hydrolysis)	n
V159	Linalool oxC /linalool oxD	"
V161	Linalool/geraniol	"
V162	Trans 8-OH linalool/cis 8-OH linalool	"
V165	Trans 8-OH linalool + cis 8-OH linalool/p-menth -1ene-7,8-diol	"
V166	3-hydroxy β-Damascenone/3-oxide α-ionol	"
V167	Linalool oxA /linalool oxB (acid hydrolysis)	"

Table 120. List of abbreviations used in the text.

The MANOVA analysis variance was conducted studying the significance of the variables in function of the factor choice (tab. 121).

Factor	Dipendent variable	F	Sign.
Year	Aliph. alc. ET1	0,371	,691
	Der. benzene ET1	29,313	,000
	Phenols ET1	2,738	,069
	Vanillins ET1	5,599	,005
	Monoterp. ET 1	2,413	,095
	Norisopren. ET1	11,626	,000
	Aldehydes ET1	8,097	,001
	Acids ET1	138,683	,000
	Esters ET1	9,283	,000
	Hydro. monot. ET2	23,965	,000
	Oxi. monot. ET2	27,172	,000
	Alc. monot. ET2	6,778	,002
	Hydr. norisopr. ET2	17,320	,000
	Ket. norisopr. ET2	15,929	,000
	Alc. norisopr. + Ether ET2	4,639	,012
	Heterosides 1	8,286	,000
	Heterosides 2	26,103	,000
	Total	26,103	,000
	V158	9,351	,000
	V159	8,722	,000
	V161	35,769	,000
	V162	43,580	,000
	V165	1,498	,228
	V166	9,688	,000
	V167	43,963	,000

Table 121. Test of the effects between subjects (p=<0,05).

In the interaction thesis by year, all the aromatic classes of the compounds (tab. 120) and the ratios between aromatic compounds, resulted statistically notable, therefore they have not been recorded on the table (tab. 121). However, if the year is the factor in the statistic analysis, some parameters are not statistically important, i.e: aliphatic alcohols, phenols, monoterpenols from enzymatic hydrolysis and the ratio trans 8-OHlinalool+cis8-OHlinalool/p-menth-1 en-7,8-diol.

Using data previously obtained the amount of the variability attributed to the different factor was calculated (tab. 122).

Variability is equally attributable to the thesis and to the year as shown in the table 6, more precisely, the compounds, originating from enzymatic hydrolysis except for aldehydes and acids, and 3- hydroxy β-damascenone/3-oxide α-ionol and linalool oxA/linalool oxB (acid hydrolysis) have a greater variability due to the thesis, while the compounds originating from acid hydrolysis and the other ratios are strongly influenced by the year effect. Aldehydes, esters and the total of heterosides 1 and hydrocarbon monoterpenols and norisoprenoids for the heterosides 2, show comparable levels of variability due to thesis and year (tab. 122).

Variable	% variability due to the thesis	% variability due to the year	% variability due to the interaction thesis/ year	% variability due to error
Aliph. alc. ET1	74,53	1,75	19,01	4,72
Der. benzene ET1	51,86	37,56	9,29	1,28
Phenols ET1	44,97	11,84	38,87	4,32
Vanillins ET1	66,23	18,95	11,43	3,38
Monoterp. ET 1	52,83	20,05	18,81	8,31
Norisopren. ET1	31,20	55,47	8,56	4,77
Aldehydes ET1	40,39	37,95	16,98	4,69
Acids ET1	37,18	52,82	9,62	0,38
Esters ET1	41,30	42,03	12,14	4,53
Hydro. monot. ET2	47,77	44,25	6,13	1,85
Oxi. monot. ET2	34,90	57,56	5,42	2,12
Alc. monot. ET2	59,92	21,37	15,56	3,15
Hydr. norisopr. ET2	42,38	47,12	7,77	2,72
Ket. norisopr. ET2	27,62	56,29	12,55	3,53
Alc. norisopr. + Ether ET2	64,49	20,91	10,09	4,51
Heterosides 1	37,79	37,51	20,17	4,53
Heterosides 2	27,05	62,65	7,90	2,40
Total	27,05	62,65	7,90	2,40
V158	38,00	39,01	18,82	4,17
V159	22,75	42,49	29,89	4,87
V161	33,03	56,29	9,11	1,57
V162	17,53	70,43	10,42	1,62
V165	37,38	19,93	29,38	13,31
V166	47,28	15,62	35,49	1,61
V167	11,25	80,28	6,64	1,83

Table 122. Level of variability attributable to the different factor.

Using Tukey test, it is possible to note that all the parameters analyzed have given rise to homogenous differentiated subsets (tab. 123-125).

The significant variables that create less differentiated homogenous subsets are the compounds from the esters classis obtained from the enzymatic way and the ratio linalool oxA /linalool oxB obtained, instead, from the acid hydrolysis.

Within the compounds freed by the enzymatic way the families of the benzene derivatives and of the norisoprenoids classes are more present in theses while the aldehydes are quantitatively lower; from a concentration of hundreds of ng/g fresh vegetal tissue weight to values close to the unit (tab. 123).

Hydrocarbon norisoprenoids and monoterpenols are the classes that are more and less represented in the hydrolyzing of aromatic compounds by acid way (tab. 124).

Comparing the theses, the 'Chianti Colline Pisane' thesis is quite distinct from the others for the quantitative inferior values of most of the aromatic classes. Samples from the province of Siena, however, have a higher aroma content: benzene derivatives, phenols, vanillins, and aldehydes. As for enzymatic hydrolysis and hydrocarbon and monoterpenol oxides for the acid one, are more present in the 'Chianti Classico' area while the rest are found in the area of the 'Brunello di Montalcino'. In the province of 'Grosseto',the 'Morellino di Scansano' thesis differs from the others for the highest levels of monoterpenol alcohols, while two thesis from 'Montecucco' for the lowest in phenols and aldehydes. The benzene derivatives class is that with the most variability within the theses. Analyzing the total quantity of aromatic compounds, those freed by enzymatic hydrolysis are more present in a thesis of the 'Brunello di Montalcino' and scarcely present in a 'Montecucco' thesis, while those freed by acid hydrolysis are more present in the province of Siena and more precisely in the 'Chianti Classico' and in a limited way in the 'Chianti Colline Pisane' thesis (tab. 123-125).

As can be seen from all the ratios examined there is perfect harmony in the results and in the values obtained by other authors for the 'Sangiovese' cultivar (Di Stefano, 1998 et Lanati 2001) The first and second ratio regarding the linalool oxides are completely favourable to the trans form compounds compared to the cis one; the linalool/geraniol ratio is much less than one in the grapes with a low linalool concentration (tab. 125).

Thesis	Aliph. alc .	Benz der	Phenols	Vanillin	Monoterp	Norisopr.	Aldehyd	Acids	Esters
CCP 1	51,54 a	281,29 a	44,80a	74,36 a	62,98 a	138,22 a	1,57 ab	55,41abc	14,03a
MC 1	140,95 def	481,98 abc	64,00 a	126,85abc	114,62 a-d	247,61 abc	1,15 a	71,87 ad	11,79a
MC 2	121,62 cd	423,82ab	38,04 a	99,19 ab	68,54 a	168,92 a	2,49 bc	77,45 ad	12,54a
MC 3	173,35 f	606,54bcd	96,92ad	164,31 be	111,47 a-d	297,80 a-e	2,84 c	106,38cd	10,95a
MC 4	164,52 ef	586,38 bcd	92,39abc	166,82 be	111,35 a-d	274,33 a-d	2,28 abc	114,98de	23,26a
MC 5	148,38def	522,82 abc	68,05 a	140,78 ad	106,16 a-d	205,01 abc	1,34 ab	84,11 ad	31,92ab
MC 6	95,50bc	592,49 bcd	175,16de	186,32cde	135,44cd	359,33 b-e	6,14 d	48,8 ab	17,65 a
MS 1	133,26 cde	800,35 de	207,40 e	186,24cde	114,22 a-d	435,53de	6,34 d	39,52 a	20,59 a
BM 1	160,58def	441,89 ab	65,19 a	125,95abc	91,09 abc	242,10 abc	2,22 abc	101,77bcd	15,60 a
BM 2	140,38 def	437,87 ab	59,21 a	120,85abc	66,11a	165,83 a	2,89 c	52,98 abc	11,04 a
BM 3	151,84 def	471,26 abc	52,60 a	111,11abc	75,28 ab	220,42 abc	1,50 ab	86,85 a-d	11,85 a
BM 4	132,60 cde	504,47 abc	71,27 ab	117,05abc	72,52ab	234,71 abc	2,49 bc	79,96 a-d	8,45 a
BM 5	268,26 g	815,22 de	115,79ad	213,84 de	147,66 d	463,41 e	3,42 c	162,38 e	13,38 a
BM 6	96,15 bc	695,46 cde	206,09 e	185,23 be	123,46bcd	481,85 e	8,11 e	39,21 a	5,38a
BM 7	74,96 ab	501,81abc	157,06cde	230,41 e	136,10 cd	388,56 cde	7,03 de	115,72 de	73,12 b
CC 1	132,28 cde	888,43 e	288,65 f	183,45 be	96,65 a-d	377,42 b-e	8,14 e	60,62 abc	26,62 a
CC 2	68,50 ab	575,22bcd	150,32 be	187,16cde	71,27ab	201,86 ab	6,42 d	68,84 a-d	17,56 a

Table 123. Significant parameters with different subsets; heterosides 1. Tukey Test (p=0,05).

Thesis	Hydroc. monot.	Oxid. monot.	Alc. monot.	Hydr. norisopr.	Ket. norisopr.	Alc. norisopr. + Ethers
CCP 1	0,21 ab	2,19 ab	2,02 a	6,65a	2,42 a	10,61 a
MC 1	0,46 b-g	4,12 de	4,76 b-g	31,01d-g	4,66 ab	30,89 de
MC 2	0,41 a-e	4,08 cde	3,72 ab	26,91 b-g	7,78 a-d	21,78 a-d
MC 3	0,27 abc	3,30 bcd	4,65 b-f	13,95a-d	5,60abc	15,58ab
MC 4	0,26 ab	3,17 a-d	4,07 bcd	19,95 a-f	5,39 abc	16,98 abc
MC 5	0,21 ab	2,31 abc	3,33 ab	11,64 ab	2,55 a	12,06 a
MC 6	0,73 gh	6,06 f	6,43 fg	32,60 efg	9,70 bcd	33,59 e
MS 1	0,58 c-g	3,70 bcd	6,58 g	17,42 a-e	11,90 de	19,57 a-d
BM 1	0,36 a-d	2,86 a-d	3,19 ab	21,10 a-g	6,29 a-d	19,58 a-d
BM 2	0,12 a	3,24 bcd	3,03 ab	22,28 a-g	6,21 a-d	15,67 ab
BM 3	0,42 a-f	3,06 a-d	3,03 ab	19,79 a-f	5,10 abc	16,20 ab
BM 4	0,24 ab	1,40 a	1,97 a	12,66 abc	3,63 a	10,20 a
BM 5	0,72 fgh	4,13 de	5,59 c-g	36,15 fg	10,64 cd	36,62 e
BM 6	0,69 fgh	3,75 bcd	4,31 b-e	22,20 a-g	5,75 abc	29,92 de
BM 7	0,62 d-g	3,72 bcd	3,87 bc	30,29 c-g	6,73 a-d	25,68 b-e
CC 1	1,01 h	5,78 ef	5,91 d-g	39,61 g	17,23 e	29,82 de
CC 2	0,75gh	7,78 g	5,96 efg	39,74 g	16,67 e	28,01 cde

Table 124. Significant parameters with different subsets; heterosides 2. Tukey Test (p=0,05).

