SIMULTANEOUS DETERMINATION OF KETOACID AND DICARBONYL COMPOUNDS, KEY MAILLARD INTERMEDIATES ON THE GENERATION OF AGED WINE AROMA

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Recently it has been demonstrated that the typical aroma of oxidative spoiled white wine are related with the presence of methional and phenylacetaldehyde, substances accountable respectively for the "boiled-potato" and "honey-like" odour notes with threshold values of 0.5 μg/L and 25 μg/L [1][2][3].

These compounds can be formed by the direct oxidation of the respective alcohol or via Strecker degradation of the respective amino acid [1][3], but the main pathway for their formation is not clearly established. Some researchers suggest that the Strecker mechanism is the main pathway for the formation of methional [3] nevertheless, due to the temperature; pH; and dissolved oxygen regimes related with the storage conditions of wines, the question remains unanswered.

The Strecker degradation is the reaction between an amino acid and a α-dicarbonyl compound, involving an intermediary ketoacid, generating an aldehyde with one carbon atom less than the amino acid known as "Strecker aldehyde".

In order to detect ketoacid compounds in wine, a method was developed based on a quinoxaline derivatives formation by the reaction in wine with diaminobenzene, currently employed to detect α-dycarbonyl compounds [4]. The quinoxaline derivatives were detected by RP-HPLC with UV detection, which allows the determination of the major dicarbonyl compounds in wine: glyoxal, methylglyoxal, diacetyl and pentane-2,3-dione. However, the UV detection is not selective to quinoxaline/ quinoxalinol derivatives (being the former the product of the reaction between ketoacid compounds and diaminobenzene). In order to improve the selectivity to quinoxaline/ quinoxalinol derivatives, a fluorescence detector was employed simultaneously with the UV detector. With this detection configuration it was also possible to quantify of α-keto-γ-(methylthio)butyric acid and β-phenylpyruvic acid (intermediary ketoacid compounds of methional and phenylacetaldehyde).

The method proposed is sensitive, linear and has good repeatability. The levels found in 15 wines analysed (white wine, Madeira wine and Port wine) varied according to the type and the age of the wine. The ketoacid compounds ranged from 0.2 to 5.7 mg/L for α-keto-γ-(methylthio)butyric acid and 0.1 to 9.6 mg/L for β-phenylpyruvic acid. The quantities observed for dicarbonyl compounds were similar to those already reported [4]. In fact, with exception of pentane-2,3-dione and methylglyoxal Madeira and Port wines (mainly old port wines) are richer in these compounds than white wines.

For the first time, α-keto-γ-(methylthio)butyric acid and β-phenylpyruvic acid were detected in wines by a simple and selective method which enables the quantification of maillard intermediates, some of which are believed to be key substances on the generation of aged wine aroma. This methodology constitutes a fundamental tool in order to gather useful information concerning the assessment of the main pathway of the formation of "Strecker aldehydes" in beverages.

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