TRADITIONAL ALGARVIAN DISTILLATS AND LIQUEURS HISTORIC SCIENTIFIC ASPECTS

Ludovina Galego
Escola Superior de Tecnologia
Universidade do Algarve
Campus da Penha
8005-139 FARO PORTUGAL
Tel 289800151
lgalego@ualg.pt

ABSTRACT

All the evidence indicates that distillation and liqueurs preparation began in Monchique mountain because this place was pointed as a possible capital of the oldest population of Algarve and an important Arabic village (Barreto, 1972: 19). It was possible to find lots of vestiges like the alembic produced by Arabic population near the X century (Telo, 1988: 77).

Traditionally the Algarvian people produce the *Arbutus unedo* L., fig, carob, grape distillates. At the same time they produce liqueur-using maceration of parts of plants or fruits in some kinds of distillates.

Most of the work about Algarvian distillates started by studying the basic compounds of *Arbutus unedo* spirits by gas chromatography (GC) and mass spectrometry (MS) as well as other physical-chemical properties. In a second phase aged distillates were studied by their phenolic compounds evolution using high resolution liquid chromatography (HPLC).

Volatile compounds of traditional liqueurs were identified by head space micro extraction solid phase (HE-SPME) and also analysed by gas chromatography mass spectrometry (GC-MS) and when possible confirmed with standards. Total phenols were determined by Folin-Ciocalteur method. Flavenoids were studied by high performance liquid chromatography (HPLC).

Sensorial analysis was also done in every drink studies.

The results showed that the arbutus distillate doesn't present a high level of methanol according to the current legislation. The excesses of acidity or ethyl acetate present normal values when the fermentation is well done (Galego, *et al*. 1995: 341; Galego, *et al*. 1995: 685).

During the aging process, the colour of spirits tend to become darker, the colour changes occurred more rapidly in the arbutus spirits located in cellars with higher temperatures (Galego, *et al*. 2001: 432).

In the sensory evaluation of samples aged during 12 months into 50 L medium toasting level oak wood barrels, panellists considered that samples of arbutus spirit had too much wood flavour and they were not able to detect the characteristic aroma of arbutus fruit (Galego, *et al*., 2001: 183).

Differences in liqueurs were observed using HS-SPME-GC, HS-SPME-GC-MS or HPLC analysis and this observation was confirmed by a sensorial panel (Galego, *et al*. 2003: 60).

1. Introduction

1.1. Distillates

Historically, alcoholic distillation began with the Arabs who, however, did not invent, but greatly improved, the methods. According to P. Bertherlot the alembic was used by the chemicals of Alexandria before the Arabic conquest, although bibliography did not exist because Alexandria library was destroyed in 48 BC, Roget and Garreau believed that the distillation operation was done in the Neolithic period (Roget J. and Garreau Ch, 1991: 54).

During the 6th century the Irish performed a primitive alcoholic distillation in the monasteries. The Irishmen monasteries, between VI and IX century, only preserve the past knowledge including the distillation secrets because of the Barbarian invasions (Brown, 1996, p: 12).

The Arabs after their conquest of Sicily during the 9th century fermented and distilled the grapes in the islands. A century later the Arabs introduced the distillation in the south of the Iberian Peninsula. During the XVI century, distillation was done in every place of Europe, as well as in Scandinavia and Russia. Before 1600 the emigrants introduced it in America (Brown, 1996, p: 12). However according to Helena Catarino (1999:63) Baixo Alentejo and Algarve were conquest by the Arabs between 712-713.

Finding historic aspects of traditional algarvian distillates or liqueurs was a hard work because these people didn't write very well, the knowledge has been passed orally from generation to generation.

In 1504, when Aljezur received the charter of King D. Manuel, people drank wine, "medronho" distillate, myrtle berry and *Menthe pulegium* liqueurs. In 2004, in the celebration of the 500th anniversary of the charter, people tried to recreate the food and drinks of 1504. But in the 1504 Manuelins charters, all the commercial transactions with significance to the kingdom, were referred distillates or liqueurs were not mentioned (O Foral Manuelino de

Aljezur, 2004: 25). In an other work about Algarvian commerce during XV century fish, dried grapes, figs, wine, salt and olive oil were indicated as products exported abroad (Fonseca, 1999: 131), distillates or liqueurs references were not described either, probably because distillates and liqueurs were only produced for family self-consumption.

It is worth mentioning that the oldest fig Algarvian distillery, located in Portimão, was founded in 1750 by Izaac Correyoles, a Swiss man, but this factory was distrained near 1760 and João Lampreia bought it and gave it different uses (Lopes, 1988: 145).

In the exportation importation maps of the 1835 year of Algarve there exist references to the exportation of 214 "almudes" (measure for liquids equivalent to 25 litres) of distillates from Lagos customs and the importation of the same quantity in Alcoutin customs, (Lopes, 1988, 8C and 9) it didn't refer the kind of distillate but it is possible that it was arbutus distillate.

Algarvian monographs from mountain areas written at the beginning of XX century refer to the high number of distilleries, 1905 in Loulé 61 (Oliveira 1998, p. 102), 1929 in São Brás de Alportel 5 (Louro, 1996, 148), 1938 in Monchique 55 (Gascon, 1993, p. 330). São Brás produce arbutus, fig, grape husk and rarely grape distillates, Monchique didn't produce fig spirits.

During visits to the oldest distilleries in the Algarve Mountain area it was possible to observe the first distillery in Cachopo (Tavira), but it was impossible to find it in Monchique. In Monchique one of the oldest legalized producer (Mr António Costa - 70 years old) knew his grandfather, with 3 alembic, selling arbutus distillate but didn't know when his family started producing *arbutus unedo* distillate or the other producer families. Mr José Custódio from Cachpo (81 years old) knew the first distillery dated near 1850. After 1925 started the second and the third distillery, in the same region. Nowadays all of then are in ruins, but others were constructed. In other places of Algarve "Sotavento" like Barranco do Velho (Loulé), São Brás de Alportel, Ameixial (Loulé) or Santa Catarina da Fonte do Bispo (Tavira) the producers know the beginning of distilleries in theirs families or in the neighbourhood. In the Algarve "Barlavento" like Monchique, Aljezur, São Bartolomeu de Messines (Silves) or São Marcos da Serra (Silves) people didn't know where the first distillery was constructed, but in all of these places arbutus distillate is the most important spirit drink.