Thesis	Heter. 1	Heter. 2	Total	V158	V159	V161	V162	V165	V166	V167
CCP 1	1155,23ab	24,22 a	1179,45abc	1,15 a	8,22 bc	0,14 f	1,43 a	11,75de	0,05abc	2,55 a
MC 1	1299,30abc	75,9 dg	1375,23 ad	1,29ab	6,95abc	0,04ab	2,68 e	2,25 ab	0,03 ab	2,49 a
MC 2	1046,24 a	64,70bg	1110,94 a	1,26ab	9,51 c	0,07ad	2,76 e	1,76 a	0,06 ad	3,19 a
MC 3	1624,16 af	43,37ad	1667,54 af	1,32abc	7,63abc	0,0 abc	2,48 de	1,68 a	0,05 ad	2,86 a
MC 4	1583,01 ae	49,84ad	1632,85 ag	1,40 ad	8,64 bc	0,05 bc	2,22 be	1,87ab	0,06 ad	2,91a
MC 5	1349,30abc	32,12abc	1381,42 ad	1,41 ad	7,48abc	0,04 ab	2,65 e	1,86 ab	0,04abc	2,73 a
MC 6	1688,44 af	89,1 efg	1777,58 bg	1,33abc	6,31 ab	0,12def	1,55 ab	5,50 bc	0,03 ab	2,94 a
MS 1	2010,67def	59,76 bf	2070,43efg	1,41 ad	6,40 ab	0,12 ef	1,36 a	2,51 ab	0,03 ab	2,59a
BM 1	1304,84abc	54,54 ae	1359,38 ad	1,42 ad	6,77abc	0,08 be	1,63abc	1,95 ab	0,05 ad	4,67 a
BM 2	1098,24ab	50,59 ad	1148,86 ab	1,59 cd	7,89abc	0,05abc	2,23 be	1,93ab	0,09 d	2,77 a
BM 3	1225,09 ab	47,69 ad	1272,77abc	1,47bcd	8,70 bc	0,04 ab	2,18 be	1,40 a	0,06 ad	4,97a
BM 4	1260,88 ab	30,12ab	1290,99abc	1,45bcd	8,44bc	0,05 ab	1,74 ad	1,50 a	0,07 cd	2,79 a
BM 5	2277,13 f	93,86 fg	2370,99 g	1,32abc	8,07abc	0,03 a	2,2 cde	2,29 ab	0,04abc	2,62a
BM 6	1927,83 cf	66,63 cg	1994,46 dg	1,47bcd	7,28abc	0,05abc	1,87 ad	2,20 ab	0,02 a	39,46b
BM 7	1754,55 bf	70,93 dg	1825,48 cg	1,68 d	5,32 a	0,06abc	2,46 de	2,08ab	0,05abc	36,03b
CC 1	2157,71 ef	99,38 g	2257,09 fg	1,47bcd	8,61 bc	0,08 a-e	1,22 a	14,77e	0,02 a	70,54b
CC 2	1394,84 ad	98,93 g	1493,78 ae	1,51bcd	12,53d	0,01 cf	1,31 a	8,70 cd	0,06bcd	2,75a

Table 125. Significant parameters with different subsets; heterosides 1, 2 and ratios. Tukey Test (p=0,05).

From the multivariate analyses, choosing the year as the factor and the Tukey test, it emerged that most of the parameters examined originated differentiated subsets in particular in the year 2011 (tab. 126). The year 2010 that stands out as having the highest level of aromatic families with the exception of aliphatic alcohols (enzymatic hydrolysis) which were quantitatively higher the year before. The aromas found in the 2011 harvest were mainly the phenols, vanillins, aldehydes, esters, hydrocarbon and ketones norisoprenoids classes even if the values were quantitatively similar to those of the other years.

Variable	2009	2010	2011
Aliphatic alcohols ET1	145,40 b	140,13 b	112,36 a
Benzene derivates ET1	549,54 a	605,50 a	543,90 a
Phenols ET1	99,23 a	114,12 ab	131,28 b
Vanillin ET1	141,28 a	158,10 a	162,06 a
Monoterpenols ET 1	94,53 a	117,60 b	88,74 a
Norisoprenoids ET1	251,96 a	337,91 b	275,35a
Aldehydes ET1	2,80 a	3,66 b	5,26 c
Acids ET1	73,10 a	96,20 b	71,92 a
Esters ET1	13,70 a	17,24 a	26,54 a
Hydroc. monot. ET2	0,32 a	0,56 b	0,55 b

Variable	2009	2010	2011
Oxid. monot. ET2	3,61 a	4,25 b	3,55 a
Alc. monot. ET2	3,78 a	4,10 b	4,01 a
Hydr. norisopr. ET2	16,96 a	26,68 b	27,80 b
Ket. norisopr. ET2	6,56 a	7,42 ab	8,65 b
Norisopr. alc.+ Ether ET2	13,05 a	27,12 b	25,61 b
Heterosides 1	1444,55 a	1722,22 b	1449,24 a
Heterosides 2	44,32 a	71,04 b	70,24 b
Total	1488,88 a	1793,27 b	1519,48 a
V158	1,34 a	1,49 b	1,40 a
V159	1,34 a	1,49 b	1,40 a
V161	0,08 b	0,09 b	0,04 a
V162	1,87 b	1,62 a	2,53 c
V165	5,00 b	3,33 a	3,32 a
V166	0,06 b	0,03 a	0,06 b
V167	7,56 a	10,93 ab	14,84 b

Table 126. Mean separation by multiple range test (Tukey) the comparison is among data shown in horizontal.

Using the factorial statistics analysis it was possible to collect all the variables found and calculated into four new complex variables (components) to represent 96,62% of the total variability of the aromatic characteristics of the berries at harvest (tab. 127). The first component is linked to most of the variables studied: to the variables that indicate varietal ratios except for linalool/geraniol, to many of the families belonging to the heterosides 1, to the total, between the heterosides 2, to the hydrocarbon and alcohols monoterpenols. The sum of linalool/geraniol, the aromatic classes freed by acid hydrolysis not previously mentioned and the aliphatic alcohols from the enzymatic hydrolysis characterize the second component. The third is linked to the esters and to the acids from the heterosides 1, and the fourth, only to vanillin from the enzymatic hydrolysis (tab. 128).

	Weights of rotated factors		
Component	Total	% variability	% cumulated
1	15,39	51,16	51,16
2	9,38	31,26	82,42
3	2,35	7,84	90,26
4	1,91	6,36	96,62

Table 127. Results of the factorial analysis: pricipal components method.

	Component			
	1	**2**	**3**	**4**
Total	,987			
Ketones norisoprenoids ET2		,983		
Hydrocarbon norisoprenoids ET2		,980		
Heterosides 2		,979		
Aliphatic alcohols ET1		-,863		
Esters ET1			,939	
Heterosides 1	,986			
Benzene derivates ET1	,972			
Norisoprenoids ET1	,935			
V162	,935			
V167	,902			
Phenols ET1	,882			
Aldehydes ET1	,873	-,402		
Monoterpenols ET 1	,741			,464
Alcohols monoterpenols ET2	,713	,499		
Hydrocarbon monoterpenols ET2	,702	,676		
Vanillin ET1	,479	,511		,687
Acids ET1	,465	,440	,702	
Alcohols + ethers norisoprenoids ET2	,451	,804		
V161	-,490	,858		
Oxides monoterpenols ET2	-,570	,755		
V165	-,789	-,461		
V159	-,856			,404
V158	-,875			
V166	-,986			

Table 128. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.

By extracting only two of the components from the total data it is possible to explain 87,49% of the total variability (tab. 129). The first component is linked to the variables that represent the ratios between specific aromas and those of the heterosides 1, while the second to the heterosides 2 (tab. 130).

On the graph (fig. 68) it is possible to see how the descriptors that are found in the same quadrant are directly correlated while those further away are correlated negatively. Both components are negatively correlated to the ratio trans 8-OH linalool+cis 8-OH linalool/p-menth-1ene-7,8-diol. Furthermore, the first component is negatively correlated to other ratios between specific components except trans 8-OH linalool/cis 8-OH linalool and linalool oxA/ linalool oxB coming from acid hydrolysis, the esters of the heterosides 1, the total of the components obtained by acid hydrolysis and the hydrocarbon norisoprenoids and oxides monoterpenols classes. The second component, is negatively correlated with the sum of the

freed components by enzymatic hydrolysis, aliphatic alcohols, benzene derivatives, aldehydes and the trans 8-OH linalool/cis 8-OHlinalool (fig. 68).

	Weights of rotated factors		
Component	Total	% variance	% cumulated
1	15,51	51,69	51,69
2	10,74	35,81	87,49

Table 129. Results of the factorial analysis extracting only the first 2 components: method of the principal components.

Variable	Component	
	1	2
Total	,998	
Aliphatic alcohols ET1		-,950
Heterosides 2		,949
Ketones norisoprenoids ET2		,919
Hydrocarbon norisoprenoids ET2		,893
Esters ET1		,555
Heterosides 1	,997	
Benzene derivates ET1	,959	
Norisoprenoids ET1	,958	
V162	,923	
V167	,913	
Phenols ET1	,906	
Aldehydes ET1	,850	-,457
Monoterpenols ET 1	,798	,441
Alcohols monoterpenols ET2	,750	,592
Hydrocarbon monoterpenols ET2	,684	,595
Vanillin ET1	,545	,672
Acids ET1	,525	,670
Alcohols + ethers norisoprenoids ET2	,470	,858
V161	-,492	,830
Oxides monoterpenols ET2	-,551	,805
V165	-,801	-,493
V159	-,818	
V158	-,853	,460
V166	-,978	

Table 130. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.
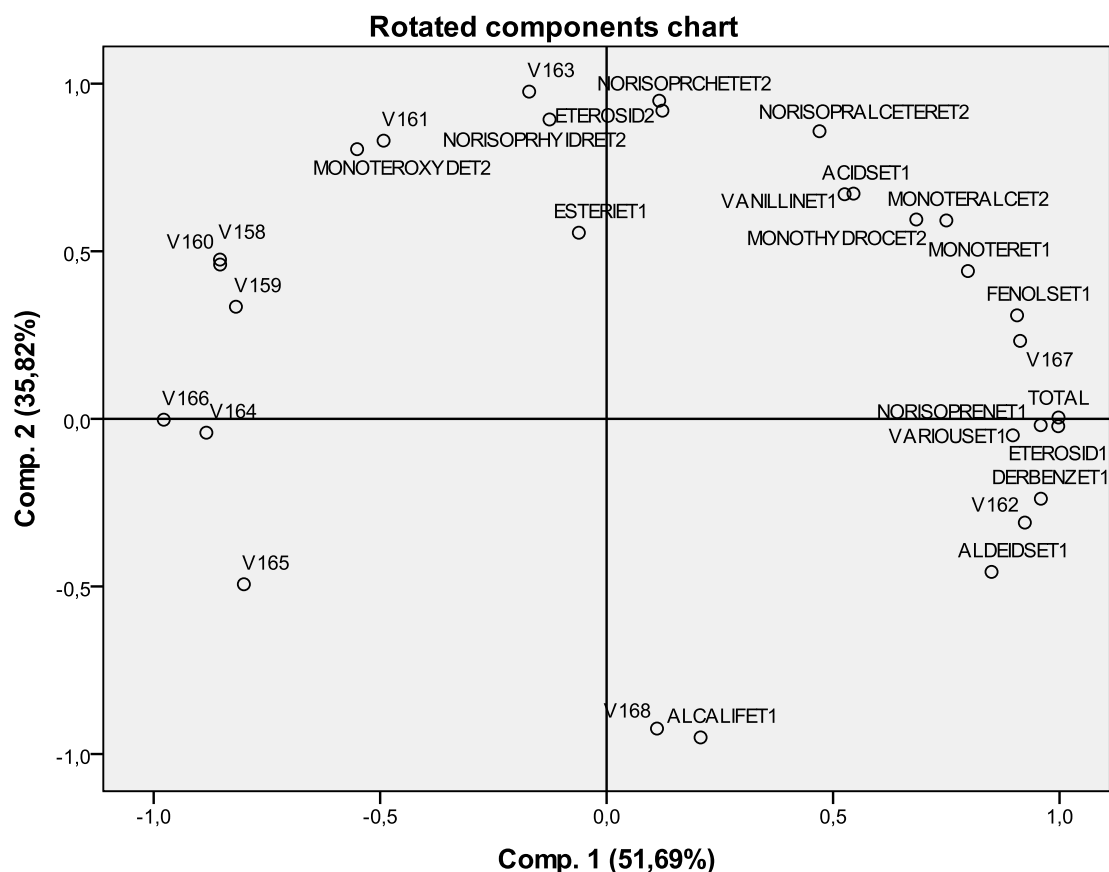
Figure 68. Rotated graph of the first two components obtained from the factorial analysis.

Considering the correlation between the parameters analyzed, only the variables characterized by a probability < 0,00001 were reported on the table. Pearson's significant correlations are mostly positive while those linked to the variables expressing the ratios between single aromatic components are negative. Correlations close to the unit value are present between the value of the heterosides 1 and the content of the benzene derivatives and norisoprenoids while the heterosides 2 are strictly linked to those of hydrocarbon norisoprenoids and alcohols plus ether monoterpenols classes. Pearson's correlations among ratios and others variables aren't so significant (tab. 131).

