2-*exo*-Hydroxy-1,8-cineole: A New Component from Grape Var. Sauvignon

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2-*exo*-Hydroxy-1,8-cineole is being reported in grape for the first time. It was extracted from var. Sauvignon must according to classical retention by XAD-2 organic resin. Identification was achieved by positive comparison of mass spectral and infrared spectral data and retention indexes on two gas chromatographic columns (polar CWAX20M and nonpolar OV-1) of the natural component with those of the corresponding synthesized compound. Possible breakdown of 2-*exo*-hydroxy-1,8-cineole following thermal treatment or fermentation in synthetic and neutral musts was investigated. Results of both investigations account for the chemical and biological stabilities of this new grape component.

1,8-Cineole, a component of many essential oils, is widely distributed in the plant kingdom. This compound has been reported as one of the major constituents responsible for the characteristic aroma note of black currant berries from various varieties (Williams, 1972; Maarse and Visscher, 1986). One of its oxidized derivatives, 2-*exo*-hydroxy-1,8-cineole, has been less frequently reported. To our knowledge, it has never been reported among the several compounds extracted from black currant berries but has recently been found, along with 1,8-cineole, in the water removed during juice concentration of ground black currant berries (Bitteur and Rosset, 1988). It has also been found in a mineral salt medium containing 1,8-cineole used as a carbon source by *Pseudomonas* bacterium isolated from the surface of eucalypt leaves (MacRae et al., 1979) as well as a result of the conversion of 1,8-cineole by a strain of *Aspergillus niger* in connection with the biomass utilization of *Eucalyptus* plants (Nishimura et al., 1982). In addition, it was recently described as one of the metabolites of 1,8-cineole in both blood and urine of rabbits (Miyazawa et al., 1989).

This paper reports on the isolation, identification, and quantification of 2-*exo*-hydroxy-1,8-cineole in the juice of grape berries var. Sauvignon. These experiments follow a previous study carried out by Italian coresearchers (Versini et al., 1988a) on the same grape variety, which had led to the report of an "unknown compound" along with its EIMS spectrum. Using the analytical procedures developed in our laboratories for the estimation of terpenic compounds in grapes (Günata et al., 1985; Versini et al., 1988b), we found that this component exists under two forms: "free" (i.e., 2-*exo*-hydroxy-1,8-cineole itself) and "bound" (i.e., liberated by the enzymic incubation with a commercial preparation of pectinol).

2-*exo*-Hydroxy-1,8-cineole is of some interest as it was not found in other white grape varieties studied so far such as Muscat, Malvoisie, Chardonnay, and Riesling and is now being reported for the first time in the Sauvignon variety.

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EXPERIMENTAL SECTION

Solvents and Chemicals. Pentane was obtained from Labosi (Oulchy-le-Chateau, France). It was washed with H_2SO_4 and then with $KMnO_4$ and was distilled from potassium hydroxide. Analytical-grade methylene chloride and ethyl acetate (Merck, Darmstadt, FRG) were redistilled before use. Subsequent distillation of pentane/methylene chloride mixtures led to the (2/1, v/v) azeotropic composition. Ultrapure water was obtained from a Milli-Q purification unit (Millipore, Bedford, MA).

4-Nonanol used as an internal standard, as well as optically pure (*R*)-α-pinene; *m*-chloroperoxybenzoic acid and formic acid were purchased from Merck. *p*-Toluenesulfonic acid was obtained from Prolabo (Paris, France).

Pectinol solution was prepared with 1.2 mg of purified pectinol (Röhm, GmbH, Darmstadt, R.F.G) in 100 μL of phosphate/citrate buffer (pH 5.0).

Preparation of Plant Material. Technologically mature Sauvignon grapes (total sugar content 180 g/L, titrable acidity 9.95 g of tartaric acid/L, pH 3.14) was collected from the vineyards of Trentino Adige Valley (San Michele all'Adige, Italy). They were rapidly cooled with liquid nitrogen and then stored at −20 °C until must preparation. Two samples of grape berries (351, 349 g) were allowed to reach 4 °C overnight and then crushed at the same temperature. Each must (238, 235 mL) was filtered and then spiked with 29 μg of 4-nonanol before centrifugation (4 °C, 12000*g*, 15 min). The final volumes were 218 and 222 mL, respectively.