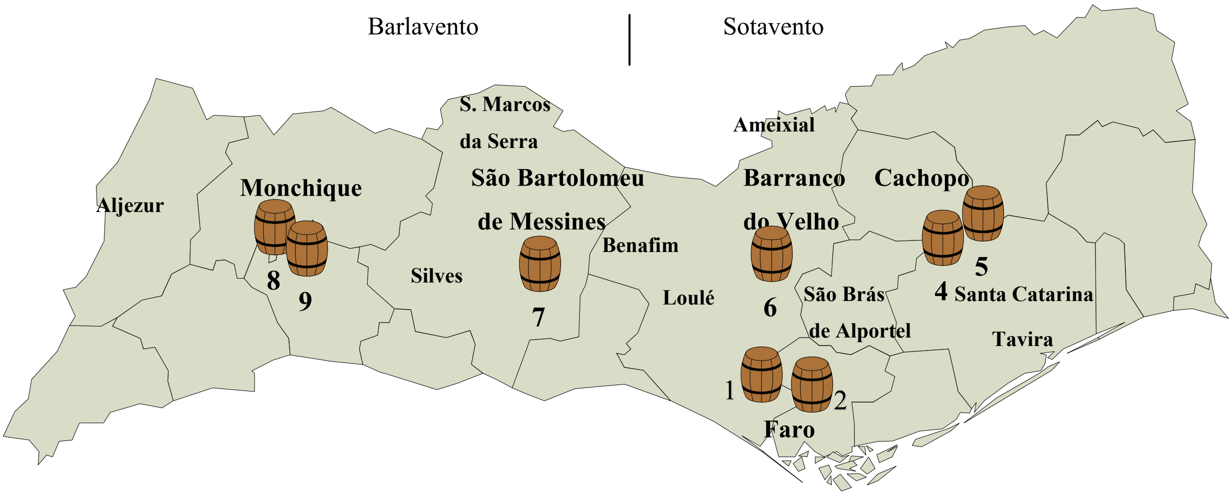


Fig 1: Algarve map indicating the location of the most important traditional spirit producer involved in the studies involved in the studies.

Arbutus unedo distillate called "Aguardente de medronho" or "Medronheira do Algarve" is only produced in Portugal, before 2000 and more typically in the Algarve Region.

Arbutus unedo distillates, was one of the three most important economic sources of the mountain area in the Algarve and the Baixo Alentejo, in a social study at 1993 (INDE, 1993).

The arbutus distillate process consists basically in joining water to the ripe arbutus fruit. Traditionally the fruits were placed in wooden casks in direct contact with the air. After two or three months, with spontaneous fermentation, the distillations are still made in copper alembics. Some years ago the producers had lots of people to work, they made the fermentation in direct contact with the air but in the end they threw away some mass (the top mass) where some compounds were in excess. The quality of the fruits, the additional water quantities, the fermentation time, the temperature at which the distillation begins, the time which the distillation take to be achieved and the way the distillate is collected are the main secrets of each producer. For the past century, small-scale distillers aimed to produce high quality distillates, competing among each other, and such a competition gave rise to very high quality products. After the 60's, with tourism development and with the increase of emigration there was a decrease in these high lands occupation, the arbutus trees stopped being well cared and fruit quality became poorer.

To make this situation even worse, a Portuguese law (Dec. L. 3/78, the 8 of January) imposed that spirits could only be sold and exported in sealed containers not bigger than 1 L, properly sealed and labelled. The same law states that the distillers or handlers must execute bottling. As some distillers workers at that time were old people, without financial ability to develop their own neither brand name nor packaging, they began selling their products to retailers. The retailers bottled them after mixing several distillates, or even other materials, like alcohol and water.

"In Loco" association obtain the first financial support from LEADER for the "medronho distillate" study to start. After Algarvian Institutions received a financial support from a Portuguese programme called PAMAF (PAMAF-IED 4057 and PAMAF-IED 8005).

Some traditionally "medronho distillates" were analysed by G. Vernini and co-workers in San Michell All Adige laboratory – Italy, and the main problem was found. The distillates had a lot of ethyl acetate and had high acidity. These problems have the same source, the fermentation in direct contact with the air (Versini *et al*. 1995: 1779). It was important to try another fermentation conditions. "In Loco" association, Algarvian Technology Department of Agriculture (DRAALG), Superior Technology School of Algarvian University (EST-UAlg) began the study by producing experimental "medronho distillate" and analysing physic-chemical characteristics.

The medronho distillate study started first in the laboratory, after obtaining positive results from laboratory experiences, G. Versini, encouraged the work with the producers. Nowadays there exists a partnership of producers and technicians. They ask us some questions but they also tell us their experiences and results.

For protecting the producer a Portuguese law (nº 238/2000 of 26 of September) established a minimum of quality parameters for *arbutus unedo* distillate.

Only Monchique producers used aging this distillate in chestnut barrel, in other place they only did the aging process if they couldn't sell it.

The quality of brandies and their organoleptic characteristics depend on the fruit fermentation and type of wood barrel used in the aging process. Oak wood and chestnut have been widely used in the cooperage for making barrels, but characteristics of the final product obtained depend on species of the tree, their geographical origin, processes used in seasoning and wood toasting level.

Other fruit distillates have similar problems and producers also try to solve them (Galego et al., 1997: 407).

1.2. Liqueurs

The industrial liqueurs preparation historically was done in Italy during the XIII century. At this time liqueurs were liquid medicines, extracted for curative virtues of parts of plants in alcohol and sweeted with honey for more agreeable flavour (Thönges, 1994: 104).

Algarvian history of liqueur production has similar problems to the distillates, it is difficult to find references, maybe liqueurs were first made in Monchique, because "melosa" is only produced by amateurs in Monchique, it was prepared with arbutus distillate, honey and cinnamon. It is important to remember that Algarvian people early used spices because of the India discovery (In 1497-1499 the first Portuguese travelled to India) and the first sugar manufactory appeared in the XVIII century (Thönges, 1994: 104), in spite of sugar production being the main activity developed between the middle of the 15th century until the middle of the 19th century by Portuguese in Brasil (Couto, 1995: 179).

In 1938 Monchique had 3 liqueur merchants (Gascon, 1993: 330), bitter almond liqueurs production was mentioned in Lopes study 1841 (Lopes, 1988: 147), as above-mentioned in the King's party in 1504, liqueurs were served.

In the visited Algarve Mountain area "Sotavento" people only started liqueur production after the middle of XX century, but in "Barlavento" area people did not know when the liqueurs production began, even producing liqueurs from every plant or edible fruits. Ms. Isabel Jesus from Monchique was invited in 2004 to recreate century liqueurs recipes for the 500th year commemoration of Charter King D. Manuel in Aljezur. She knew all of these recipes because she worked with important Monchique families who used prepared typical liqueurs and she, also told us about some technical facts, such as, the time of maceration or the degree of alcohol for preparing liqueurs.

Some distillates have no market, because they have a strong taste or have fermentation problems. Traditionally people use them to prepare liqueurs by maceration of fruits or parts of plants. The fig distillate is a cheap distillate and Algarvian people don't appreciate it very much. They prefer to do other drinks with the fig distillates. Some years ago this distillate was sold for less than 1 euro per litre. After 1993 because of the alcohol high tax on all the distillates, the fig distillate is now sold for more than 6 euro. The fig distillate producers haven't conditions to continue the work, it is necessary to transform this type of distillate because Algarve has lots of figs for this kind of preparation. The figs used for preparing distillates are the smallest and those bitten by the birds.