	Aliph. Alc ET1	Benz. Der. ET1	Phen ET1	Van. ET1	Mon. ET 1	Nor. ET1	Ald. ET1	Acid ET1	Est. ET1	Hydr. Monot ET2	Oxid Monot. ET2	Alc. Monot ET2	Hydr. Noris. ET2	Ket. Noris. ET2	Alc+Et. Noris. ET2	Heter. 1	Heter. 2	Tot.
Aliph. Alc.ET1		0,37						0,54								0,34		0,33
Benz. Der ET1	0,37		0,78	0,62	0,42	0,78	0,39			0,31						0,92		0,92
Phenols ET1		0,78		0,73	0,43	0,79	0,64			0,52		0,39		0,45	0,31	0,83	0,32	0,83
Vanillins ET1		0,62	0,73		0,58	0,77	0,40	0,32		0,39					0,32	0,77		0,78
Monoterpenols ET 1		0,42	0,43	0,58		0,58		0,40		0,32		0,40			0,38	0,59		0,60
Norisoprenoids ET1		0,78	0,79	0,77	0,58		0,47			0,40					0,34	0,90		0,90
Aldehydes ET1		0,39	0,64	0,40		0,47				0,49	0,35			0,44	0,38	0,41	0,37	0,43
Acids ET1	0,54			0,32	0,40				0,33							0,37		0,36
Esters ET1								0,33										
Oxid. Monot. ET2							0,35			0,61		0,71	0,72	0,66	0,59		0,76	
Alcohols Monot. ET2			0,39		0,40					0,65	0,71		0,61	0,63	0,67		0,73	
Hydrocarbon Norisop.ET2										0,69	0,72	0,61		0,73	0,84		0,97	
Ketones Norisop.ET2			0,45				0,44			0,61	0,66	0,63	0,73		0,55		0,77	0,26
Alcoh.+ Eters Norisop.ET2			0,31	0,32	0,38	0,34	0,38			0,77	0,59	0,67	0,84	0,55			0,92	0,32
Heterosides 1	0,34	0,92	0,83	0,77	0,59	0,90	0,41	0,37		0,38								
Heterosides 2			0,32				0,37			0,78	0,76	0,73	0,97	0,77	0,92			
Total	0,33	0,92	0,83	0,78	0,60	0,90	0,43	0,36		0,42		0,34			0,32			

Table. 131 Pearson's correlations. Legend abbreviations is on the previous pages.

The Stepwise discriminant analysis gave the best results compared to the traditional method; analysis of the most relevant variables for statistics purposes were inserted in stepwise (tab. 132).

Aliphatic alcohols (enzymatic hydrolysis)
Linalool oxA/linalool oxB (acid hydrolysis)
Trans 8-OH linalool + cis 8-OH linalool/p-menth -1ene-7,8-diol
Ketones norisoprenoids (acid hydrolysis)
Compounds released by enzymatic hydrolysis
Benzene derivates (enzymatic hydrolysis)
Aldehydes (enzymatic hydrolysis)
Vanillins (enzymatic hydrolysis)

Table 132. Variables inserted in the analysis.

Discriminating analysis on the aroma characteristics of the berries at harvest has highlighted differences in the winegrowing areas examined, some of these are distinct (fig. 64). In particular the first two functions explain over 60% of total variability (tab. 133).

Function	Eingenvalue	% of variance	% cumulated	Canonical correlation
1	34,702	48,6	48,6	,986
2	10,145	14,2	62,8	,954
3	7,885	11,0	73,9	,942
4	5,592	7,8	81,7	,921
5	3,680	5,2	86,9	,887
6	2,809	3,9	90,8	,859
7	2,193	3,1	93,9	,829
8	1,541	2,2	96,0	,779
9	1,231	1,7	97,8	,743
10	,773	1,1	98,8	,660
11	,363	,5	99,3	,516
12	,170	,2	99,6	,381
13	,155	,2	99,8	,367
14	,076	,1	99,9	,265
15	,065	,1	100,0	,247

Table 133. Eigenvalues of discriminant analysis.

Looking at the graph (fig. 69) of the centroids obtained from the discriminating analysis data subdivided by area (tab. 134), one thesis in the 'Chianti Classico' area stands out. The other thesis are close to one another and some points overlap. The two 'Montecucco' theses do not appear very close differently from those of the 'Brunello and Montalcino'. In the 'Chianti Classico' the two theses are very different. 100% of the original cases grouped are correctly classified (tab. 135).

Area	Denomination area	Estate
1	Colline Pisane	Beconcini
2	Montecucco	Collemassari
3	Montecucco	Salustri
4	Morellino di Scansano	Fattoria di Magliano
5	Brunello di Montalcino	Col D'Orcia
6	Brunello di Montalcino	Casanova di Neri
7	Brunello di Montalcino	La Mannella
8	Chianti Classico	Capannelle
9	Chianti Classico	Castello di Albola

Table 134. Area subdivision.
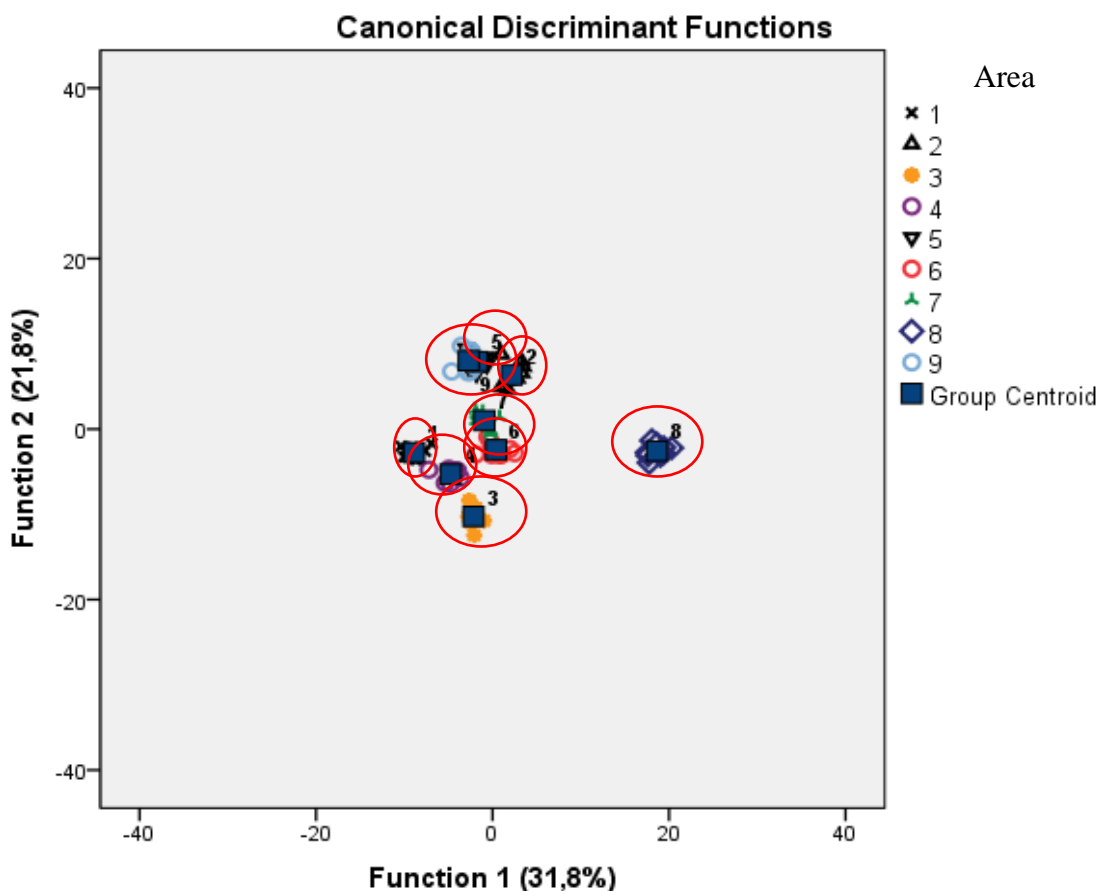
Figure 69. Centroids obtained from the cluster analysis of the aromatic characteristics of the grapes at harvest's time.

		Thesis	Group expected									Total
			1	2	3	4	5	6	7	8	9	
Cross-validatoa	%	1	100,0	,0	,0	,0	,0	,0	,0	,0	,0	100,0
		2	,0	100,0	,0	,0	,0	,0	,0	,0	,0	100,0
		3	,0	,0	100,0	,0	,0	,0	,0	,0	,0	100,0
		4	,0	,0	,0	100,0	,0	,0	,0	,0	,0	100,0
		5	,0	,0	,0	,0	100,0	,0	,0	,0	,0	100,0
		6	,0	,0	,0	,0	,0	100,0	,0	,0	,0	100,0
		7	,0	,0	,0	,0	,0	,0	100,0	,0	,0	100,0
		8	,0	,0	,0	,0	,0	,0	,0	100,0	,0	100,0
		9	,0	,0	,0	,0	,0	,0	,0	,0	100,0	100,0

Table 135. Classification results.
a. Cross validation is done only for those cases in the analysis in cross validation, each case is classified by the functions derived from all cases other than that case.
b. 100,0% of original grouped cases correctly classified.
c. 100,0% of cross-validated grouped cases correctly classified.

Statistics analysis was also carried out on the aromatic compounds to study the characteristics and possible important statistical differences of the grapes from the theses belonging to the same Denomination of Origin. This is the case of to 'Montecucco' area where multivariate, factorial, discriminating and correlation analyses were carried out.

In addition, among the theses coming from the area of 'Montalcino' was also studied the case of 'Col D'Orcia' estate in order to study in detail the clone effect grown in the same site of cultivation.

3.9.1. 'Montecucco' area

MANOVA analysis was conducted studying the significance of the variables in function of the factor choice (tab. 136).

Factor	Dipendent variable	F	Sig.	Factor	Dipendent variable	F	Sig.
Year	Aliph. alc. ET1	0,22	,804	Thesis* Year	Aliph. alc. ET1	1,07	,413
	Der. benzene ET1	52,55	,000		Der. benzene ET1	5,69	,000
	Phenols ET1	7,81	,002		Phenols ET1	3,73	,002
	Vanillins ET1	0,00	,998		Vanillins ET1	2,13	,049
	Monoterp. ET 1	0,68	,514		Monoterp. ET 1	4,41	,000
	Norisopren. ET1	8,14	,001		Norisopren. ET1	4,96	,000
	Aldehydes ET1	5,48	,009		Aldehydes ET1	3,47	,003
	Acids ET1	101,53	,000		Acids ET1	9,87	,000
	Esters ET1	0,16	,850		Esters ET1	2,16	,045
	Hydro. monot. ET2	2,81	,074		Hydro. monot. ET2	4,35	,001
	Oxi. monot. ET2	3,07	,059		Oxi. monot. ET2	3,49	,003
	Alc. monot. ET2	14,21	,000		Alc. monot. ET2	12,06	,000
	Hydr. norisopr. ET2	21,51	,000		Hydr. norisopr. ET2	2,91	,009
	Ket. norisopr. ET2	8,49	,001		Ket. norisopr. ET2	19,22	,000
	Alc. norisopr. + Ether ET2	6,71	,003		Alc. norisopr. + Ether ET2	10,90	,000
	Heterosides 1	3,390	,045		Heterosides 1	3,210	,005
	Heterosides 2	12,572	,000		Heterosides 2	16,391	,000
	Total	12,57	,000		Total	16,39	,000
	V158	3,17	,054		V158	3,10	,006
	V159	19,79	,000		V159	4,31	,001
	V161	29,33	,000		V161	71,11	,000
	V162	33,80	,000		V162	35,09	,000
	V165	2,09	,139		V165	1,52	,174
	V166	48,16	,000		V166	60,15	,000
	V167	27,50	,000		V167	3,59	,002

Table 136. Test of the effects between subjects (p=<0,05).

From MANOVA analysis, the only variable that, apart from the choice of factor, remains statistically non significant is the ratio trans 8-OH linalool + cis8-OH linalool/p-menth-1-ene-7,8-diol. Moreover this ratio is the only parameter statistically significant selecting the thesis as the factor and to this, aliphatic alcohols from enzymatic hydrolysis are added if the interaction thesis by year is indicated. Vanillins, monoterpenols and esters obteined from enzymatic hydrolysis and hydrocarbon and monoterpenols oxides from hydrolysis acid, are

the aromatic classes that appear statistically non important when the factor is the year. Ratios between single compounds, linalool oxA/linalool oxB lose importance with the year change.

