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ScienceDirect
Bioresource Technology 99 (2008) 260–268
BIORESOURCE TECHNOLOGY

Volatile components of grape pomaces from different cultivars of Sicilian *Vitis vinifera* L.

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Received 30 August 2006; received in revised form 22 December 2006; accepted 23 December 2006
Available online 23 February 2007

Dedicated to the memory of Dr. Gianfranco Borin.

Abstract

The volatile components of grape pomace coming from the processing of some of the most important varieties of grape (*Vitis vinifera* L.) cultivated in Sicily, namely Nero d'Avola, Nerello Mascalese, Frappato and Cabernet Sauvignon, have been determined by gas-chromatography (GC) and gas-chromatography–mass spectrometry (GC–MS). According to the winemaking procedure that entails the removal of stalks before fermentation, two kinds of grape pomace are obtained. The first consists of skins, pulp residues and seeds, the proper grape pomace, which is partially used for grappa, a typical Italian spirit, and alcohol production, the second consists almost exclusively of stalks. On the whole, 38 components have been characterized in the samples of grape pomaces, with Frappato cv. showing the richest composition; instead, 88 components have been detected in the stalks of Frappato, Nero d'Avola, Nerello Mascalese and Cabernet Sauvignon varieties. In order to make a comparison between the grape varieties easier, the volatile components detected in the two sets of samples (grape pomaces and stalks) have been grouped in different classes. Significant differences among varieties have been detected and statistical treatment of data is also reported. This study is part of a wider project aimed at the possible exploitation of the main agro-industrial by-products. At the same time it is one of the first reports on the volatile components of this waste material.

Keywords: *Vitis vinifera* L.; Grape pomace; Stalks; Volatile components; GC–MS

1. Introduction

Agro-industrial by-products present two rather conflicting aspects: on one hand their disposal represents a great economical and ecological problem, further complicated by legal restrictions, while on the other, they may be considered a promising and renewable source of useful compounds for their technological and nutritional properties (Laufenberg et al., 2003; Montgomery, 2004; Schieber et al., 2001).

It is likely that the most immediate and economic use of this material is as feed and as fertilizer, even though some pre-treatments and composting procedures are necessary in most cases. It also is true that these wastes are rich in several micronutrients such as carotenoids, polyphenols, tocopherols, vitamins, oligo elements and others, whose beneficial effects on human health are frequently highlighted, therefore this large amount of waste material could be a very cheap source of the aforesaid components. Of course, such potential exploitation would not avoid the disposal of a still substantial amount of waste, but the economic profit should make it more bearable.

Grape (*Vitis vinifera* L.) is one of the world's largest fruit crops, in excess of 60 million metric tons (www.fao.org), and is mainly grown for wine production. Grape pomace, the main by-product of wine production, consists of skins, seeds and stalks, reaching an estimated amount of 13% by weight of processed grape (Torres et al., 2002). In line with different winemaking procedures,

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0960-8524/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2006.12.025

two kinds of grape pomaces are obtained after the removal of stalks before maceration and successive fermentation steps. The first consists of skins, pulp residues and seeds, the proper grape pomace, which is partially used for grappa and alcohol production; the second consists almost exclusively of stalks.

The chemical composition of grape pomace is rather complex: alcohols, acids, aldehydes, esters, pectins, polyphenols, mineral substances, sugars etc. are the most represented classes of compounds (Bonilla et al., 1999; Mantell et al., 2003; Murthy et al., 2002; Saquet et al., 2000). The evaluation of the qualitative aspects of a grape pomace is carried out in view of the production of high quality grappa; otherwise the grape pomace is used for alcohol distillation, or thrown away. The best grape pomaces are highly rich in vinous liquid, namely not exhaustively pressed, with a moisture degree ranging from 55% to 70%, which allows to exploit the raw material better and to extract the organoleptic characteristics of the native vine. Concerning the pool of the volatile components of a grape pomace which confer its particular aroma, few studies have so far been reported (Park et al., 1991; Silva et al., 1996; Hashizume and Samuta, 1997), if compared with the analogous studies made on wine (Aznar et al., 2001; Flamini, 2005).