It was possible to reduce the fig flavour or other flavours problems if the distillate was deodorized by active coal. This process was done in laboratory or with producers using a minimum of 5 g of active coal per litre of fig distillate (Galego *et al*., 2004: 421).

The quality of the liqueurs and their organoleptic properties depend on the characteristics of spirits of plants or fruits used as well as on the preparation procedures, including maceration and maturation processes. After the maceration occurs the first filtration and sugar syrup is added before a maturation period starts. Chemical components may be extracted from the raw material into the spirit in order to obtain a product with colour, aroma and taste characteristics of the fruit or plant. Chemical reactions may also occur during the maceration process and maturation of final products (Galego *et al*., 2001: 184; Galego *et al*., 2004: 421). Some liqueurs have similar proprieties to wine as are widely described in the literature, because of their polyphenolic content (Vacca, *et al*., 2003: 442).

2. Materials and methods

2.1.1. Experimental production of distillate

The production of arbutus distillate started in the laboratory of Agriculture Technology of Algarve (DRAALG) at the end of 1993 controlling the process conditions, from the picking of the fruits, fermentation to distillation. 15 anaerobic fermentations were prepared, according to 5 different methods. In all methods it was used plastic or inox fermenting vessel containing 22 kg of "medronho" fruits and 3, 5 and 7 L of water. In some cases pH was corrected to 3 with sulphuric acid. The fermentation time was 21 days at 17 ºC for every trial. At the end of the process, some trials rested for 40 days before distillation, in such cases, potassium metabissulfite was added in the concentration of 60 mg/l (Galego *et al*. 1997:381).

The distillations proceeded in a 30 L copper alembic, heated in liquid paraffin melted by electrical heating units. During the distillation samples were collected every 100 cm^3 in the first 500 cm^3 and every 330 cm^3 after that, completing 14 samples per distillation.

Finally all the distillation portions were analysed according to the quantification of their physical/chemical properties (ethanol, pH, volatile and total acidity) performed in DRAALG, using Official methods (Official Methods, 1990). And analysis of volatile compounds (acetaldehyde, ethyl acetate, methanol, 1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol + 3 methyl-1-butanol), which exist in the distillates were performed at EST-UAlg.

In 1995 the work stared with traditional producers in their distilleries using bigger fermentaters and 5 samples were collected during the distillation process (Galego *et al*. 1997:381).

Other fruits distillates studied had similar proceedings (Galego et al., 1997: 407).

2.1.2. Arbutus distillate aging process

In the first study it was used oak wood (treated to medium toasting level) during 18 months in barrel of 50 L (samples were collected every 3 months). Three barrels were in the laboratory with humidity and temperature controlled, the other five were in cellars where the humidily and the temperature were only registered.

2.1.3. Sensorial analysis

During all the experiences (6 years) a group of technicians and producers were trained for sensorial analysis. Every month they had a meeting. At the beginning some aqueous solution with compounds problems (ethyl acetate, acetaldehyde or acetic acid) of distillates were tasted at different concentrations. In a second phase the panellists taste ethanol/water solution with these problems compounds, and finally different distillates. Because of alcohol concentration quantity only 3 samples were possible to taste during a session and only two session during one day.

2.2.1. Production of liqueurs

The study started by preparing small quantities of traditional recipes by maceration of lemon peels, fig leaves, *Mirtus communis* leaves or *Mirtus communis* fruits into fig distillate. The first filtration occurs in the end of the maceration (10 days) after sugar syrup was added and then begins the maturation period (3 months).

Different maceration procedures were tested: maceration into fig distillate with 45 % V/V of alcohol; maceration into concentrated fig distillate (75 % V/V); maceration into deodorized concentrated fig distillate (75 % V/V).

2.2.2. Sensorial analysis of liqueurs

During two years every week a group of 20 assessors, started training to differentiate liqueurs concerning acidity, bitterness, sweetness, metallic flavour, fig flavour and general flavour first using paired comparison in the first year and in the last year assessors differentiated liqueur samples by triangular tests, in partially blue coloured liqueur glasses.

2.3 Solid phase micro extraction procedure

To 5 cm^3 of liqueur it was added 5 cm^3 of water, in a 20 ml vial, with a minimum of 1 g of salt. Two different coated fibers were used a 65 µm PDMS-DVB (polydimethylsiloxane – divinylbenzene) and a 50/30 µm DVB-Carboxen-PDMS.

The SPME fiber was exposed for fixed time (5 minutes for more volatile compounds or 40 minutes for lessen volatile compounds) in the head-space of the vial at laboratory temperature (20 ± 2 ºC) with magnetic stirring. After the fibre was withdrawn into the needle and transferred to the injector of the GC or GC-MS, where the analytes were thermally desorbed from the fibre during 5 or 8 min depending if it was a PDMS-DVB or a DVB-Carboxen-PDMS respectively.

Similar proceeding was used for analysing aged distillates.

2.4. GC analysis

2.4.1 Distillates

Gas chromatographic analysis was carried out using a Hewlett Packard 5890 Série II equipped with a FID detector. Helium was used as carrier gas. The components were separated on a DB Wax column 30 m x 0,32 mm i.d., 0,25 µm film thickness from J & W Scientific. Fid detector temperature was set at 270 ºC and all injections were made in split mode (split, 30:1).

The operation conditions were injector temperature 250 ºC, programme temperature: 3 minutes at 35 ºC, 5 ºC/min up to 80 ºC, 10 ºC/min up to 180 ºC. The internal standard method was used, with 4-methyl-2-pentanol as standard. Samples were injected without any prior treatment.

2.4.2 Liqueurs

The components were separated on 30 m x 0,25 mm i.d., 0,25 μm film thickness DB-1701P column from J & W Scientific using SPME fibres. The column was initially maintained at 50 ºC for 5 minutes; subsequently the temperature was increased to 210 ºC at a rate of 5 ºC/min and finally held for 5 minutes. Injector temperature 250 ºC and FID detector temperature was set at 270 ºC. Data acquisition and data processing using *Chromulan* software.

2.5 GC-MS analysis

A Shimadzu 17-A chromatograph equipped with Shimadzu QP-5000 mass spectrometer was used. The separation was achieved using a J&W Scientific DB-1701P column of 30 m x 0,25 mm i. d. and 0,25 μm of film thickness. GC oven temperature was programmed from 40 ºC (5 min), to 230 ºC at a rate of 5 ºC/min and then 5 min at 230 ºC. The carrier gas was helium with a column-head pressure of 1,4 x 10^5 Pa.

Mass spectra were recorded in the electron impact (EI) mode at 70 eV, scanning the m/z 30 to 300. Interface temperature was 250 ºC. Data acquisition and data processing were carried using Class5K software.

Peaks in TIC (total ion current) or MIC (Multi Ion Chromatogram) profiles for both analyses were characterized or tentatively identified from their mass spectral data using National Institute of Standards and Technology (NIST12 or NIST62) and Wiley 229 mass spectrometry libraries. Identification was confirmed using standard compounds when available.