Using data previously obtained, the amount of the variability attributed to the different factor, was calculated (tab. 137). For most of the parameters the variability is attributable to the thesis; the year, however, shows more variability as concerns benzene derivates, phenols, acids and hydrocarbon norisoprenoids. The parameters linked to the ratios show comparable levels of variability attributable to the different source, except of linalool oxA/linalool oxB (acid hydrolysis) and linalool/geraniol (tab. 137).

Variable	% variability due to the thesis	% variability due to the year	% variability due to interaction thesis/year	% variability due to error
Aliph. alc. ET1	79,61	1,95	9,51	8,92
Benzene der. ET1	18,40	72,38	7,84	1,38
Phenols ET1	17,31	51,50	24,60	6,60
Vanillins ET1	81,77	0,01	12,39	5,83
Monoterp. ET 1	52,46	5,29	34,45	7,80
Norisopren. ET1	43,76	32,48	19,77	3,99
Aldehydes ET1	47,85	28,70	18,21	5,24
Acids ET1	35,23	58,51	5,69	0,58
Esters ET1	54,06	2,25	29,88	13,81
Hydro. monot. ET2	58,89	14,16	21,91	5,03
Oxi. monot. ET2	61,06	15,80	17,98	5,16
Alc. monot. ET2	44,30	29,03	24,63	2,04
Hydr. norisopr. ET2	30,11	59,13	8,00	2,75
Ket. norisopr. ET2	42,72	16,95	38,34	2,00
Alc. norisopr. + Ether ET2	45,19	19,76	32,10	2,95
Heterosides 1	40,67	26,47	25,06	7,81
Heterosides 2	45,59	22,83	29,77	1,82
Total	45,59	22,83	29,77	1,82
V158	41,48	25,53	24,94	8,05
V159	9,02	71,74	15,61	3,63
V161	27,33	21,01	50,94	0,72
V162	32,34	32,72	33,97	0,97
V165	24,97	34,01	24,73	16,29
V166	36,83	27,83	34,76	0,58
V167	10,71	76,52	10,00	2,78

Table 137. Level of variability attributable to the different factor.

Using Tukey test, it is possible to note that all the parameters analyzed have given rise to homogenous differentiated subsets (tab. 138-140).

The compounds originated by enzymatic way, except for benzene derivates and esters classis and the compounds obtained by acid hidrolysis, create differentiated homogenous subsets (tab. 138-139).

The variables describing the ratios create both type of homogenous subsets (tab. 140).

Regarding heterosides 1, the most quantitatively present class is that of the benzene derivatives while the aldehydes and esters the least. The thesis with the highest values in most of the different families is the same as the one having lower aliphatic alcohols and acid levels and it is the only thesis not from the 'ColleMassari' wine farm (tab. 138).

Among the compounds extractedby acid hydrolysis the most present are those from the hydrocarbon norisoprenoids class and in a minor way those from monoterpenols oxides and ketones norisoprenoids (tab. 138).

In addition, the grapes from the above mentioned thesis also stand out for the highest aroma levels from heterosides 2, while the lowest levels belong to another single thesis (tab. 139).

The ratios examined accord perfectly well with each other and with the values obtained by other authors on the 'Sangiovese' cultivar (Di Stefano et al, 1998; Lanati et al., 2001) (tab. 140).

Thesis	Aliph. alcohols	Phenols	Vanil.	Monot.	Norisop.	Aldeh.	Acids	Esters	Benzene der.
MC 1	140,95 bc	64,00 ab	126,85 ab	114,62 bc	247,61 ab	1,15 a	71,87 ab	11,80 a	481,98 a
MC 2	121,62 ab	38,04 a	99,19 a	68,54 a	168,92 a	2,49 c	77,45 ab	12,55 a	423,82 a
MC 3	173,35 d	96,92 b	164,31 bc	111,47 b	297,80 bc	2,84 c	106,38 b	10,95 a	606,54 a
MC 4	164,52 cd	92,39 b	166,82 bc	111,35 b	274,33 b	2,28 bc	114,98 b	23,26 a	586,38 a
MC 5	148,38 bcd	68,05 ab	140,78 abc	106,16 b	205,01 ab	1,34 ab	84,11 ab	31,92 a	522,82 a
MC 6	96,51 a	182,14 c	192,39 c	142,11 c	376,85 c	6,01 d	51,10 a	18,58 a	612,49 a

Table 138. Significant parameters with different and no differentiated subsets; heterosides 1. Tukey Test (p=0,05).

Thesis	Hydroc. monot.	Oxid. monot.	Alcoh. monot.	Hydr. norisopr.	Ket. norisopr	Alc. norisopr. + Ethers
MC 1	0,47 b	4,12 b	4,76 b	31,01 d	4,66 ab	30,89 c
MC 2	0,41 ab	4,09 b	3,72 b	26,91 cd	7,78 cd	21,78 b
MC 3	0,27 ab	3,30 ab	4,65 ab	13,95 ab	5,60 bc	15,58 ab
MC 4	0,26 ab	3,17 ab	4,07 ab	19,95 bc	5,40 b	16,99 ab
MC 5	0,22 a	2,31 a	3,33 a	11,64 a	2,55 a	12,06 a
MC 6	0,72 c	5,84 c	6,46 c	29,03 d	8,11 d	31,37 c

Table 139. Significant parameters with different subsets; heterosides 2. Tukey Test (p=0,05).

Thesis	Heter. 1	Heter. 2	Total	V159	V161	V162	V166	V158	V167	V165
MC 1	1299,30 ab	75,92 de	1375,23 ab	6,95 ab	0,04 a	2,69 b	0,04 ab	1,29 a	2,50 a	2,25 a
MC 2	1046,24 a	64,70 cd	1110,94 a	9,51 c	0,07 b	2,76 b	0,06 b	1,26 a	3,19 a	1,76 a
MC 3	1624,16 b	43,37 ab	1667,54 b	7,63 abc	0,06 ab	2,48 b	0,05 b	1,32 a	2,86 a	1,68 a
MC 4	1583,01 b	49,83 bc	1632,85 b	8,64 bc	0,05 ab	2,22 ab	0,06 b	1,40 a	2,90 a	1,87 a
MC 5	1349,30 ab	32,12 a	1381,42 ab	7,49 ab	0,04 a	2,65 b	0,04 ab	1,41 a	2,73 a	1,86 a
MC 6	1755,93 c	81,55 e	1837,48 b	6,41 a	0,13 c	1,53 a	0,03 a	1,34 a	2,97 a	5,21 b

Table 140. Significant parameters with different and no differentiated subsets; heterosides 1,2 and ratios. Tukey Test (p=0,05).

From the multivariate analysis, choosing the year as the source and from the Tukey test, it emerged that most of the parameters examined originate differentiated subsets (tab. 141).

The grapes harvested in 2009 and those of the following year stand out in equal measure, for the highest levels of the aromatic families, with the exception of vanillins, esters and ketones norisoprenoids classes which were predominant in 2011. The variables indicating the ratios between single compounds do not predominate in any one year in particular.

Variable	2009	2010	2011
Aliphatic alcohols ET1	174,25 c	150,63 b	97,87 a
Benzene derivates ET1	633,55 c	537,15 ab	436,54 a
Phenols ET1	89,92 a	89,95 a	85,54 a
Vanillins ET1	150,20 a	140,86 a	151,86 a
Monoterpenols ET 1	116,51 b	116,71 b	91,06 a
Norisoprenoids ET1	241,83 a	307,48 b	227,65 a

Variable	2009	2010	2011
Aldehydes ET1	1,50 a	2,10 b	4,37 c
Acids ET1	88,05 a	82,52 a	84,22 a
Esters ET1	8,99 a	13,27 a	33,07 b
Hydroc. monot. ET2	0,33 a	0,46 b	0,36 ab
Oxid. monot. ET2	4,51 c	3,71 b	3,03 a
Alc. monot. ET2	4,66 b	5,42 b	3,23 a
Hydr. norisopr. ET2	18,04 a	24,63 b	23,25 b
Ket. norisopr. ET2	6,14 b	4,59 a	6,22 b
Norisopr. alc.+ Ether ET2	14,17 a	28,40 c	21,20 b
Heterosides 1	1560,67 b	1491,68 ab	1248,42 a
Heterosides 2	47,86 a	67,23 b	57,30 a
Total	1608,54 b	1558,91 ab	1305,73 a
V158	1,24 a	1,30 a	1,48 b
V159	8,98 b	6,73 a	7,68 a
V161	0,07 b	0,08 b	0,04 a
V162	2,71 b	1,59 a	2,94 b
V165	3,22 b	1,91 a	2,01 a
V166	0,05 b	0,02 a	0,06 b
V167	2,62 a	2,79 a	3,17 a

Tabella 141. Mean separation by multiple range test (Tukey), the comparison is among data shown in horizontal.

Using the factorial statistics analysis it was possible to collect all the variables found and calculated into five new complex variables to represent 94,47% of the total variability of the aromatic characteristics of the berries at harvest (tab. 142).

The descriptors that represent the highest coefficients (tab. 143) operate in a more reliable way in determining the aromatic profile of the berries at harvest.

The first component is linked to the total aromatic content of compounds generated by enzymatic hydrolysis and alcohols monoterpenols classes. Monoterpenols, aliphatic alcohols, ketones norisoprenoids, oxides monoterpenols, trans 8-OH linalool + cis 8-OH linalool/p-menth -1-ene-7,8-diol and linalool/geraniol characterize the second component.

The third is linked to 3-hydroxy β-damascenone/3-oxide α-ionol, to trans 8-OH linalool/cis 8-OH linalool, to hydrocarbon, to monoterpenols and to norisoprenoids. Acids and linalool oxA /linalool oxB are the only two variables correlated to fourth component.

The last component shows coefficient values below 0,4 (tab. 143).

	Weights of rotated factors		
Component	Total	% variability	% cumulated
1	8,88	29,59	29,59
2	8,80	29,34	58,93
3	6,33	21,10	80,03
4	2,99	9,99	90,03
5	1,33	4,44	94,47

Table 142. Results of the factorial analysis: principal components method.

Variable	Component				
	1	2	3	4	5
Total	,964				
Heterosides 1	,958				
Phenols ET1	,953				
Benzene derivates ET1	,948				
Norisoprenoids ET1	,865	-,466			
Vanillins ET1	,825				
Esters ET1	,789			,458	
V159	-,693		-,449	,441	
Alcohols monoterpenols ET2	-,681	,615			
Monoterpenols ET 1		,981			
V165		,970			
V161		,934			
Ketones norisoprenoids ET2		,904			
Oxides monoterpenols ET2		,852			
Aliphatic alcohols ET1		-,766		,469	
V167		,447			
Alcohols + ethers norisoprenoids ET2			,975		
Heterosides 2			,896		
Hydrocarbon norisoprenoids ET2			,893		
Hydrocarbon monoterpenols ET2			,844	-,425	
V162		-,575	,767		
V166			,748		
Aldeids ET1			,740		
V158				-,925	
Acids ET1				,803	

Table 143. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.

By extracting only two of the components from the total data it is possible to explain 64,32% of the total variability (tab. 144). The variables examined are subdivided into equal parts between the two extracted components (tab. 145).

The graph (fig. 70) shows how the descriptors that are in the same quadrant and that are close to the ripening index of the berry are directly correlated to it while those further away are correlated negatively. The first and the second component are negatively correlated only with the linalool oxC /linalool oxD e linalool/geraniol. The first component is negatively correlated with the ratios and the monoterpenols, with oxides e alcohols ,with monoterpenols, and with ketones norisoprenoids. Most aromatic compounds classes and total are, on the contrary, negatively correlated with the second component (fig. 70).

Component	Weights of rotated factors		
	Total	% variance	% cumulated
1	10,59	35,30	35,29
2	8,71	29,03	64,32

Table 144. Results of the factorial analysis extracting only the first two components: method of the principal components.