Extraction of Free and Bound 2-*exo*-Hydroxy-1,8-cineole. Each centrifugated must was divided into three samples (3 × 50 mL) that were extracted separately. Extraction was carried out according to the analytical procedure described previously (Günata et al., 1985) with the following modifications: Each 50 mL of must was allowed to pass through a 0.9 × 10 cm XAD-2 column at 1.5 mL/min flow rate. After the chromatographic system was flushed with 70 mL of ultrapure water, recovery of the "free" compounds was achieved by elution with 70 mL of pentane, while the "bound" fraction was obtained by subsequent elution with 70 mL of ethyl acetate.

Analysis of Must Extracts. The pentane fraction containing the free 2-*exo*-hydroxy-1,8-cineole was dried over sodium sulfate and then concentrated under reflux in Dufton columns to approximately 200 μL. A 3-μL portion was then analyzed by high-resolution gas chromatography on a capillary CPWAX57CB column. The ethyl acetate fraction was dried over sodium sulfate, evaporated under a gentle stream of nitrogen, and taken up in 100 μL of phosphate/citrate aqueous buffer (pH 5.0). After

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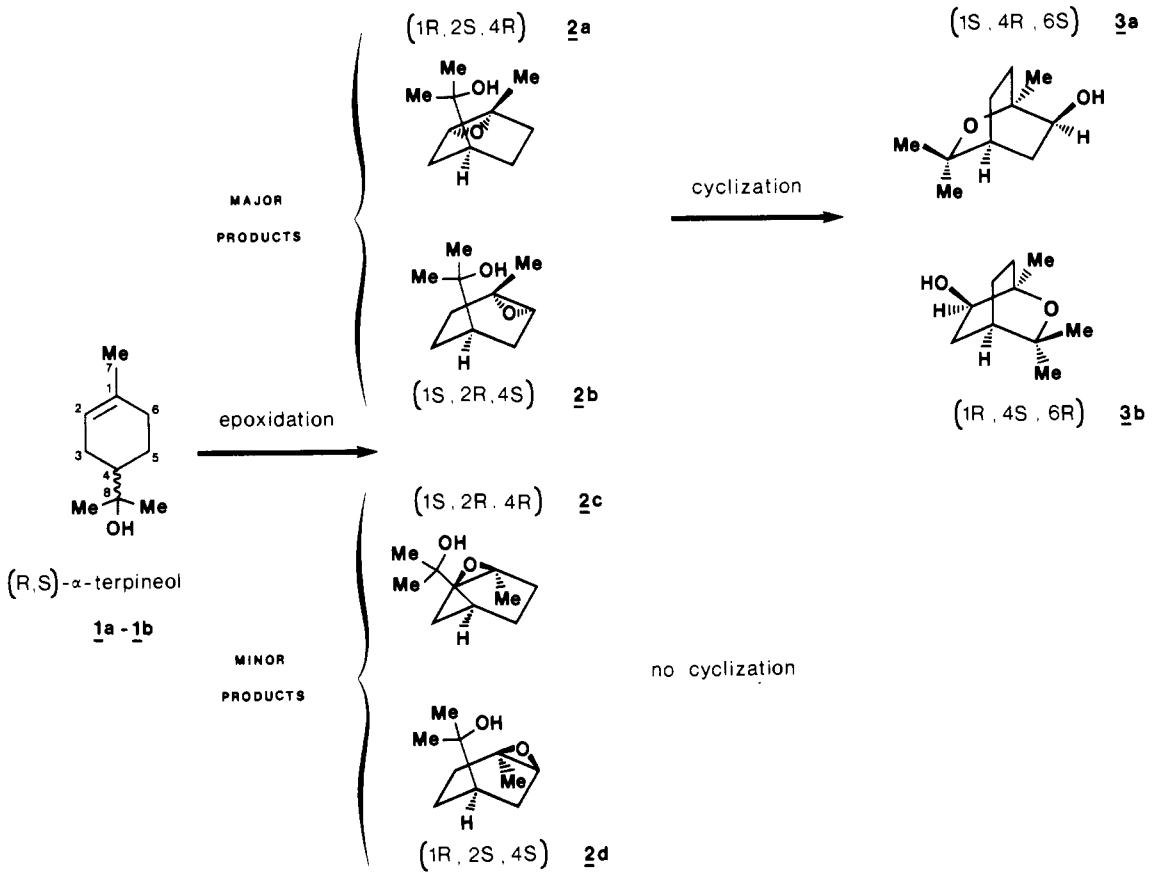