The same methodology was used in direct analysis or in SPME analysis.

2.6 HPLC analysis

A LKB Bromma 2152 LC was used equipped with a UV/Vis variable-wavelength LKB Bromma 2151 detector set at 280 or 500 nm depending if it was study yellow drinks (only use 280 nm) or red drinks (280 and 500 nm) and conneted to a LKB Bromma 2221 integrator. Data acquisition and data processing using *Chromulan* software.

A C18 Chrompack INERTSIL ODS2 column (25,0 cm x 4,6 mm; 5 μm particle size) connected a pre-column with the same phase (1,0 cm x 3 mm) to protect analytical columns was used.

Two eluents were used: A - 0,1 % of orthophosphoric acid (H_3PO_4) (Merck); B - 0,1 % of H_3PO_4 and 40 % of acetonitrile (C_2H_3N). The flow rate was 0,7 ml/min. Gradient was run as following: 0-15 min 0-20 % B; 15-25 min 20 % B; 25-70 min 20 -70 % B; 70-75 min 70 % B; 75-85 min 70-100 % B; 85-100 min 100 % B.

The samples were filtered through 0,45 μm *milipore* filter DAWP01300 and 20 μl of this solution was injected into the chromatograph.

2.7. Copper content

A GBC Avanta atomic absorption spectrometer was used to determinate copper in distillates. Five stands with the concentration of: 2,00; 4,00; 6,00; 8,00 and 10,00 mg/L of copper were prepared from a standard solution (Spec pure Cu 1000 mg/ml with 5 % of HNO_3 reference 088061). The samples were prepared adding 5 ml of distillate and 250 μl de HNO_3 at 5 %. If samples have more copper then maximum concentration standard of calibration, the samples were diluted. All the samples was analysed in triplicate, and each 10 readings calibration was checked using the 6,00 mg/L standard.

2.8. Other physic-chemistry analyses

Other analyses were done in order to characterise spirits and liqueurs like: colour (L*, a*, b*), density, total acidity, alcohol degree, absorption at 440 nm, total phenolic compounds and ºBrix, using reference methods (Regulamento CEE nº 2676/90).

3. Results

3.1. Distillates production

Before arbutus distillate study started it was communicate to the producer the main problems found the heigh level of ethyl acetate in both sides of Algarve as it possible to observe in fig 2.

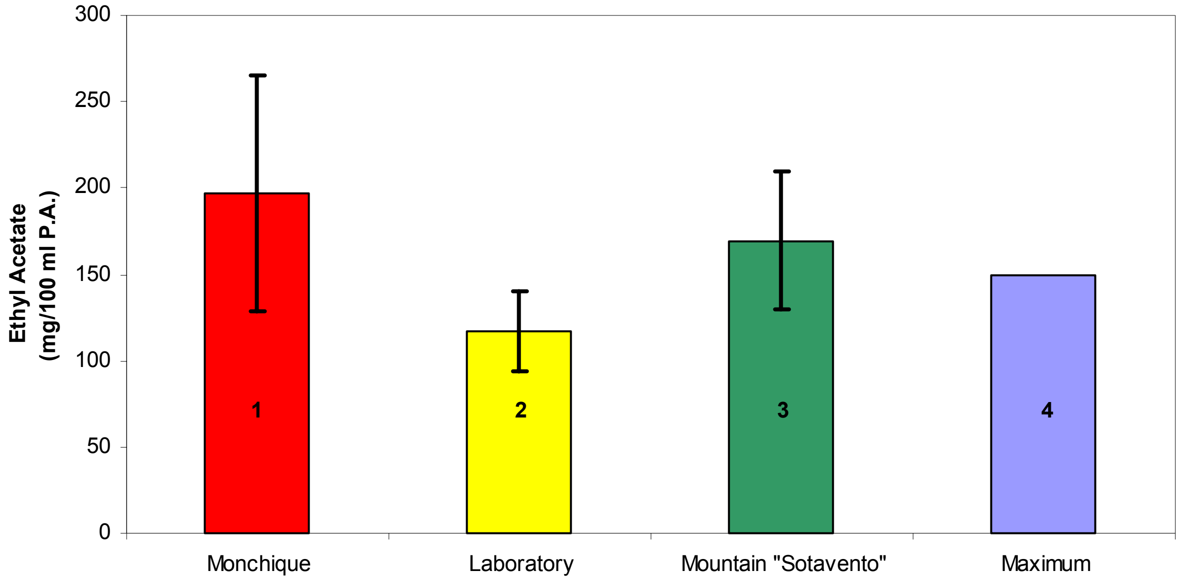


Fig 2: Ethyl acetate found in different samples collected in Mountain areas compared with the laboratory samples and the maximum recommended, before arbutus study was communicated.

All the distillation compounds have typical conduct, the ethyl acetate decrease during the distillation as it can be observed in fig 3, acidity and methanol increase in the same conditions, fig 4 and 5 (Galego *et al*. 1995: 341; Galego *et al*., 1995: 685). Copper, first decreases, but at the end increases as well as the acidity, fig 6. If fermentation process could be completed at pH 3, the final distillate would present less methanol, ethyl acetate, acidity and consequently less copper (Galego *et al*., 1998: 5.02).

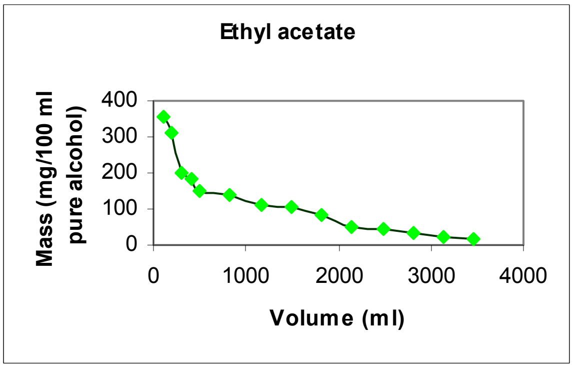


Fig 3: Ethyl acetate conduct during a distillation

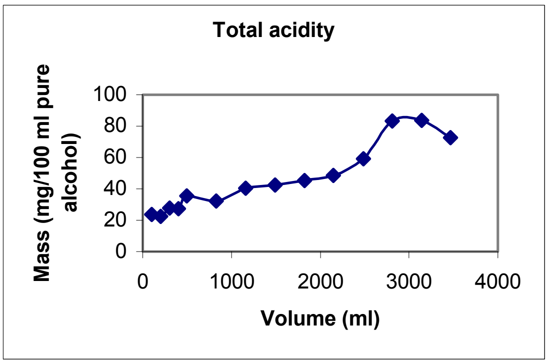
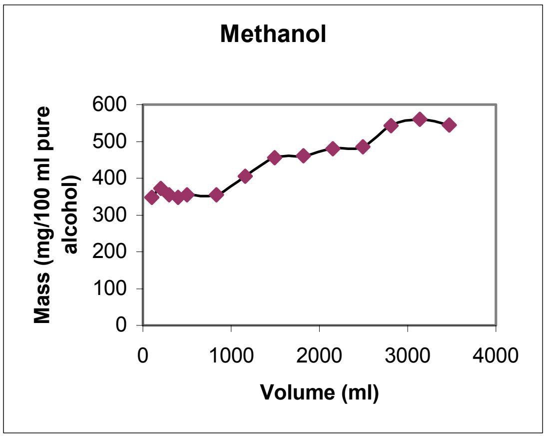