Variable	Component	
	1	2
Aldeids ET1	,853	
V 162	,821	,516
Vanillis ET1	,781	-,410
Norisoprenoids ET1	,746	-,509
Hydrocarbon monoterpenols ET2	,643	,731
Benzene derivates ET1	,576	-,659
Total	,575	-,635
Heterosides 1	,563	-,665
Alcohols + ethers norisoprenoids ET2	,518	,791
Esters ET1	,478	-,685
V167		
Heterosides 2		,874
Hydrocarbon norisoprenoids ET2		,868
V166		,745
Acids ET1		-,732
Phenols ET1		-,600
V158		,547
Aliphatic alcohols ET1		
Ketones norisoprenoids ET2	-,533	,546

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Oxides monoterpenols ET2	-,573	,572
V159	-,574	
Monoterpenols ET 1	-,691	
V165	-,812	
V161	-,879	
Alcohols monoterpenols ET2	-,959	

Table 145. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.
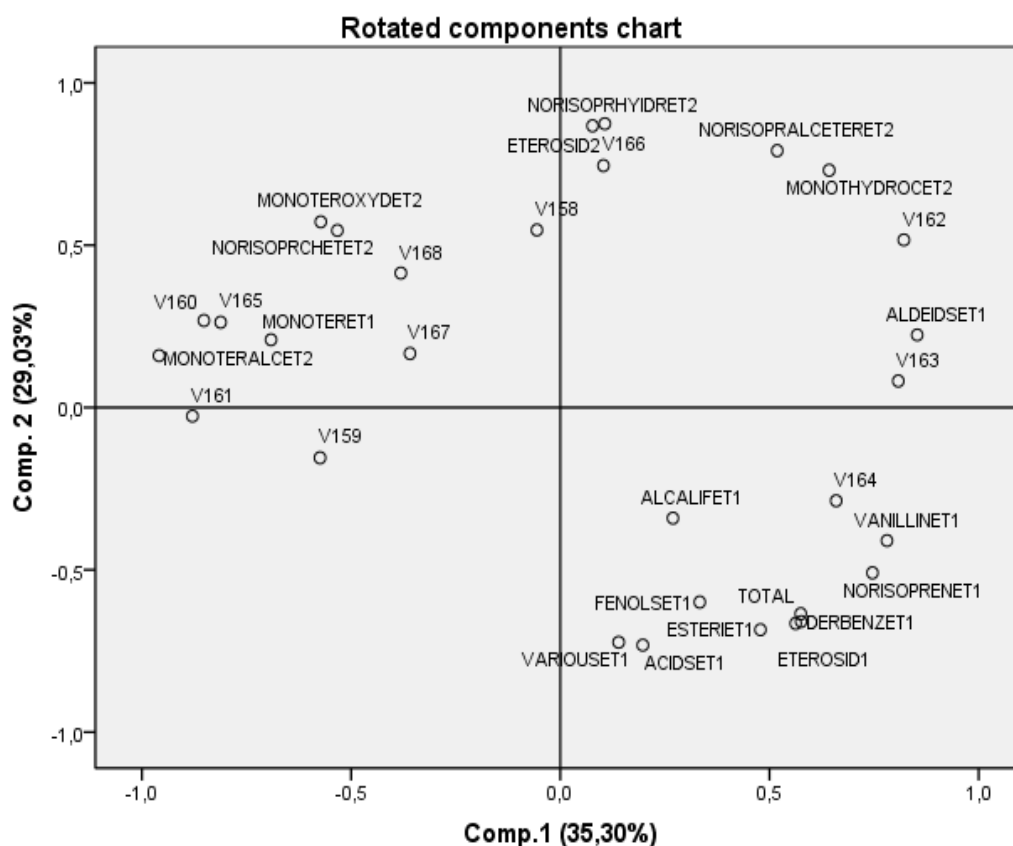
Figure 70. Rotated graph of the first two components obtained from the factorial analysis

Examining the correlation between the parameters analyzed, in the table, only the variables with a probability <0,00001 are reported and the characters in bold indicate the negativity of the value indicated. Esters, linalool oxA /linalool oxB, linalool oxC /linalool oxD, 3-hydroxy β-damascenone/3-oxyde α-ionol and linalool oxA /linalool oxB, are the parameters that don't present significant Pearson's correlations (tab. 146). Pearson's significant correlations are mostly positive except for linalool/geraniol, trans 8-OH linalool/cis 8-OH linalool and alcohols monoterpenols.

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Variable	Aliph. Alc ET1	Benz. Der. ET1	Phen ET1	Van. ET1	Mon. ET 1	Nor. ET1	Ald. ET1	Acid ET1	Hydr. Monot. ET2	Oxid Monot. ET2	Alc. Monot ET2	Hydr. Noris. ET2	Ket. Noris. ET2	Alc+Et. Noris. ET2	Heter. 1	Heter. 2	Tot.	V 161	V 162	V 165
Aliph. Alc. ET1		0,57																		
Benz. Deriv. ET1	0,57		0,66	0,78		0,70									0,95		0,94			
Phenols ET1		0,66		0,79		0,82	0,60								0,79		0,80			
Vanillins ET1		0,78	0,79			0,76									0,88		0,88			
Monoterp. ET 1											0,54				0,53		0,55	0,53		0,64
Norisopr.ET1		0,70	0,82	0,76											0,86		0,87			
Aldehyd.ET1			0,60																	
Acids ET1															0,52					
Hydroc. Monot. ET2										0,67	0,55	0,71		0,70		0,76				
Oxid. Monot. ET2									0,67		0,71	0,74	0,71	0,57		0,76		0,63		0,61
Alcohols Monot. ET2					0,54				0,55	0,71				0,59		0,63		0,56	**0,62**	
Hydrocarbon Norisop.ET2									0,71	0,74			0,65	0,86		0,97				
Ketones Norisop.ET2										0,71		0,65				0,63		0,53		
Alcoh.+ Eters Norisop.ET2									0,70	0,57	0,59	0,86				0,93				
Heterosides 1		0,95	0,79	0,88	0,53	0,86		0,52												
Heterosides 2									0,76	0,76	0,63	0,97	0,63	0,93						
Total		0,94	0,80	0,88	0,55	0,87														
V161					0,53					0,63	0,56		0,53						**0,69**	0,84
V162											0,62								**0,69**	
V165					0,64					0,61								0,84		

Table 146. Pearson's correlations. Bold numbers are preceded by the minus sign. Legend abbreviations is on the previous pages.

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The Stepwise discriminant analysis gave the best results to study the characteristics and possible important statistical differences of the grapes from the theses belonging to the same Denomination of Origin (fig. 71).

The first two canonical functions represent more than 94,0 % of the total variability (tab. 147).

Function	Eingenvalue	% of variance	% cumulated	Canonical correlation
1	231,771	83,6	83,6	,998
2	31,404	11,3	94,9	,984
3	8,452	3,0	97,9	,946
4	4,525	1,6	99,6	,905
5	1,219	,4	100,0	,741

Table 147. Eigenvalues of discriminant analysis.

Looking at the graph of the centroids obtained from the discriminating analysis data (fig. 71), is observed that the points relative to centroids present a limited dispersion. In the centroid there are two distinct groups, the first belonging to a thesis from a different estate from the other five and it is the only one that stands out. In the second group the other theses: among these, the second stands out more from the others, while numbers four and five overlap in some points.

The 100,0% of the original grouping are classified correctly, while 88,7% of the cases grouped cross-validated are reclassified correctly (tab. 148).
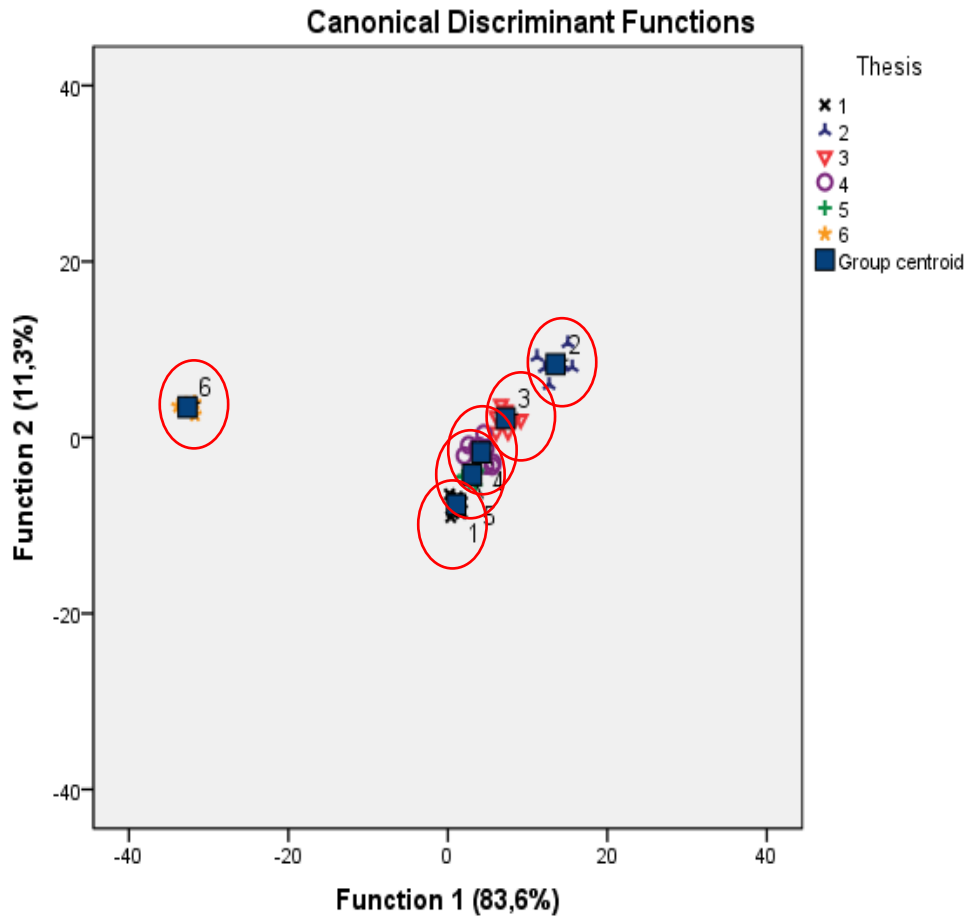
Figure 71. Centroids obtained from the cluster analysis of the aromatic characteristics of the grapes at harvest's time.

		Thesis	Group expected						Totals
			1	2	3	4	5	6	
Cross-validation a	%	1	100,0	,0	,0	,0	,0	,0	100,0
		2	,0	100,0	,0	,0	,0	,0	100,0
		3	,0	,0	77,8	22,2	,0	,0	100,0
		4	,0	,0	,0	66,7	33,3	,0	100,0
		5	,0	,0	,0	11,1	88,9	,0	100,0
		6	,0	,0	,0	,0	,0	100,0	100,0

Table 148. Classification results.
a. Cross validation is done only for those cases in the analysis in cross validation, each case is classified by the functions derived from all cases other than that case.
b. 100,0% of original grouped cases correctly classified.
c. 88,7% of cross-validated grouped cases correctly classified.

3.9.2 'Col d'Orcia' estate

In the multivariate analysis, if the factor is the thesis, all the variables examined appear to be statistically important, however, if in the course of the analysis the factor choice is the year the alcohol aliphatic, the vanillins and the aldehydes derived from the enzymatic hydrolysis lose their statistical significance. From the interaction thesis by year, some variables are not statistically different for instance: the benzene derivates, esters, hydrocarbon and monoterpenols alcohols, ketones norisoprenoids, the total compounds originated by acid hydrolysis and the content of the identified aromatic compounds expressed in ng/g fresh weight. The ratios linalool oxC/linalool oxD, linalool/geraniol, trans 8-OH linalool/cis 8-OH linalool and 3-hydroxi β-damascenone/3-oxo-ionol do not appear statistically relevant only by the interaction thesis by year (tab. 149).

Factor	Dipendent variable	F	Sign.	Factor	Dipendent variable	F	Sign.
Year	Aliph. alc. ET1	1,077	,353	Thesis* Year	Aliph. alc. ET1	2,138	,063
	Der.b enzene ET1	11,022	,000		Der. benzene ET1	1,541	,185
	Phenols ET1	3,823	,033		Phenols ET1	2,633	,026
	Vanillins ET1	,232	,794		Vanillins ET1	1,523	,191
	Monoterp. ET 1	4,390	,021		Monoterp. ET 1	2,582	,028
	Norisopren. ET1	20,674	,000		Norisopren. ET1	4,548	,001
	Aldehydes ET1	,023	,977		Aldehydes ET1	6,453	,000
	Acids ET1	203,831	,000		Acids ET1	12,527	,000
	Esters ET1	16,687	,000		Esters ET1	1,780	,121
	Hydro. monot. ET2	13,380	,000		Hydro. monot. ET2	1,414	,231
	Oxi. monot. ET2	16,655	,000		Oxi. monot. ET2	2,493	,033
	Alc. monot. ET2	7,753	,002		Alc. monot. ET2	1,312	,276
	Hydr. norisopr. ET2	12,937	,000		norisopr. ET2	2,756	,021
	Ket. norisopr. ET2	14,228	,000		Ket. norisopr. ET2	1,201	,331
	Alc.nor. + Ether ET2	18,947	,000		Alc. nor. + Ether ET2	2,325	,045
	Heterosides 1	3,434	,045		Heterosides 1	2,678	,024
	Heterosides 2	19,036	,000		Heterosides 2	1,425	,227
	Total	19,036	,000		Total	1,425	,227
	V158	3,375	,048		V158	2,924	,015
	V159	13,964	,000		V159	1,696	,140
	V161	30,696	,000		V161	1,373	,248
	V162	44,142	,000		V162	2,140	,063
	V165	27,556	,000		V165	3,607	,005
	V166	8,854	,001		V166	2,162	,060
	V167	4,450	,020		V167	3,441	,006

Table 149. Test of the effects between subjects, p= <0,05.