Figure 1. Two-step pathway involved in synthesis of 2-*exo*-hydroxy-1,8-cineole (**3a**).

removal of eventual traces of free compounds by extraction with 4 × 100 μL of pentane, enzymic assay was achieved by the addition of 100 μL of pectinol solution and incubation at 40 °C for 15 h. Incubated samples were then extracted with 5 × 100 μL of pentane. These five organic fractions were pooled, dried over sodium sulfate, spiked with 29 μg of 4-nonanol, and then concentrated and analyzed by GC according to the procedure applied for the free fraction.

Synthesis of 2-*exo*-Hydroxy-1,8-cineole. The pathway chosen for this synthesis is depicted in Figure 1. It involves epoxidation of the C1=C2 double bond of α-terpineol, followed by ring opening according to Markovnikov addition of the C8-hydroxyl moiety. The first step could result in the formation of four epoxides, but steric hindrance of the isopropylhydroxy group is expected to favor endo attack of the double bond and formation of the corresponding enantiomeric pair **2a** and **2b** as major epoxidation products. As for the second step, requirements of the transition state for ring closure (Baldwin, 1976) should lead to the enantiomeric pair **3a** and **3b** only. So to minimize the number of products involved, the synthesis of 2-*exo*-hydroxy-1,8-cineole was achieved by the *m*-chloroperoxybenzoic acid epoxidation of optically pure (*R*)-α-terpineol.

(+)-(*R*)-α-Terpineol was synthesized according to the method described by Colonge and Crabalona (1959). This involved the action of formic acid on optically pure (*R*)-α-pinene and subsequent saponification of intermediate terpinyl formate. The final product was purified by distillation under reduced pressure (0.2 bar) followed by fractionation on silica gel (60 mesh) and elution with 50/50 petroleum ether/diethyl ether (v/v).

Epoxidation of (+)-(*R*)-α-terpineol was carried out under the same conditions as those described by Kopperman et al. (1976) who used (*R,S*)-α-terpineol and reported that two major components (**2c/2d**, **3a/3b**) were obtained after 2 h. Monitoring our reaction mixture by GC/ITD showed that, after 22 h, only 5% of compound **3a** was obtained, along with 9% of the starting material (**1a**) (Figure 1) and 86% of a major component (probably **2a**). The conversion rate of **2a** to **3a** was then improved by acid catalysis. Thirty hours after the addition of *p*-toluenesulfonic acid, **3a** was obtained as a major component (70%) of the reaction mixture. Subsequent purification by silica gel chromatography and recrystallization in pentane afforded compound **3a**.

Gas Chromatography. Gas chromatographic analyses were performed on a Vista 6000 apparatus (Varian, Sunnyvale, CA) equipped with a flame ionization detector and a CPWAX57CB fused silica capillary column (26 m × 0.32 mm (i.d.)) (Chrompack, Middleburg, The Netherlands). The WCOT film of the polar phase was 1.2 μm thick, hydrogen was used as the carrier gas (4.2 mL/min flow rate), and 3-μL aliquots of organic samples were injected through a split/splitless injector (ratio 1/10). Detector and injector were kept at 250 °C while the oven temperature program was 60 °C for 3 min, up to 220 °C at 2 °C/min, and 220 °C for 10 min.