Fig 4: Total acidity conduct during a distillation



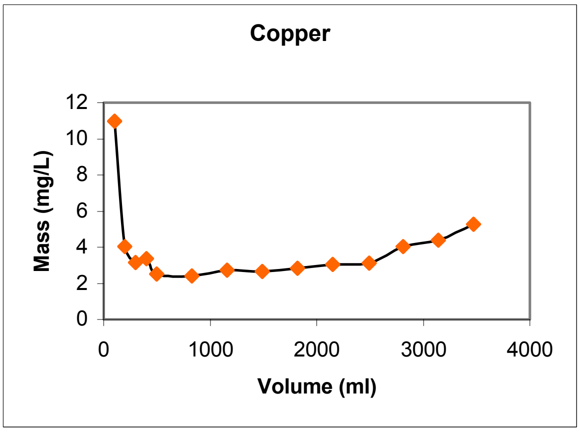


Fig 5: Methanol conduct during a distillation   Fig 6: Copper conduct during a distillation

The water quantity used depends on the sugar and water content of the fruits, the more water the less final alcohol. In order to reduce the alcohol degree it is better to add water in the begging of distillation than after.

The better results were obtained if distillation occurred immediately after the end of fermentation (Galego *et al*., 1997: 371).

3.2 Aging distillates

The results obtained from the analysis of 53 samples of arbutus spirit aged in oak wood were compared by multivariate analysis (Principal Component Analysis). Figure 7 shows a projection of the samples on a two dimensional plane defined by the 1st and 2nd principal components extract from the oak wood barrel and detected in the analysis by HPLC.

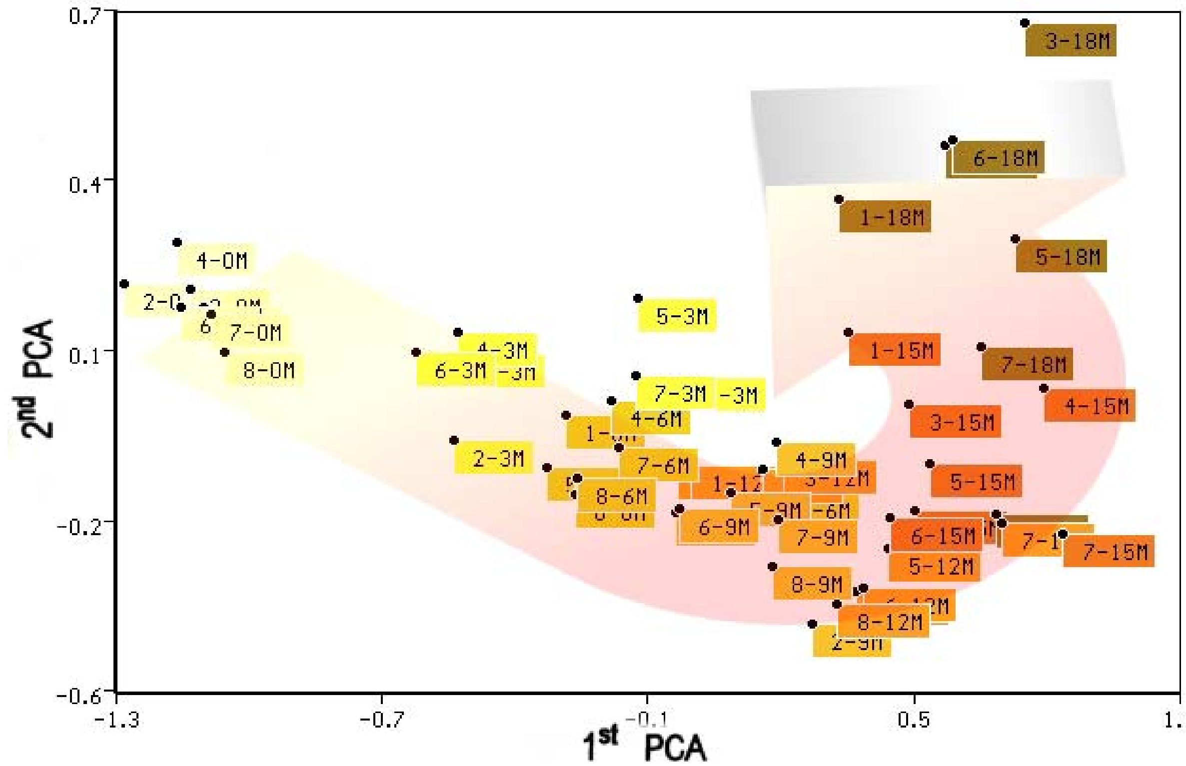


Figure 7. Projection of 53 samples of arbutus spirit in the two dimensional plane defined by the first two principal components (total variance accumulated – 61 %). Each samples is identified by its producer number (1-8) and months of aging in oak barrel (0M-18M) (Galego *et al*, 2001: 183; Galego *et al*., 2001: 432).

It was also possible to observe that initial characteristics of distillate didn't change significantty during the aging process (Galego *et al*., 2001: 513).

When comparing the HPLC profile of experimental arbutus spirits aging in oak wood and arbutus spirits aging in chestnut wood from Monchique producers it was possible to observe that aromatic compounds were in less concentration and/or in less number when chestnut was used, figure 8.

