

HS-SPME USING A CARBOWAX/DIVINILBENZENE COATING FIBRE AS A POWERFUL TOOL FOR CHARACTERIZATION OF SESQUITERPENOIDS FROM *Vitis vinífera* L. GRAPES AND WINES

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Volatile varietal characterization of grapes and wines from *Vitis vinífera* L., Baga variety, were studied by HS-SPME-GC-MS using a partially cross-linked with 65 μm carbowax-divinylbenzene coating fibre. This fibre was able to extract small, medium and large molecules and it is also recommended for polar compounds present in trace levels in the matrix. This study allowed the detection of 66 and 45 varietal compounds in the grapes from two Bairrada Appellation vineyards. Twenty three sesquiterpenoids were detected in both vineyards. The common and most abundant sesquiterpenoids were α -ylangene, germacrene D, β -bourbonene and γ -cadinene and these compounds seem to be a varietal marker for this variety. The sesquiterpenoids have been related with medicinal plants with different health applications, mainly anti-inflammatory, anti-HIV, antibacterial and antitumor activity [1]. The odour descriptors of sesquiterpenoids, like woody, spicy, sweet, floral, clove, oily, musty and fresh, may contribute positively for the wine aroma [1].

The volatile composition of Baga wine was studied by liquid-liquid dichloromethane continuous extraction to confirm the presence of the sesquiterpenoid compounds [2]. This methodology allowed the detection of aliphatic and aromatic alcohols, aliphatic acids, esters, phenols, lactones, amides, among others, but no sesquiterpenoid was detected. The analyses by

HS-SPME-GC-MS in the same conditions as used in grapes were carried out in four Baga wines from different winemakers and two vintages (2002 and 2004). Using this methodology about 90 volatile compounds were detected and identified. They were grouped as terpenoids, sesquiterpenoids, C₁₃ norisoprenoids, aliphatic and aromatic alcohols, aliphatic acids, esters, phenols, lactones, amides and others.

The sesquiterpenoids α -muurolene, α -calacorene and cadalene were detected in all Baga wines as well as in grapes (Table 1). Compounds not identified in grapes such as α -chamigrene, nerolidol, calarene, γ -eudesmol, α -cedrene and 1(5),3- aromadenedradiene, were detected in some of these wines. The presence of different sesquiterpenoids in Baga grapes and wines can be explained by their lability.

Table 1- Sesquiterpenoids found in monovarietal *Vitis vinifera* L. cv 'Baga' wine obtained from different winemakers (MC2, PP, CTD and QB) and vintages (2002 and 2004).

Compound	GC peak area x 10 ⁻⁵ (arbitrary units)			
	MC2 2002	PP 2004	CTD 2004	QB 2002
α -chamigrene	119 (6) ^a	--	--	--
α -muurolene*	153 (11)	76 (16)	118 (4)	130 (26)
α -calacorene*	173 (13)	39 (31)	63 (15)	283 (26)
Calamenene	--	--	--	13 (33)
(E)-nerolidol	--	83 (28)	208 (3)	--
Calarene	--	10 (29)	--	--
Calamene	--	--	--	135 (35)
γ -eudesmol	32 (6)	--	15 (17)	--
cadalene*	75 (2)	32 (6)	38 (5)	49 (20)
α -cedrene	--	--	64 (46)	--
1(5),3-aromadenedradiene	--	13 (79)	13 (12)	41 (14)

^a Number in parenthesis represent the coefficient of variation expressed in percentage (standard deviation * 100 / mean). *sesquiterpenoids detected in grapes and wines

These results show that the sesquiterpenoids present in grapes were extracted during the winemaking process from the raw material (grape), to the fermented product (wine). However, the detection of these compounds seems to be highly dependent of the methodology of extraction used. The HS-SPME-GC-MS methodology using a partially cross-linked with 65 μ m carbowax-divinylbenzene coating fibre allows the detection of varietal compounds such as sesquiterpenoids that were present in trace levels in *Vitis vinifera* L. Baga grapes and wines.

[1] Rocha, S. M.; Coelho, E.; Vinholes, J.; Coimbra, M. A. In: Recent Progress in Medicinal Plants, Vol. 15, studium Pres LLC, Houston, Texas, USA, 2005.

[2] Rocha, S. M.; Rodrigues, F.; Coutinho, P.; Delgadillo, I. and Coimbra, M. A. Anal. Chim. Acta. 2004, 513, 257-262.

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