Using data previously obtained the amount of variability attributed to the different factor was calculated (tab. 150). The variability of none of the variables examined is due in percentage to the interaction thesis by year. The thesis, however, shows more variability as concerns aroma compounds generated by enzymatic hydrolysis; on the contrary aroma compounds originated by acid hydrolysis are the variables that show more variability when the factor is represented by the year. The ratios between the compounds show higher percentage values of variability for the year.

Variable	% variability due to the thesis	% variability due to the year	% variability due to interaction thesis/year	% variability due to error
Aliph. alc. ET1	55,29	11,42	22,67	10,61
Derivates benzene ET1	64,01	29,25	4,09	2,65
Phenols ET1	77,26	11,66	8,03	3,05
Vanillins ET1	73,61	2,23	14,59	9,58
Monoterpenols ET 1	69,71	16,68	9,81	3,80
Norisoprenoids ET1	59,35	32,05	7,05	1,55
Aldehydes ET1	84,07	0,05	13,75	2,13
Acids ET1	8,95	85,38	5,25	0,42
Esters ET1	35,95	54,90	5,86	3,29
Hydro. monot. ET2	37,58	52,88	5,59	3,95
Oxi. monot. ET2	43,98	46,31	6,93	2,78
Alc. monot. ET2	42,41	44,37	7,51	5,72
Norisopr. ET2	46,56	41,42	8,82	3,20
Ket. norisopr. ET2	24,86	65,07	5,49	4,57
Alc. nor. + Ether ET2	34,06	56,10	6,88	2,96
Heterosides 1	80,88	9,23	7,20	2,69
Heterosides 2	31,24	60,99	4,56	3,20
Total	31,24	60,99	4,56	3,20
V158	82,46	8,11	7,03	2,40
V159	15,48	70,85	8,60	5,07
V161	23,04	71,44	3,20	2,33
V162	30,35	65,03	3,15	1,47
V165	8,89	78,06	10,22	2,83
V166	31,57	50,42	12,31	5,70
V167	28,89	35,59	27,52	8,00

Table 150. Level of variability attributable to the different factor.

From Tukey test it is possible to note the table with the different subsets and those non differentiated (tab. 151-153).

Within the heterosides 1 classis, only the esters class creates non differentiated homogeneous subsets while in the heterosides 2 there is not even one. In the compounds released by enzymes, the benzene derivates family is the most prominent in the theses while the aldehydes are quantitatively inferior; from a concentration of hundreds of ng/g fresh weight of vegetable tissue to values close to the unit (tab. 151).

Comparing the theses in the study, the second and third show lower levels of compounds freed by enzymatic way and the fifth, BM5, stands out for the highest heterosides 1 and 2 content and therefore for total aromas. The grapes from the BM4 sample contain lower quantities of compounds originated by acid hydrolysis, except for the hydrocarbon monoterpenols class (tab. 152).

As can be seen from all the ratios examined there is perfect harmony in the results and in the values obtained in literature by other authors for the 'Sangiovese' cultivar (Di Stefano et al., 1998; Lanati et al., 2001). The first and second ratio regarding the linalool oxides are completely favourable to the trans form compounds compared to the cis one; the linalool/geraniol ratio is much less than one in the grapes with a low linalool concentration (tab. 153).

Thesis	Aliph. alcoh.	Der. benzene	Phenols	Vanillins	Monoter.	Norisopr.	Aldeids	Acids	Esters
BM 1	160,58 a	441,89 a	65,19 a	125,95 a	91,09 b	242,10 b	2,2 b	101,77 a	15,60 a
BM 2	140,38 a	437,87 a	59,21 a	120,85 a	66,11 a	165,83 a	2,89 cd	52,98 a	11,04 a
BM 3	151,84 a	471,26 a	52,60 a	111,11 a	75,28 ab	220,42 ab	1,50 a	86,85 a	11,84 a
BM 4	132,60 a	504,47 a	71,27 a	117,05 a	72,52 ab	234,71 ab	2,48 bc	79,96 a	8,45 a
BM 5	268,26 b	815,22 b	115,79 b	213,84 b	147,66 c	463,41 c	3,42 d	162,38 b	13,38 a

Table 151. Significant parameters with different and no differentiated subsets; heterosides 1. Tukey Test (p=0,05).

Thesis	Hydroc. monot.	Oxid. monot.	Alc. monot.	Hydr. norisopr.	Ket. norisopr.	Alc. norisopr + Ethers
BM 1	0,36 b	2,86 ab	3,19 a	21,99 ab	6,30 a	19,58 a
BM 2	0,12 a	3,24 b	3,03 a	22,28 ab	6,22 a	15,67 a
BM 3	0,42 b	3,06 b	3,03 a	19,79 a	5,10 a	16,20 a
BM 4	0,24 ab	1,40 a	1,97 a	12,66 a	3,63 a	10,20 a
BM 5	0,72 c	4,13 b	5,59 b	36,15 b	10,63 b	36,62 b

Table 152. Significant parameters with different subsets; heterosides 2. Tukey Test (p=0,05).

Thesis	Heter. 1	Heter. 2	Total	V158	V159	V161	V162	V165	V166	V167
BM 1	1304,84 a	54,54 a	1359,38 a	1,42 ab	6,77 a	0,08 c	1,63 a	1,95 ab	0,06 ab	4,67 a
BM 2	1098,24 a	50,59 a	1148,86 a	1,59 b	7,89 ab	0,05 b	2,23 b	1,93 ab	0,09 b	2,77 a
BM 3	1225,09 a	47,69 a	1272,77 a	1,47 ab	8,70 b	0,04 ab	2,18 ab	1,40 a	0,06 ab	4,97 a
BM 4	1260,88 a	30,12 a	129,00 a	1,45 ab	8,44 b	0,05 ab	1,74 ab	1,50 a	0,07 ab	2,80 a
BM 5	2277,13 b	93,86 b	2370,99 b	1,33 a	8,07 ab	0,03 a	2,29 b	2,29 b	0,05 a	2,63 a

Table 153. Significant parameters with different subsets; heterosides 1, 2 and ratios. Tukey Test (p=0,05).

From the multivariate analysis where factor choice is the year and from the Tukey test, it appears that most of the parameters tested originate homogenous differentiated subsets, exception made for phenols, norisoprenoids and esters classes. Linalool oxA/linalool oxB generated by acid hydrolysis is the only ratio between specific compounds that creates homogenous non differentiated subsets.

The grapes harvested in 2010 stand out for the highest levels of the aromatic families, with the exception of esters classes which were predominant in 2009. On the contrary, vanillins, oxides monoterpenols, norisoprenoids, alcohols + ethers monoterpenols, were predominant in 2011 (tab. 154).

Variable	2009	2010	2011
Aliphatic alcohols ET1	181,65 b	192,78 b	137,77 a
Benzene derivates ET1	565,99 b	557,44 ab	478,99 a
Phenols ET1	69,38 a	76,11 a	72,95 a
Vanillins ET1	130,91 ab	126,06 a	156,31 b
Monoterpenols ET 1	79,04 a	112,37 b	80,18 a
Norisoprenoids ET1	265,76 a	267,16 a	262,96 a
Aldehydes ET1	1,47 a	1,54 a	4,49 b
Acids ET1	86,36 a	139,91 b	64,10 a
Esters ET1	14,83 a	12,83 a	8,53 a
Hydroc. monot. ET2	0,17 a	0,44 b	0,51 b
Oxid. monot. ET2	2,04 a	3,35 b	3,43 b
Alc. monot. ET2	2,28 a	4,18 b	3,62 b
Hydr. norisopr. ET2	10,64 a	25,84 b	31,25 b
Ket. norisopr. ET2	4,19 a	5,69 a	9,25 b
Norisopr. alc.+ Ether ET2	7,52 a	24,10 b	27,34 b
Heterosides 1	1435,53 ab	1557,14 b	1307,02 a
Heterosides 2	26,86 a	63,63 b	75,58 b
Total	1462,39 ab	1620,80 b	1382,61 a

Variable	2009	2010	2011
V158	1,28 a	1,58 b	1,49 b
V159	6,67 a	9,94 b	7,31 a
V161	0,07 b	0,06 b	0,02 a
V162	1,66 a	2,06 b	2,34 b
V165	1,62 a	2,23 b	1,59 a
V166	0,06 ab	0,05 a	0,08 b
V167	2,71 a	4,99 a	3,01 a

Table 154. Mean separation by multiple range test (Tukey) the comparison is among data shown in horizontal.

Using the factorial statistics analysis it was possible to collect all the variables found and calculated into six new complex variables (components) to represent 95,08% of the total variability of the aromatic characteristics of the berries at harvest (tab. 155).

The first component is linked to aromatic compounds released by acid hydrolysis, on the other hand, the second to classes belonging to the heterosides 1. Monoterpenols, esters and the most of the variables studied characterize the third component. The fourth and the fifth component are linked to only one variable precisely trans 8-OH linalool/cis 8-OH linalool e linalool oxA/linalool oxB respectively. Finally the last component shows coefficient values below 0,4 (tab. 156).

Component	Total	Weights of rotated factors	
		% variability	% cumulated
1	7,84	26,15	26,15
2	7,09	23,63	49,78
3	6,90	23,01	72,79
4	2,63	8,76	81,55
5	2,40	8,00	89,55
6	1,66	5,53	95,08

Tab 155. Results of the factorial analysis: principal components method.

Variable	Component					
	1	2	3	4	5	6
Heterosides 2	,961					
Hydrocarbon norisoprenoids ET2	,961					
Hydrocarbon monoterpenols ET2	,956					
Alcohols + ethers norisoprenoids ET2	,936					
Ketones norisoprenoids ET2	,806					
Alcohols monoterpenols ET2	,698		,484			
Oxides monoterpenols ET2	,624					-,492
Aldehydes ET1	,595	,613				
Benzene derivates ET1		,953				
Phenols ET1		,939				
Vanillins ET1		,919				
Monoterpenols ET 1			,882			
Norisoprenoids ET1		,881				
Heterosides 1		,969				
Total		,951				
V158			,784			
V159			,822			
V162		,472		,834		
V165			,759			
V166			-,961			
V167					-,954	
Acids ET1	-,400		,513		,413	,430
V161	-,490					
Esters ET1	-,601					
Aliphatic alcohols ET1	-,701					,482

Table 156. Matrix of the rotated components (Varimax) in order of importance. Coefficient values below 0,4 are not included as of little relevance.

Extracting only two components from all the data collected it is possible to explain 62,02 % of the total variability (tab. 157).

In particular the first component is greatly linked to the most of the ratios analysed, to the classes generated by enzymatic hydrolysis and to ketones norisoprenoids by acid one.

The second, on the other hand, to herterosides 2, to aliphatic alcohols, to monoterpenols and to acids classes (tab. 158).

The graph (fig. 72) shows how both of the components are negatively correlated with the esters, the aliphatic alcohols and the linalool/geraniol. The first component is negatively correlated with the acids and the monoterpenols derived from enzymatic hydrolysis, with oxides e alcohols monoterpenols from acid hydrolysis, and with the most of ratios between

specific aromatic compounds. Benzene derivates, phenols, vanillins, heterosides 1 and 3-hydroxi β-damascenone/3-oxo-ionol are negatively correlated with the second component.

	Weights of rotated factors		
Component	Total	% variance	% cumulated
1	9,70	32,32	32,32
2	8,91	29,70	62,02

Table 157. Results of the factorial analysis extracting only the first two components: method of the principal components.