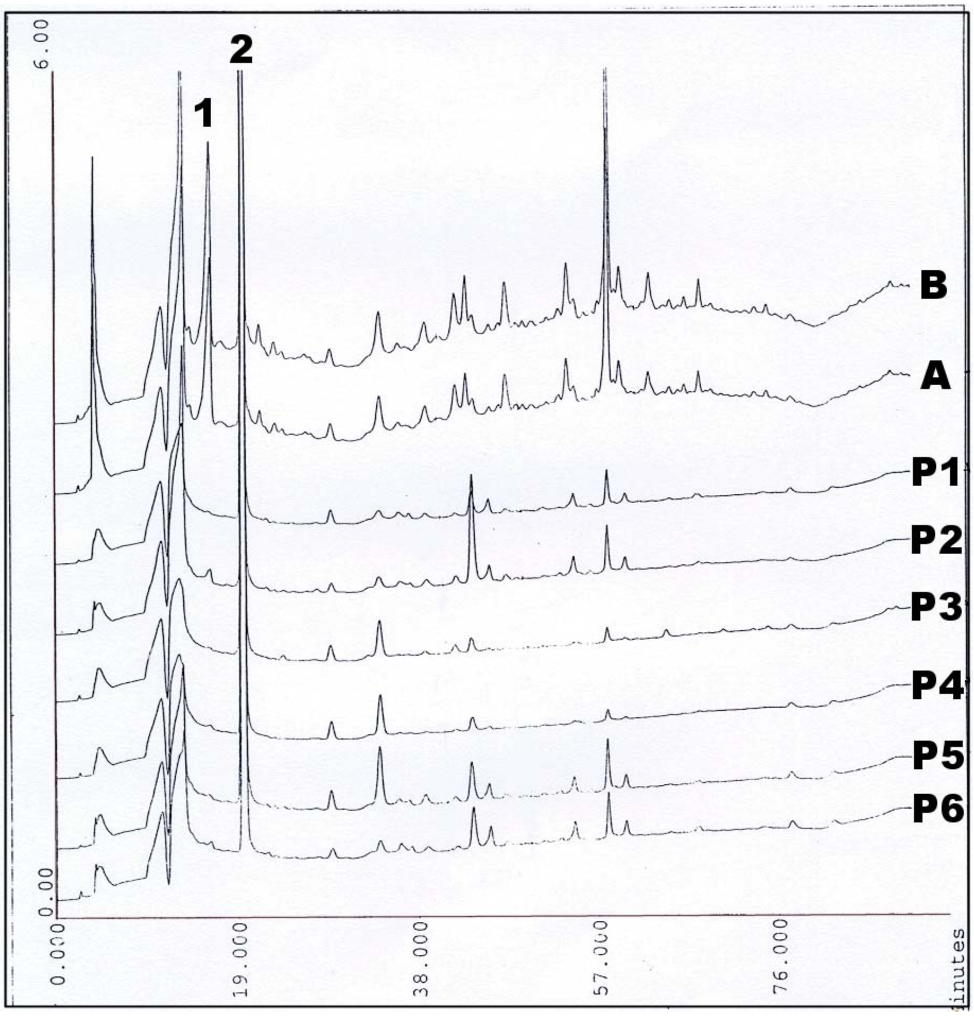


Figure 8: Chromatograms of aging arbutus spirits at controlled conditions in oak wood (A and B) and samples of Monchique producers in chestnuts wood (P1, P2, P3, P4, P5, P6). (1) 5-hidroximethyfurfural, (2) – furfural (Galego et. al., 2001: 432; Galego, 2001: 513)

Chestnut wood gives more colour and lesse taste than oak wood, this is an important characteristic to fruits distillates, where the fruit flavour is appreciate (Galego, 2001: 513).

3.3 Distillates sensory analysis

Acidity was the most difficult characteristic for training assessors (Colaço *et al*., 1995: 693; Jesus *et al.*, 1999: 42)

More than 70 % of the assessors, after having been trained, differentiate distillates with excess of aromatic compounds: ethyl acetate, acetaldehyde or vanilla. Tiredness implicates fewer results (Quintas, *et al*., 38).

In aged distillates two groups of assessors were found, a group prefers less wood flavour, and other group prefer a strong wood flavour, but after 12 months in 50 L oak wood barrels, treated to medium toasting level, all panellists considered these samples of distillates had too much wood flavour and they were not able to detect the characteristic aroma of arbutus fruit (Galego *et al.*, 2001: 183; Galego, *et al*, 2001: 513)

3.4. Liqueur analysis

Generally when maceration was done with concentrate distillate they present high quantity of volatile and non-volatile compounds (Galego *et al*., 2004: 421).

If the distillate was deodorized and/or concentrated before maceration, acidity presents lower values and less typical distillate flavour. These factors contribute to the assessor preference (Galego *et al*., 2004: 421).

Experimental produced liqueurs were in good conditions in according to all the physic-chemical analysis fixed by Portuguese law (decree nº 257/87), but these analysis were insufficient to differentiate flavour types. For a contribution to the characterization of this kind of drinks other analysis were done like volatile and/or polyphenolic profiles.

Liqueurs are complex matrix systems with compounds of different characteristics, it is not possible to get standards for most of the compounds, some are isomerous. Fig 9 TIC present an example GC-MS volatile analyse of a liqueur made by fig distillate and lemon peel using DVB-CAR-PDMS fibre. It is a particularly complex matrix, as can be seen by the high number of volatile compounds presented. Some come from the fig distillate, mostly ethyl esters, and others from the lemon peel, mainly monoterpenes (Galego *et al*., 2004: 421; Galego *et. al*., 2005: P 1.32).

With the aim of obtaining a profile of these two groups of compounds, and for their more effective identification, fragmentograms are used in figure 9-MIC. The first uses a typical ion of m/z = 88, to show ethyl esters (from fig distillate). The second fragmentogram uses m/z = 121, 136 and 154 as typical ions to reveal the monoterpenic compounds of lemon peel.