Instrumention. ^{13}C and ^{1}H NMR spectra were measured on a Brüker AC 300 apparatus with tetramethylsilane as the internal standard.

Vapor-phase GC/FTIR spectra were recorded on a HP 5965 IRD (Hewlett-Packard Italiana, Cernusco sul Naviglio, Milano, Italy). Transfer line temperature was 200 °C.

GC/EIMS (70-eV) spectra were obtained on a 5979 Hewlett-Packard mass detector connected to a Carlo Erba HRGC 5300 chromatograph equipped with a HP-20M fused silica capillary column. Additional experimental details are as in Versini et al. (1988a).

MS monitoring of the compounds formed during synthesis of 2-*exo*-hydroxy-1,8-cineole was achieved by gas chromatography and ion trap detection (Finnigan MAT, San Jose, CA). GC/ITD conditions have been described by Baumes et al. (1988).

Recovery of 2-*exo*-Hydroxy-1,8-cineole. To quantify the original content of this 1,8-cineole derivative in Sauvignon must, an aqueous solution containing 200 g/L glucose and 4 g/L potassium hydrogen tartrate (pH 3.47) was added with 4-nonanol (54 mg/L) and 2-*exo*-hydroxy-1,8-cineole (31 mg/L). The whole extraction and concentration procedure was applied twice to 2 × 50 mL model solutions, and the average final 2-*exo*-hydroxy-1,8-cineole to 4-nonanol area ratio was compared to its original value. Mean relative recovery was 66%.

Chemical Stability Experiments. These trials were performed as described by Strauss et al. (1988). A 2.3-mg sample of synthetic 2-*exo*-hydroxy-1,8-cineole in 13 mL of tartrate aqueous buffer (pH 3.0) was allowed to stand in a boiling water bath for 15 min. After being rapidly cooled in ice, the reaction mixture was extracted with 2 × 10 and then 3 × 5 mL of dichloromethane. The pooled organic extract was dried over sodium sulfate, filtered, concentrated to 2.5 mL, and then analyzed by gas chromatography.

Biological Stability Experiments. Fermentation trials were carried out on two different media. The first was a culture medium simulating a grape must, the composition of which was given in Sablayrolles and Barre, 1989. The second medium was an actual var. Grenache Blanc must previously centrifugated at 4 °C and 12000*g* for 15 min. The yeast was *Saccharomyces cerevisiae*, strain K1 (ICV-INRA, Montpellier, France) for both trials. Four 200-mL culture media (two control samples of each kind and two samples previously spiked with 1 mg of 2-*exo*-hydroxy-1,8-cineole) were inoculated with 10^6 cells/mL previously grown at 28 °C for 24 h in the synthetic culture medium. After 10 days at 26 °C, fermentated media were analyzed according to the procedure already described for must samples with two differences: A 10 cm × 0.9 cm strong anion-exchange resin (Dowex, Fluka Chemie, Buchs, Switzerland) was used before the XAD-2 resin during the extraction step in order to avoid interference of organic acids during GC analyses, and pentane/dichloromethane (2/1) was used as an eluting solvent of medium polarity.