Variable	Component	
	1	2
Aldehydes ET1	,921	
Norisoprenoids ET1	,895	
Derivates Benzene ET1	,786	
Vanillins ET1	,781	
Total	,734	
Ketones norisoprenoids ET2	,727	
Phenols ET1	,706	
Heterosides 1	,691	
V162	,666	
V166		-,700
Acids ET1	-,588	
V159	-,644	,706
V158	-,730	,482
V161	-,851	
Aliphatic alcohols ET1		-,473
Monoterpenols ET 1		,759
Esters ET1		-,530
Hydrocarbon monoterpenols ET2		,866
Oxides monoterpenols ET2		,838
Alcohols monoterpenols ET2		,952
Hydrocarbon norisoprenoids ET2		,879
Alcohols + ethers norisoprenoids ET2		,898
Heterosides 2		,882
V165		,829
V167		

Table 158. Matrix rotated (Varimax) of the first two components extracted. Descriptors ordered in order of importance excluding the <0,4 coefficients as of little relevance.
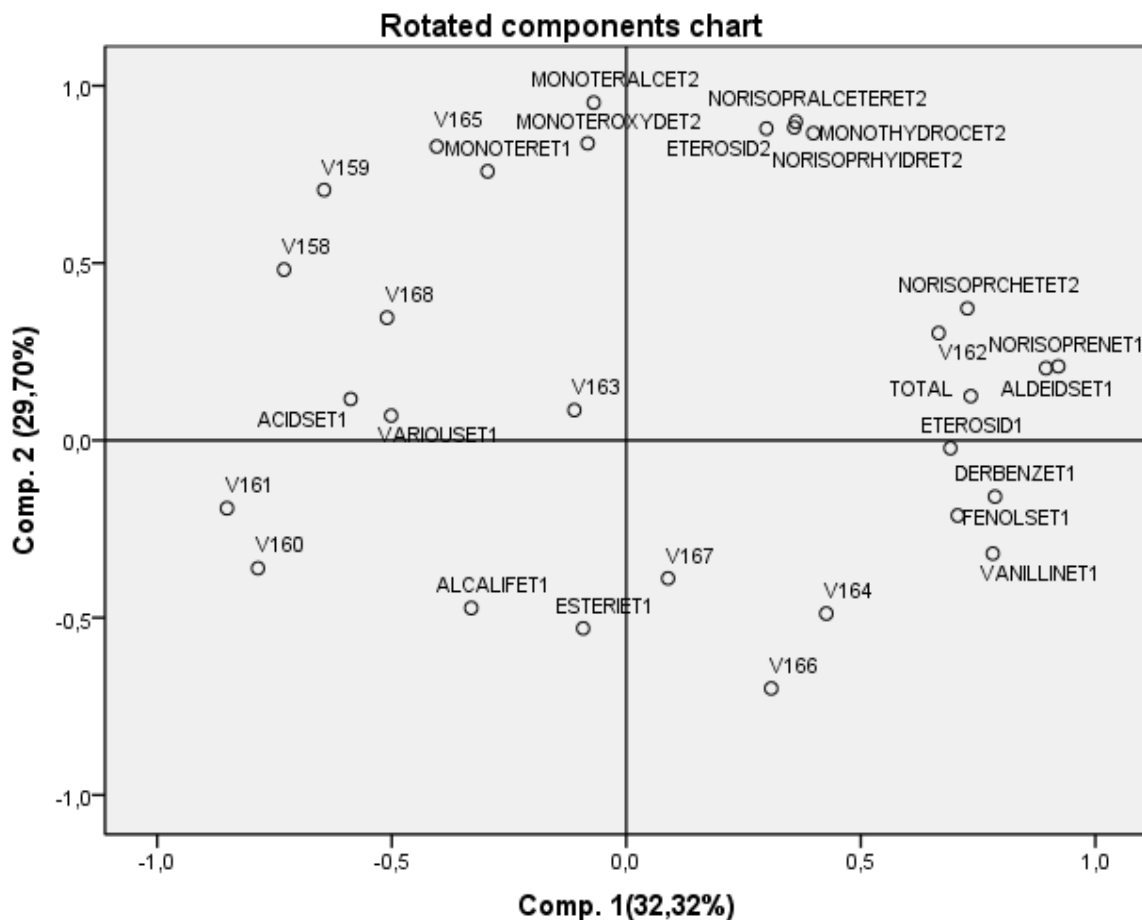
Figure 72. Rotated graph of the first two components obtained from the factorial analysis.

Examining the correlation between the parameters analyzed, in the table only the variables with a probability <0,00001 are reported and the characters in bold indicate the negativity of the value indicated.

Esters, trans 8-OH linalool/cis 8-OH linalool, 3-hydroxi β-damascenone/3-oxo-ionol, linalool oxA/linalool oxB, are the parameters that don't present significant Pearson's correlations. In most cases there are values of Pearson's correlation positive. However Pearson's correlations among ratios and others variables, are negatively correlated and show lower values (tab. 159). The following variables show Pearson values close to the unit and thus are closely correlated to each other: aromatic compounds derivated by enzymatic hydrolysis and total aromatic compounds, the benzene derivates and the norisoprenoids. Those derived from acid hydrolysis are closely correlated to hydrocarbon norisoprenoids and alcohols + ethers monoterpenols (tab. 159).

	Aliph. Alc ET1	Benz. Der. ET1	Phen ET1	Van. ET1	Mon. ET 1	Nor. ET1	Ald. ET1	Acid ET1	Hydr. Monot. ET2	Oxid Monot. ET2	Alc. Monot ET2	Hydr. Noris. ET2	Ket. Noris. ET2	Alc+Et. Noris. ET2	Heter. 1	Heter. 2	Tot.	V 158	V 159	V 161	V 165
Aliph. Alc. ET1		0,84	0,69	0,63	0,82	0,72		0,82							0,90		0,89				
Benz. Deriv. ET1	0,84		0,85	0,81	0,74	0,90		0,59							0,96		0,95				
Phenols ET1	0,69	0,85		0,82	0,68	0,84									0,88		0,87				
Vanillins ET1	0,63	0,81	0,82		0,59	0,85	0,55						0,56		0,83		0,84				
Monoterp. ET 1	0,82	0,74	0,68	0,59		0,75		0,83	0,56		0,68		0,59		0,85		0,87				0,57
Norisopr. ET1	0,72	0,90	0,84	0,85				0,55	0,57						0,93		0,94				
Aldehyd.ET1				0,55									0,68							**0,59**	
Acids ET1	0,82	0,59			0,83	0,55									0,74		0,73				
Hydroc. Monot. ET2					0,56	0,57				0,62	0,73	0,79	0,71			0,85					
Oxid. Monot. ET2									0,62		0,86	0,82	0,64	0,74		0,81					
Alcohols Monot. ET2					0,68				0,73	0,86		0,83	0,68	0,84		0,86					
Hydrocarbon Norisop.ET2									0,79	0,82	0,83		0,86	0,94		0,99					
Ketones Norisop.ET2				0,56			0,68		0,71	0,64	0,68	0,86		0,81		0,88				**0,56**	
Alcoh.+ Eters Norisop.ET2					0,59				0,90	0,74	0,84	0,94	0,81			0,98					
Heterosides 1	0,90	0,96	0,88	0,83	0,85	0,93		0,74									1,00				
Heterosides 2									0,85	0,81	0,86	0,99	0,88	0,98							
Total	0,89	0,95	0,87	0,84	0,87	0,94		0,73							1,00						
V158																			0,60		
V159																		0,60			
V161							**0,59**						**0,56**								
V165					0,57																

Table 159. Pearson's correlations. Bold numbers are preceded by the minus sign. Legend abbreviations is on the previous pages.

The Stepwise discriminant analysis gave the best results to study the characteristics and possible important statistical differences of the grapes from the theses belonging to the same estate (fig. 68).

Discriminant analysis on the aromatic characteristics of the grapes at harvest's time highlighted differences between clones examined and some of which may be distinct.

The first two canonical functions represent more than 95,0 % of the total variability (tab. 160).

Function	Eingenvalue	% of variance	% cumulated	Canonical correlation
1	71,504	79,3	79,3	,993
2	14,350	15,9	95,2	,967
3	3,266	3,6	98,9	,875
4	1,029	1,1	100,0	,712

Table 160. Eigenvalues of discriminant analysis.

In the centroids graph obtained from the discriminant analysis (fig. 73), three distinct groups appear: the first includes the thesis BM2, BM3 e BM4 that intersect each others. The second only BM1 and the third BM5 which well differs from the others, because well detached from the other theses.

The original grouping classified correctly 97,8% of the data, while 84,4% of the cases grouped cross-validated were reclassified correctly (tab. 161).
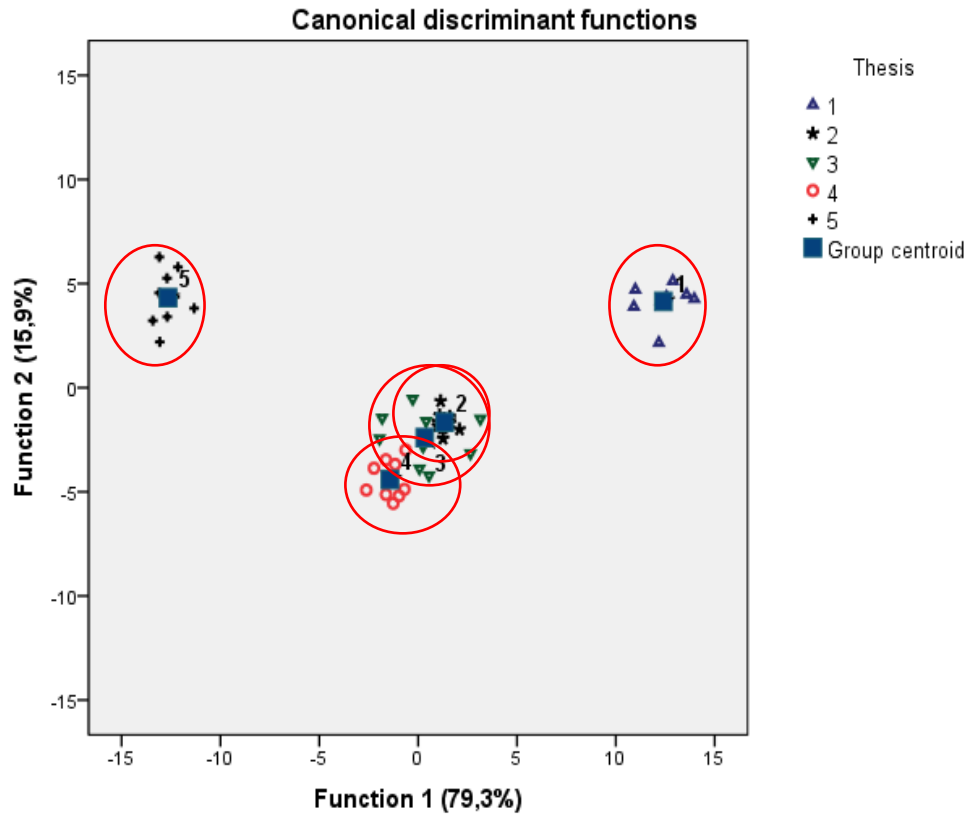
Figure 73. Centroids obtained from the cluster analysis of the characteristics of the grapes at harvest's time.

		Thesis	**Group expected**					**Totals**
			1	**2**	**3**	**4**	**5**	
Cross- validatoa	%	1	100,0	,0	,0	,0	,0	100,0
		2	,0	77,8	22,2	,0	,0	100,0
		3	,0	11,1	66,7	22,2	,0	100,0
		4	,0	,0	22,2	77,8	,0	100,0
		5	,0	,0	,0	,0	100,0	100,0

Table 161. Classification results.

a. Cross validation is done only for those cases in the analysis In cross validation, each case is classified by the functions derived from all cases other than that case.
 b. 97,8% of original grouped cases correctly classified.
 c. 84,4% of cross-validated grouped cases correctly classified.

4. DISCUSSION AND CONCUSIONS

The variety 'Sangiovese' is a genotype characterized by a wide variation of expression due to its high responsiveness to the environment so it would be possible to obtain in different areas wines with quality levels very similar, though differentiated between them, thus expressing the varietal potential in response to a specific *terroir* (Brancadoro et al., 2006; Bucelli et al., 2013; Scalabrelli, 2013*)*. These studies of the wines produced with 'Sangiovese' as the main variety in Tuscany mainly identify by Denomination of Origin DOCG and DOC suggest that possible terroirs identifiable, could be still more numerous (Costantini et al., 2006, 2008; Scalabrelli, 2013). Research carried out in Tuscany showed that measuring several variables of vine performance could be used to predict wine quality (Bucelli et al., 2010) although the grape aroma compound were not determined. This method of testing the wine-making production allowed us to evaluate phenotypic expression of growing and of quality as a consequence of interaction between genotype and environment (Scienza *et al.*, 1990; Asselin, 2000; Panont *et al.*, 1994). Generally the product of a genotype isn't set strictly but it can have a broad range of expressions, this range is as extensive as greater is the responsiveness to local influences.