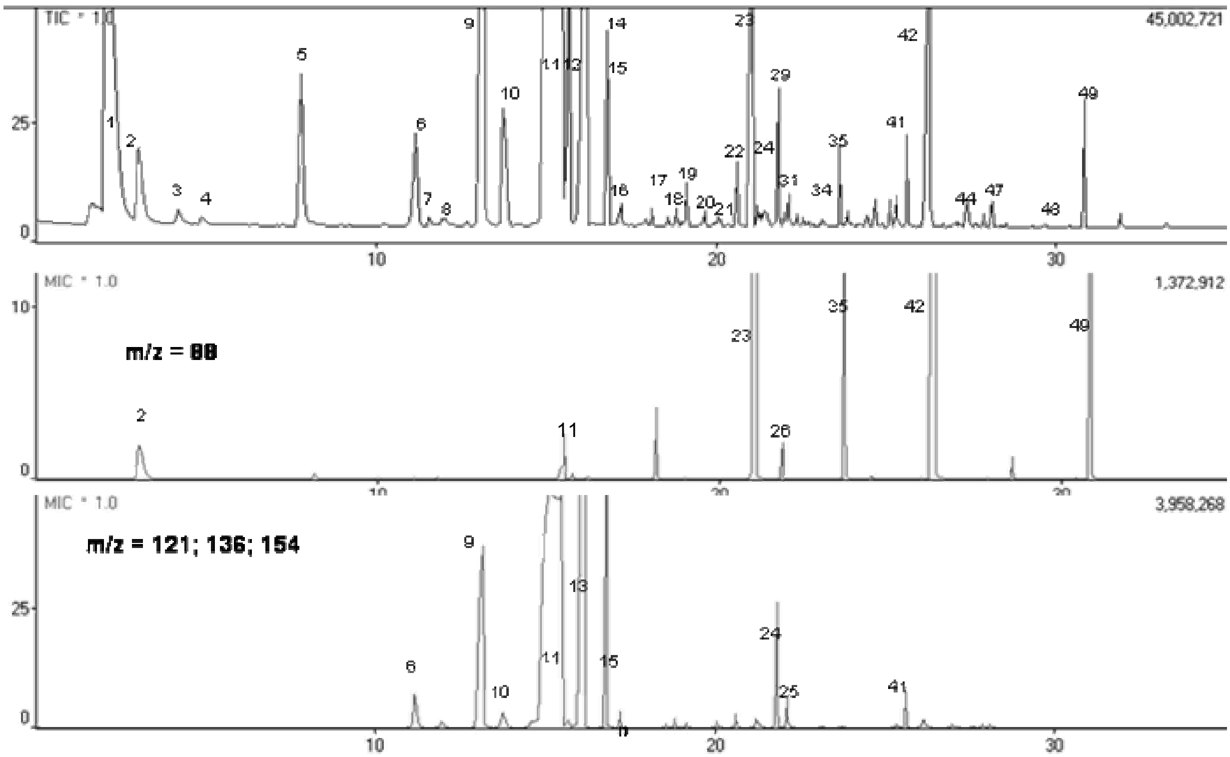


Figure 9: Lemon peel liqueur. Identification: **1**- Ethanol; **2**– Ethyl acetate , **3**- Isobutanol; **4**– Diethyl acetal; **5**– Isopentanol; **6**– α Pinene; **7**– Cardene; **8**– Canfene; **9**- β Pinene; **10**– β Mircene; **11**– Limonene + ethyl caproate; **12**–Tujene; **13**– p-Cymene; **14**- γ-Terpinene; **15** – Terpinolene; **16**- Fenchol; **17** – Ethyl heptanoate; **18** – Borneol; **19** – Nonana + Linalool; **20**– 1-Noneno-2-ol; **21**– Isoborneol + N.I.; **22**– N.I; **23**– Ethyl caprilate; **24** e **25**– Monoterpenes; **26**– Ethylic phenyl alcohol; **27**– Carveol; **28**– N.I.; **29**– Terpineol; **30**– Decanal – **31** - α Terpineol; **32**- Isopenthil caproate; **33** – Octanal diethyl acetal; **34** – Linalol acetate; **35**– Ethyl nonanoate; **36**– Citral; **37**– Methyl caprate; **38**–Nerol; **39**– Nonanal diethyl acetal; **40**- Citronellyl acetate; **41**– Geranyl acetate + caryophyllene; **42**- Ethyl caprate; **43**– Ascarideol; **44**– Isoamyl caprylate; **45**– Isocaryophyllene; **46**– N. I.; **47**– β Bisabolene; **48**– Buthyl decanoate; **49**– Ethyl laurate. (N.I.-unidentified)

As can be seen, there is clear discrimination of the terpenic compounds that come from the lemon peel in relation to those other compounds that come from fig distillate. Using selected typical ions it was possible to identify compounds unresolved by gas chromatography. It’s the case of ethyl caproate that coeluates with limonene, due to the great amount of the last (Galego *et al*., 2004: 421; Galego *et. al*., 2005: P 1.32).

The profile by HPLC can also contribute to differentiate liqueur characteristics, figure 10 present a comparison with two myrtle liqueurs with the same alcoholic degree, the red present a liqueur made with a non deodorized nor concentrated fig distillate and the black a liqueur made by fig deodorized and concentrated fig distillate, both with 5 months after preparation.

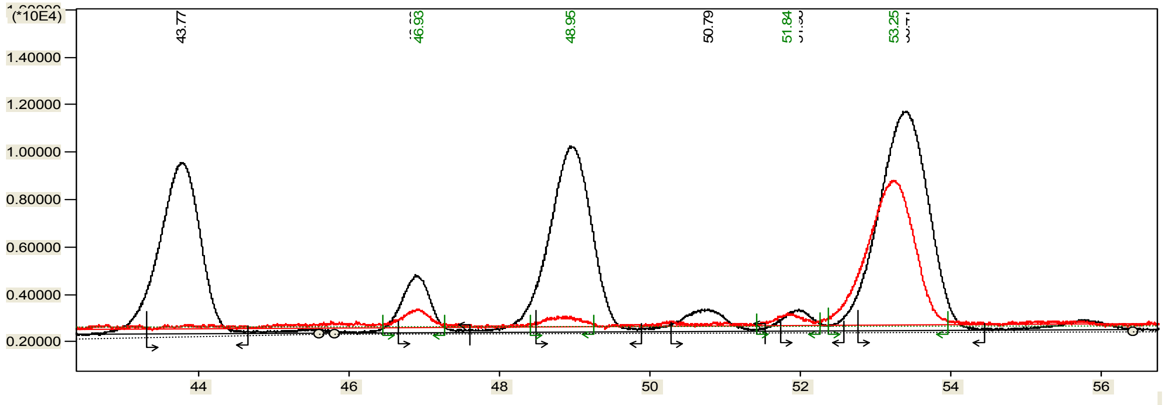


Figure 10: Comparison of myrtle liqueurs after 5 months of preparation. The red one was prepared with a non deodorized and nor concentrated fig distillate and the black one a liqueur made by deodorized and concentrated fig distillate (Galego *et al*., 2004: 421).

These examples confirm that most non volatile compounds are extracted by concentrated distillate, in all the liqueurs have the same alcoholic degree when analysed.

This case showed some possibilities of liqueurs analysis and how it is possible to investigate the producer process or the subject-matter used.

Acknowledgements:

I would like to thank Professors Valentim Almeida and Luis Vilas Boas for the incentive to do this contribution to the Algarvian distillates and liqueurs history.

Also I would like to thank Eng. Teresa Cavaco, Dr. Américo Telo and In Loco Association because of the contact that they established with traditionally Mountain producers.

I would like to thank all the producers that told me about their experiences and their knowledge: Mr Manuel Sousa Martins and Mr Analídio Gonçalves from São Bartolomeu de Messines, Mr José Cavaco, Mr José Custódio, Mr Manuel Rodrigues Palma and Mr Manuel Belchior from Cachopo, Mr Jorge Lima from São Marcos da Serra, Ms Mealha Guerreiro from Barranco do Velho, Mr José Manuel Gonçalves from Ameixial, Mr Jorge Pires from São Brás de Alportel, Engª Conceição Silva and Mr Manuel Gregório from Benafim, Mr António Costa, Mr José António André, Mr José Paulo Nunes and Ms Isabel de Jesus from Monchique the firms Percolive – São Brás de Alportel, "Baga-mel" – Silves, Cooperative Society – Santa Catarina da Fonte do Bispo, Aljezur town, and lots of other anonymous people that have helped in this work.

REFERENCES:

American Society of Enologists, 1990. Official Methods of Anaysis, Kenneth Helrich, Virgínia.

Barreto J. M., “O Algarve”, 1972. Ministério da Educação Nacional Direcção-Geral da Educação Permanente.

Brown G.,1996. L’art des Alcools à Travers le Monde, Hachette.

Catarino H., 1999. A chegada dos Árabes à Península Ibérica: A invasão de Tarique em 711 e a ocupação do território. In: O Algarve da Antiguidade aos Nossos Dias, Marques M. G. M., Lisboa, Colibri, p. 61-67.

