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Review

A critical review on extraction techniques and gas chromatography based determination of grapevine derived sesquiterpenes

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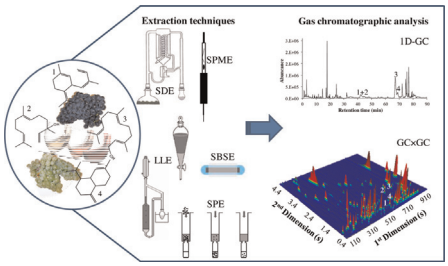
HIGHLIGHTS

- Grapevine is known to present several dozens of sesquiterpenic compounds.
- A critical overview of the sampling devices and GC methods is provided.
- Solvent and microextraction techniques are widely used.
- GC × GC offers substantial advantages for sesquiterpenes determination over conventional 1D-GC.
- Future trends on these techniques were described.

GRAPHICAL ABSTRACT



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ABSTRACT

Vitis vinifera L. (common grapevine) is considered one of the major world fruit crops based on the extent of cultivated land and on its economic value. Grapevine is composed by several different chemical compounds, including sesquiterpenic ones. Sesquiterpenic compounds play a significant role in varietal aromas, contributing to fruity and flowery odours, and are also well known for their potential health benefits. The advantages and drawbacks of different extraction and gas chromatographic techniques used for the determination of sesquiterpenic compounds are critically presented. Also, the future trends of sample preparation and gas chromatographic tools are discussed. This review provides the state-of-the-art and the technical know-how for the researchers who want to start studying sesquiterpenic compounds on complex matrices such as grapevine products.

Contents

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Sílvia Petronilho is a PhD student at University of Aveiro (Portugal). In order to evaluate the variety adequacy regarding the Appellation characteristics, she is currently studying the physico-chemical attributes of several grape varieties under the supervision of Prof. Sílvia M. Rocha and Prof. Manuel A. Coimbra. The research interests are related with the development and implementation of solvent free methodologies for the analysis of volatile and semi-volatile compounds, combined with one- (GC–FID, GC–MS) and two-dimensional (GC × GC) gas chromatography. She is the author of seven articles in international scientific journals and one book chapter.

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1. Introduction

Vitis vinifera L. is a species of *Vitis* that belongs to the Vitaceae family. This species is a perennial woody vine native to the South-Western Asia and then introduced in Mediterranean region, in Europe, and in other continents, being spread throughout the world [1]. Grapevine is considered one of the major world fruit crops based on the extent of cultivated land and on its economic value. Grapes are used mainly for wine production, but they are also consumed in fresh and as dried fruits or in juice. Their bioactive components have been used in cosmetic and healthy products.

The terpenic compounds, namely the sesquiterpenic ones, play a significant role in the varietal aroma of wines due to their flowery, fruity, and fresh odours [2–4]. The sesquiterpenic compounds present in wines may arise directly from grape and/or may have their origin on the rearrangement processes during winemaking process and/or aging [5]. These secondary metabolites are predominantly formed from farnesyl pyrophosphate or nerolidyl pyrophosphate [5]. After losing the pyrophosphate residue, different ways of cyclisations are followed. Skeletal rearrangement via carbocation intermediates with hydride or methyl group migration at low pH or temperature conditions [6] can give rise to an enormous type of structures [7] (Fig. 1).

The determination of secondary metabolites of natural products, such as terpenic compounds, represents an essential need for the valuation of these products. Besides grapevine related matrices, sesquiterpenic compounds have also been found on several natural products of different species of plants [8–15], liverworts [16,17], fruits [5,18–20], marine algae [21–23], corals [24,25], and sponges [26,27], among others. The increasing interest on sesquiterpenic compounds comes from the fact that they are present in many natural products claimed as presenting health benefits [5,11]. For instance, these compounds have been included in cosmetics and functional food products due to their aroma and preservative and bioactive health properties.

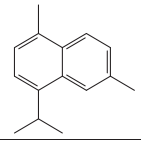
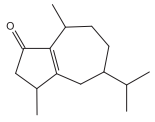
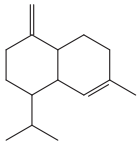
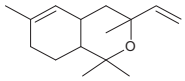
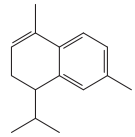
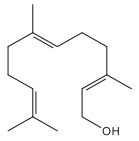
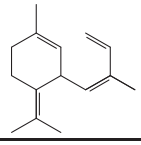
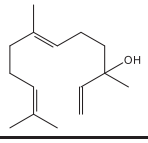
Compound	Chemical Structure	Compound	Chemical Structure
Cadalene		Rotundone	
δ-Cadinene		Cabreuva oxide D	
α-Calacorene		Farnesol	
α-Farnesene		Nerolidol	

Fig. 1. Sesquiterpenic compounds identified in grapevine related matrices, representing the four detected chemical families: hydrocarbons, ketones, oxides and alcohols.