RESULTS AND DISCUSSION

Identification of 2-*exo*-Hydroxy-1,8-cineole. The 70-eV EIMS data of the natural compound are as follows: *m/z* (relative intensity) 43 (100), 71 (39), 108 (35), 69 (24), 126 (23), 55 (20), 93 (19), 39 (19), 111 (17), 58 (14), 83 (13), 170 (5). They are similar to that of 6-methyl-5-hepten-2-one (Thomas et al., 1969) and to those of 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6-ols (racemic (1*SR*,4*RS*,6*SR*)-2-*exo*-hydroxy-1,8-cineole (Nishimura et al., 1982) and optically pure (1*S*,4*R*,6*S*-(+)-2-*exo*-hydroxy-1,8-cineole and (1*S*,4*R*,6*R*-(−)-2-*endo*-hydroxy-1,8-cineole (Gandini et al., 1972; MacRae et al., 1979). However, the various ions may have different relative intensities. Similarity between these spectra probably comes from the common fragment at *m/z* 126 (molecular ion for the first compound and loss of CH_3CHO for the others) and subsequent fragmentation as reported by Thomas et al. (1969). However, the EIMS of the octan-6-ols and that of the natural compound found in our extracts exhibited an additional fragment at *m/z* 170 (relative intensity 5.2% for the natural compound and from 7 to 47% reported in the literature; Nishimura et al., 1982; Gandini et al., 1972; MacRae et al., 1979). Moreover, the retention index of 6-methyl-5-hepten-2-one (1335 on CW20M) is very different from that of the natural product. Accordingly, this chemical structure was excluded. We finally distinguished between the two 2-hydroxy-1,8-cineoles by synthesizing one of them. As presented in the introduction, 2-*exo*-hydroxy-1,8-cineole has been reported as an oxidation product of 1,8-cineole but the corresponding 2-*endo*-hydroxy-1,8-cineole isomer was either not formed or formed as a minor compound. We therefore focused on the synthesis of the former compound.

This synthetic component obtained exhibited the following NMR spectral characteristics: ^1H NMR (300.13 MHz, $CDCl_3$) δ 3.72 (ddd, H6, $J_{6,5}$ = 9.7 Hz, $J_{6,5'}$ = 4.3 Hz, $J^{w}_{6,7}$ = 1.3 Hz), 2.51 (dddd, H5 endo, $J_{5,5'}$ = 13.3 Hz, $J_{5,6}$ = 9.7 Hz, $J_{5,4} \simeq J^{w}_{5,8} \simeq$ 3.5 Hz), 1.27, 1.18, 1.09 (3 s, Me9, Me10, Me11), other signals between 1.04 and 2.03; ^{13}C NMR (75.469 MHz, noise decoupling, $CDCl_3$) δ 73.4 (C3), 72.5 (C1), 71.1 (C6), 34.7 (C5), 34.4 (C4), 29.0, 28.6 ($(CH_3)_2$C3), 25.0 (C7), 24.0 (CH_3C1), 22.2 (C8), which favorably compared with data published previously (MacRae et al., 1979; Nishimura et al., 1982).

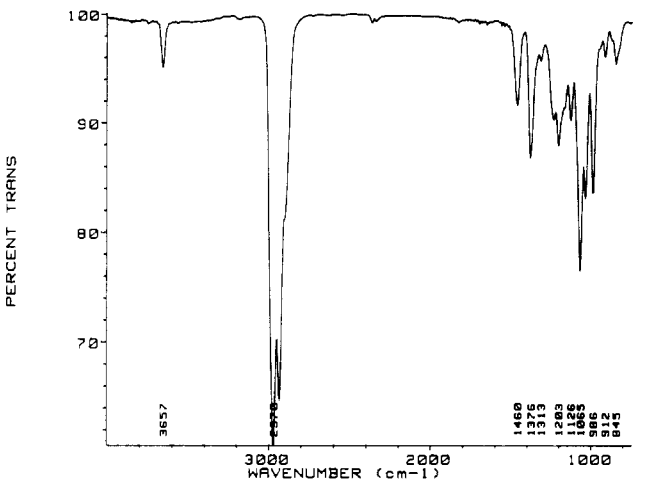

Figure 2. Vapor-phase FTIR spectrum of synthetic 2-*exo*-hydroxy-1,8-cineole.

Moreover, EIMS data of the synthesized hydroxycineole were identical with those of the natural compound extracted from grape, and vapor-phase FTIR spectra (Figure 2) were totally consistent with one another (as for the CH 2970-cm^{-1} and the OH 3655-cm^{-1} vibration bands, but more specifically in the 1000–1400-cm^{-1} fingerprint zone). Both components also exhibited the same GC retention indexes on two different phases (1822 for CWAX-20M and 1210 for OV-1). Accordingly, the natural component extracted from Sauvignon must was proved to be compound **3a** and/or its enantiomer **3b**. No further attempt was made to determine its absolute configuration.