Colaço A. C. C., Quintas P. M. B., Galego L. R., Varela J. L. M., 1995 Valorização da Aguardente de Medronho - Análise Sensorial, Actas do VIII Congresso do Algarve, Vilamoura, 693-700.

Couto, J. 1995. A Construção do Brasil. In: Azevedo A. M. Na Colonização do Brasil: a Cana-de–açúcar dos Campos Algarvios às Plantações Brasileiras. In: O Algarve da Antiguidade aos Nossos Dias, Marques M. G. M., Lisboa, Colibri, p. 179-183.

Decreto-Lei nº 3/74 de 8 de Janeiro, 1974. Diário da Republica I Série, Imprensa Nacional, 6, p.17 – 20.

Decreto-Lei nº 238/2000 de 26 de Setembro, 2000. Diário da Republica I série A, Imprensa Nacional, 223, p. 5145-5147.

Fonseca L. A., 1999. A ligação do Algarve aos Grandes Centros do Comércio Internacional. In: O Algarve da Antiguidade aos Nossos Dias, Marques M. G. M., Lisboa, Colibri, p. 131-141.

Galego L. R., Almeida R. N. , Martins A. N. , Versini G., 1995. Valorisation of Arbutus Distillate, Euro Food Chem VIII, Austria, p. 341-344.

Galego L. R., Martins A. N., Almeida V. R., 1995. Valorização da Aguardente de Medronho – Estudo do Processo Tecnológico, Actas do VIII Congresso do Algarve, Vilamoura, p. 685-691.

Galego L. R., Almeida V. R, Martins A. N., Jesus J. P., Varela J. J. L. M., Soares M. P., Quintas P. B., 1997. Investigação-Acção Sobre Aguardente de Medronho, Actas do 9º Congresso do Algarve, Vilamoura, p. 381-387.

Galego L. R., Almeida R. N., Martins A. N., Jesus J.P., Versini G., 1997. Primeira Fase da Comparação das Características dos Destilados Produzidos no Algarve, Actas do 3º Encontro de Química de Alimentos, Faro, 407-409.

Galego L. R., Bento F., Almeida V. R., Martins A. N., Jesus J. P., Vilas Boas L., 1998. Variação do teor em cobre ao longo de uma destilação experimental para obtenção de aguardente de medronho, Actas do XII encontro Luso-Galego de Química, Porto, 5.02.

Galego L.R, Bento F. J. A., Almeida V.R., Marques O. S., 1999. Contributo para a optimização da produção de licores tendo por base a aguardente de figo, Actas do X Congresso do Algarve, Alvor, p. 655-658.

Galego L. R., Almeida V. R, Martins A. N. Teixeira A. N. M., Bronze M. R., Vilas Boas L., 1999. Aguardente de medronho: envelhecimento em madeira de carvalho, Actas do 4º Encontro de Química dos Alimentos, Coimbra, F13.

Galego L. R., Bento F. J. A, Almeida V.R., Teixeira A. J., Jesus J.P., Bronze M.R., Vilas Boas L.F., 2001. Contributo para a caracterização da aguardente de medronho envelhecida, Actas do 5º Encontro de Química de Alimentos, Porto, p. 432-434.

Galego L. R., Almeida V. R, Bento F. J. A., Teixeira A. J., Jesus J. P., Bronze M. R., Vilas Boas L., 2001. Envelhecer Aguardente de Medronho, Actas do 11º Congresso do Algarve, Albufeira, 513-516.

Galego L.R, Bento F. J. A., Almeida V.R., Bronze M.R., Vilas Boas L.F., 2001. Charactrisation of Arbutus Brandies by Chemical Analysis, Actas do 2º Simposio IN Vino Analytica Scientia, Bordeaux, p. 183.

Galego L.R, Bento F. J. A., Almeida V.R., Bronze M.R., Vilas Boas L.F., 2001. Contribution to the Chemical Characterisation of Myrtle Liqueur, Actas do 2º Simposio IN Vino Analytica Scientia, Bordeaux, p. 184.

Galego L. R., Almeida V. R, Vilas Boas L., Bronze M. R., 2003. Analysis of Monoterpenic Compounds in Myrtle Liqueur Using solid Phase Micro Extraction, Actas do 3º Simpósio IN Vino analytica Scientia, Aveiro, 60.

Galego L., Almeida V., Vilas Boas L, 2004. Contributo para a Caracterização de Licores do Algarve, Actas do 12 º Congresso do Algarve, Tavira, 421-428.

Galego L. R., Bento F., Almeida V. R, Vilas Boas L., 2005. The use of typical ions for the differentiation of terpenic compounds in liqueurs, Actas do 7º Encontro de Química dos Alimentos, Viseu, P 1.32.

Gascom J. A. G., 1993. Subsídio para a Monografia de Monchique, Algarve em Foco, Faro.

INDE, 1993. Documentos de trabalho produzido para a Associação In Loco, Lisboa.

Jesus, J. P., Quintas, P. M. B., 1999. Avanços da Câmara de Provadores, Actas do 2º Colóquio de Valorização da Aguardente de Medronho, São Brás de Alportel, 42-47.

Lopes J. B. S., 1988. Corografia ou memória económica. Estatística e topografia do reino do Algarve, Algarve em Foco, Vol 1 e 2, Faro.

Louro E., 1996. O livro de Alportel Monografia, 3ª Edição, Câmara Municipal de São Brás de Alportel, p. 148.

"O Foral Manuelino de Aljezur" 2004. Câmara Municipal de Aljezur.

Oliveira A., 1998. Monografia do Conselho de Loulé, 4º edição, Algarve em Foco, Faro.

Quintas, P. M. B.; Jesus, J. P., 1997. Formação da Câmara de Provadores de Aguardente de Medronho, Actas do 1º Colóquio de Valorização da Aguardente de Medronho, São Brás de Alportel, 38-40.

Regulamento (CEE) nº 2676/90 da Comissão de 17 de Setembro de 1990. Métodos de análise Comunitários aplicáveis no Sector do Vinho. Jornal oficial nº L 272 de =3/10/1990, p. 1-192.

Roget J., Garreau Ch., 1991. Recherches sur Lórigine de la Distillation et la Preparation de L'alcool. IN: Les Eaux-de-Vie Traditionnelles d' Origine Viticole, Alain Bertrand, Lavoisier - Tec & Doc, p. 54-59.

Telo A., 1988. Destilados e Comércio de Aguardente na Serra de Monchique – Uma abordagem Ecológica. In: 5º Congresso do Algarve, Racal Clube de Silves, p.77 - 93.

Thönges H., 1994. Zumos, Vinos y Licores, Ediciones omega, Barcelona.

Vacca V., Piga A., Caro A., Fenu P. A. M. and Agabbio M., (2003), Nahrung/food, 47 No. 6, p. 442-447.

Versini G., Seeber R., Dalla Serra A., Sferlazzo G., Carvalho B., Reniero F., 1995. Aroma compounds of arbutus distillate. In: Food Flavors, Charalambous, Elsevier Science, p. 1779-1790.