Although the 'Sangiovese' grapevine was well studied, it is not possible to indicate a generalized vineyard model adapt to all situations. Our investigations performed on the grapes at maturity does not aim to make a hierarchical scale of oenological products of a specific terroir, but to provide a way to understand the potential of a territory in order to enhance its specificity.

Our research was conducted in three consecutive years (2009, 2010 and 2011), on 'Sangiovese' vineyards in five areas of production located in 'Grosseto', 'Pisa', and 'Siena' provinces, involving a total of 17 theses. The corresponding Denomination areas of wine production were: 'Brunello di Montalcino', 'Chianti Classico', 'Chianti Colline Pisane', 'Montecucco' and 'Morellino di Scansano': the vineyards are similar as the age, training system, vine density, bud load and yield were maintained close to the limit imposed by the denominations (7-8 t/ha).

The examined areas are not homogeneous, as for pedological and climatic characteristics, these ones are modulated by exposure, altitude and by interaction year by site. It follows that some grapes presented clearly differences attributable to several factors and in other cases the effects are difficult to generalize because of phenomena of compensation or of complex

interaction among factors. Technical soil and canopy management (shoot trimming and cluster thinning) were necessary to compensate for the factors that act negatively on quality parameters of 'Sangiovese' vines, known to be more sensitive to the ecopedological variables, compared to other international varieties. In this context, we underline the importance of the winegrower in order to ensure obtaining a product in conformity with the standards of production and at the same time having specific quality requirements, and possibly a strong territorial character (Scalabrelli et al., 2004).

Sometimes the climatic parameters among distant areas are more similar than those ones among areas very close.

The weather conditions affected significantly several parameter of yield and grape quality according to the year and the site. In fact, 2010 was the coldest year and 2011, instead, the hottest in June, August and September determining a generalized advanced of the harvest's time in all the Denomination areas. In 2009, however, the temperature reached in some locations the highest peaks. Most probably the high temperatures of 2009 brought a degradation of the aromatic substances which remained the same the following year as a result of the lower temperatures (D'Onofrio, oral communications). The maximum, minimum and mean temperature were negatively correlated with most of the aroma compounds (tab. 162) especially regarding to the compounds released by acid hydrolysis.

Aroma classes		T Max June-Sept	T Min June-Sept	T Mean June-Sept	T Max Aug-Sept	T Min Aug-Sept	T Mean Aug-Sept
Monoterpenols ET 1	P.C.	-,605			-,586		
	Sig.	,004			,005		
Acids ET1	P.C.	-,537			-,503		-,469
	Sig.	,011			,017		,025
Hydroc. monot. ET2	P.C.		-,552	-,585		-,566	-,499
	Sig.		,009	,005		,007	,017
Oxide monoterp. ET2	P.C.		-,715	-,658		-,710	-,617
	Sig.		,000	,002		,000	,003
Hydroc. norisop. ET2	P.C.		-,672	-,731		-,671	-,599
	Sig.		,001	,000		,001	,004
Ketones norisop. ET2	P.C.		-,600			-,581	
	Sig.		,004			,006	
Alcoh. + Eters norisop. ET2	P.C.		-,428	-,591		-,487	-,537
	Sig.		,038	,005		,020	,011
Compounds released by acid hydrolysis	P.C.		-,636	-,680		-,654	-,588
	Sig.		,002	,001		,002	,005

Table 162. Pearson's correlations.

Maximum, minimum and mean temperature in the period June-July were negatively correlated with aldehydes and esters, too.

Daily excursion, nevertheless, were negatively correlated with most of the aroma compounds originating from acid hydrolysis and with terpenols from enzymatic hydrolysis because of the high peak of maximum temperatures.

Minimun and mean temperature in the period June-September, were negatively correlated with titratable acidity and positively correlated to ripening technological index. Analysing only June-July period, were found negative correlation between maximum temperature and skin berry weight and the total berry polyphenols content.

On the basis of the mean climatic data observed during the three years studied, three distinct groups were obtained: the first represented by the stations of 'San Miniato' ('Chianti Colline Pisane') and 'Magliano' ('Morellino di Scansano') that appear less distinct and by the two stations belonging to the 'Montalcino' area. The second is constituted by the station of 'Gaiole', and the third by 'Cinigiano' ('Montecucco') which is the most distinguishable.

The 2011 was the year with the most mature grapes from a sensory point of view, especially as regards the pulp. The 2010, instead, showed more seeds phenolic maturity.

Regarding the berry sensorial maturity the lowest values were shown in the thesis of 'Chianti Colline Pisane' characterized by modest rainfall, high maximum temperatures, by having silt, alkaline, calcareous soils, poor of organic matter and potassium and with a mean amount of magnesium and phosphorus. These characteristics, had a negative effect on concentration of most of the aroma compounds found in the grapes.

In general, optimal value of sensory maturity were observed in 'Siena's province and precisely in the vineyards located in the 'Chianti Classico': they are characterized by medium to high content of sand, medium silt and a variable amount of clay. Both soils are alkaline, moderately rich in active limestone, organic matter and mineral elements. In addition we observed in this area lower mean temperature during the summer months and slower grape ripening along two years which assured higher concentration of aroma compounds (tab. 162) and a better seed phenolic maturity.

Although the training systems utilized, e.g. spur cordon and Guyot cannot be compared, it was observed a tendency on the grapes brought by the last pruning system to induce lower values of sensorial maturity of berries.

In the year 2009 grapes achieved the highest values of the Ripening Index parameter (sugar content/titratable acidity) while on 2011 it was observed generally a better phenolic maturity.

Regarding the sensorial maturity the values shown are the highest in one thesis of the 'Chianti Classico' area and the lowest in the thesis of 'Chianti Colline Pisane', which showed the lower seed phenolic maturity while a thesis belonging to 'Brunello di Montalcino' showed the ripening technological index highest and the highest value of total polyphenols.

As it was not found any correlation between the amount of aromas perceived in sensory analysis with aroma analysed by the GC-MS; this fact could be depending on several reasons: the non contemporary sensorial analysis between the tested thesis, the different threshold of perception of the several aroma compounds, (De Rosso et al., 2010) and the saturation of perception of the panelist which occurs when the threshold was overcame.

As for sensory analysis of the grapes and for the technological parameters, the effect due to the year appeared much more relevant than those dependent on the site.

It was found that the mean bunch weight was positively correlated to the nitrogen concentration of the soil.

Sugar and polyphenols content showed the highest values in theses characterized by good daily excursion, an average rainfall able to increase the available water content of the soil (AWC) and soils for the prevalence of silty particles, alkaline pH, medium quantity of active limestone, poor of organic matter and of other macro elements (Brancadoro et al., 2006).

The lowest °Brix and the highest value of titratable acidity, on the other hand, were found in soils characterized by medium to high content of sand, medium silt and variable amount of clay; alkaline, moderately rich in active limestone, organic matter and mineral elements; altogether the annual thermal regime can play an important role on sugar accumulation and final titratable acidity. A direct positive correlation was found between sugar accumulation and potassium content of the soil.

Soils characterized by a prevalence of sand, sub-alkaline pH, moderate presence of limestone, low organic matter, and average potassium, magnesium and exchange cation capacity positively influenced anthocyanins level as in most vineyards of 'Montecucco' area; on the contrary they were negatively conditioned by soils clay-sandy (with a consistent content of clay), poor in organic matter and phosphorus, rich in potassium and with an excess of magnesium (BM 6).

With regard to the aroma profile of 'Sangiovese''s grapes, we can observe how the results here reported for all the theses examined are in perfect agreement between them and with the general profiles obtained by other authors for the 'Sangiovese' (Di Stefano et al., l.c.; Lanati et al., l.c.). Specifically typical ratios of 'Sangiovese' aroma compounds are linalool oxA/linalool oxB, linalool oxC/linalool oxD, linalool/α-terpineol, linalool/geraniol, trans 8-

OH linalool/cis 8-OH linalool, trans 8-OH linalool + cis 8-OH linalool/p- menth-1en-7,8-di and 3-hydroxy β-damascenone/3-oxide α-ionol.

Inside of the compounds released by enzymes hydrolysis, the classes of benzene derivates and norisoprenoids are present in the most quantity in the samples analyses, while aldehydes are quantitatively less represented. Chemical hydrolysis to pH 3 made on aglycones obtained by enzymatic hydrolysis of glycosides precursors has shown that the most represented category is that of the norisoprenoids hydrocarbon while that of monoterpenols is the less abundant.

Comparing the grapes coming from the different locations we can observe how the 'Chianti Colline Pisane' thesis is relatively distinct from the others for the quantitative inferior values of most aroma classes, which can be attributed to the lower soil content of potassium in this vineyard. In fact, a positive correlation ($r^2 = 0,631$) with the aroma concentration with soil potassium content was found.

Samples from the province of 'Siena', however, had in general a high aroma content. In particular only one thesis belonging to 'Brunello di Montalcino' mentioned for the highest ripening technological index and the value of total polyphenols, besides showed the highest aroma's content.

Among the soil studied, one thesis in the 'Chianti Classico' area stood out while the other ones are close to one another and some points overlap: the soil of this vineyard is sub-alkaline, with prevalence of clay and it is characterized by the highest altitude.

Besides, a good daily excursion, a medium rainfall, a soil alkaline, with the prevalence of silty particles, with a fair quantity of active limestone but poor of organic matter and of other macro elements, positively affect the aroma's content. Moreover the percentage of the sand in the soils appeared positively correlated to the level of hydrocarbon, alcohols and ethers norisoprenoids derivates.

The year 2010 was characterized by the highest level of the most aroma classes while on 2009 the final concentrations were lower, as reported before. Variability was equally attributable to the thesis and to the year more precisely, the compounds, originating from enzymatic hydrolysis except for aldehydes and acids, have a greater variability due to the thesis, while the compounds originating from acid hydrolysis and the other ratios are strongly influenced by the year effect. Most of the compounds derived by acid hydrolysis and some derived by enzymatic hydrolysis were negatively correlated to the temperature occurred in the period of berry growth and ripening (from the beginning of June to the end of September). Moreover, sugar content and the ripening technological index were negatively correlated with most of the aroma compounds, while titratable acidity and mean bunch weight showed a positive

correlation. Only the class of acids obtained from enzymatic hydrolysis was positive correlated with °Brix.

Berry size was correlated negatively with anthocyanins and polyphenols concentration while was not correlated with the aroma content, also it can be highlighted that a positive relationship with the content of limestone and aroma compounds, referred in literature (Fregoni, 2005) was not evidenced.

Regarding to the focus of the vineyards of 'Montecucco' area there were several differences among them: soil of the vineyard MC7 has a lower pH than the others, almost no limestone, low organic matter and available nitrogen, meanwhile it has a good amount in phosphorus, magnesium and potassium content. This thesis which differs from other ones as regards the characteristics of the soil, not for the climate, because is very close, showed different results of sensorial, technological and aroma analysis, more provided mainly of norisoprenoids, phenols and monoterpenols. These differences were partially accounted by the high content of sand and potassium as resulted by the positive correlation previously indicated.

As for the clone effect grown in the same site of cultivation ('Col d'Orcia' estate), three distinct groups appeared during technological and aromatic analysis: the first comprises the thesis BM2, BM3 e BM4 that intersect each others. The second only BM1 and the third BM5 which well differs from the others. The five theses appear well detached when they were examined for sensorial description. It was confirmed that genetic variability affect the characteristics of 'Sangiovese' (Egger et al. 2001; Bertuccioli, 2006) although it was less relevant than the year and the site.

Secondary metabolites are so sensitive to environmental and cultural variables as can be synthesized in very different levels depending on the influence of the cultivation conditions, while preserving their quality profile essentially unchanged. It seems that rainfall didn't generate significant correlation with variables linked to the characteristics of the grape.

Some aroma classes (aliphatic alcohols, benzene derivates, phenols), especially as regards the compounds released by enzymatic hydrolysis, didn't correlated with climatic characteristics. We should suppose that the biosynthesis of these compounds in 'Sangiovese' are less influenced by the climatic conditions. It also could be hypothesized that in the area of cultivation tested even though we had variable conditions, there were not reached limiting conditions able to modify their biosynthesis.

The main hypothesis of this study was that soil and climate might have a direct relation upon grape characteristics but there were many consistent grapes effects that could be linked to both site and climatic characteristics. So, as already highlighted by Reynolds (2012), if we

would have studied also the wines, probably we could have generated several questions: '*what factors exert the greatest control over the terroir effect?; do winemakers exert more influence over wines than site characteristics?; do viticultural and/or oenological practices exert the greatest influence over wine varietal typicity?*'

Questions which suggest to continue to study the 'Sangiovese' in Tuscany, a place in which is able to give several expressions.

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