In our ongoing studies aimed at the possible exploitation of the main agro-industrial by-products obtained in Sicily, we wish to report here the results of a study of the volatile components of grape pomaces and stalks of the most important varieties of grape cultivated in Sicily for wine production, namely Nero d'Avola, Nerello Mascalese, Frappato and Cabernet Sauvignon.

2. Methods

2.1. Plant material

Grape pomaces and stalks of Nero d'Avola and Frappato were donated by the ''Valle dell'Acate'' wine firm, Acate, RG, Italy – those from Nerello Mascalese and Cabernet Sauvignon were given by the ''Emanuele Scammacca Barone del Murgo'' wine firm, Santa Venerina, CT, Italy. The winemaking procedures were similar for all samples, namely grape clusters were crushed and destemmed using a destemmer-crusher. The crushed grapes were treated with sulphur dioxide (0.2–0.5% total mash) and with selected strains of *Saccharomyces cerevisiae* to start up the fermentation. After 6–8 days of maceration, when alcoholic fermentation was finished, the mash was pressed. Stalks coming from destemming procedure and grape pomace coming from the maceration procedure were subjected to the distillation procedures within 24 h of their collection. All materials were collected during the 2004 vintage.

2.2. Isolation and analysis of volatile components

Fresh grape pomace and stalks (300 g each) were subjected to simultaneous steam distillation-extraction (SDE) for 3 h with a modified Likens–Nickerson apparatus using hexane (1 ml) as the solvent (Koedman, 1987). The SDE procedure was also carried out after adjusting the initial pH of the grape pomace and stalks suspensions to 7, by adding the necessary amount of 2 N NaOH solution.

The mixtures were immediately analysed on a Shimadzu gas chromatograph, Model 17-A equipped with a flame ionization detector (FID). Analytical conditions: DB-5 MS capillary column (30 m × 0.25 mm × 0.25 μm), helium as carrier gas. Injection in split mode (1:50), injected volume 1 μl, injector and detector temperature 250 and 280 °C, respectively. Linear velocity in column 19 cm/s. The oven temperature was held at 60 °C for 6 min, then programmed from 60 to 300 °C at 2 °C/min. Percentages of compounds were determined from their peak areas in the GC–FID profiles.

Gas-chromatography–mass spectrometry (GC–MS) was carried out in the fast mode on a Shimadzu GC–MS mod. GCMS-QP5050A, ionization voltage 70 eV, electron multiplier 900 V, transfer line temperature 280 °C. Analytical conditions: SPB-5 capillary column (15 m × 0.10 mm × 0.15 μm), helium as carrier gas. Injection in split mode (1:100), injected volume 1 μl, injector and detector temperature 250 °C. Constant linear velocity in column 50 cm/s. The oven temperature was held at 60 °C for 1 min, then programmed from 60 to 280 °C at 10 °C/min.

Identification of components was based on GC retention indexes, computer matching with Wiley 275 and NIST (Versions 21 and 75) libraries, comparison of the fragmentation patterns with those reported in the literature and whenever possible, coinjection with authentic samples (Jennings and Shibamoto, 1980; Adams, 2001).

Pure standards were purchased from Aldrich Chemical Co., Extrasynthese, France, and Fluka Chemie AG, Switzerland.

2.3. Statistical analysis

SPSS software, 14.1 version, was used to carry out statistical analysis of the data. ANOVA and Duncan's multiple range test were applied to the data to determine significant differences between the analysed volatile components; the model was statistically significant with a value of $P \leqslant 0.01$.

3. Results and discussion

3.1. Volatile components of grape pomace

Table 1 lists the 38 volatile components characterized in all samples of grape pomaces, whereas Fig. 1 shows a typical GC–FID profile. The Frappato cultivar showed the richest composition with 35 compounds; Nerello Mascalese and Nero d'Avola cultivars had a comparable composition with 21 and 19 components, respectively; finally the Cabernet Sauvignon cultivar gave the simplest mixture with only 17 identified components. The most represented class of