Origin of 2-*exo*-Hydroxy-1,8-cineole in Grape. When considering that 2-*exo*-hydroxy-1,8-cineole can originate from α-terpineol or from 1,8-cineole, we must stress that α-terpineol was found in our grape extracts (at trace levels as a free compound and more abundant as a bound compound) whereas 1,8-cineole was not. If the hypothesis of production of 2-*exo*-hydroxy-1,8-cineole from α-terpineol is to be put forward, two main pathways can be considered. The first pathway, by which our synthesis was carried out, involves epoxidation of the C1=C2 double bond of α-terpineol as previously reported by Banthorpe et al. (1977). The second pathway involves allylic oxidation of the sensitive C1=C2 trisubstituted double bond according either to a concerted mechanism similar to that of the dye-sensitized photooxygenation of limonene (Ohloff, 1975) or to a radical mechanism as for the autoxidation of limonene (Ohloff, 1975; Hammer and Scott, 1982), leading to a mixture of C1 and C2 oxidation products. The subsequent cyclization reactions should then lead to a complex mixture of oxidized compounds that we did not find in our extracts. The absence of any isomer other than **3a**/**3b** in our grape extracts suggests that the former mechanism proposed for the synthesis of 2-*exo*-hydroxy-1,8-cineole be biomimetic of the one involved in formation of the identified compound.

The analytical procedures applied here for the enzymic liberation of bound 2-*exo*-hydroxy-1,8-cineole were identical with those classically applied for the hydrolysis of glycosidically bound terpenols extracted from var. Muscat grapes (Günata et al., 1985). This involved use of commercially available pectinol, which has revealed enzymic α-L-rhamnopyranosidase, α-L-arabinofuranosidase, and β-D-glucopyranosidase activities (Cordonnier et al., 1989). As such activities have been reported to be

Table I. Quantification of 2-*exo*-Hydroxy-1,8-cineole under Free and Bound Forms in Two Samples of Sauvignon Must[a]

	free 2-*exo*-1,8-hydroxycineole		bound 2-*exo*-1,8-hydroxycineole	
	must I	must II	must I	must II
mean, μg/kg	8.0	7.0	1.7	3.5
std dev ($n-1$)	3.2	4.0	0.78	0.87
coeff var	0.41	0.56	0.47	0.25

[a] Results refer to the amount per kilogram of grape berries and correspond to triplicate determinations.

involved in sequential enzymic hydrolysis of terpenyl glycosides from grapes (Günata et al., 1988), one may put forward the hypothesis that the bound form(s) of 2-*exo*-hydroxy-1,8-cineole found in the must of Sauvignon grape be of glycosidic nature.

Quantification of 2-*exo*-Hydroxy-1,8-cineole. This compound was quantified under both free and bound forms in two samples of Sauvignon must prepared separately. Each sample was extracted in triplicate. The results in Table I take into account the GC analysis response factor of 2-*exo*-hydroxy-1,8-cineole, relative to that of 4-nonanol (1.65). As for the free compound, the recovery factor during the extraction/concentration process (0.66) was considered as well. No such factor was accessible for the bound form, as we do not know and accordingly cannot dispose of the exact compounds under concern. This can partly explain why 2-*exo*-hydroxy-1,8-cineole is more abundant as a free compound.

Tests show that mean values 1.7 and 3.5 μg/kg of grape berries are statistically different. These two figures correspond to two distinct determinations of bound 2-*exo*-hydroxy-1,8-cineole. On the other hand, the six individual values obtained for the free form can be regarded as a unique statistical population defined by a mean of 7.5 μg/kg and a standard deviation of 3.3 μg/kg.

Stability of 2-*exo*-Hydroxy-1,8-cineole. Unlike 1,8-cineole, 2-*exo*-hydroxy-1,8-cineole is hardly odorous. Possible breakdown of the latter compound into odorous volatile components was therefore investigated in two different ways. The first one was achieved according to the chemical stability experiments already described in the Experimental Section. 2-*exo*-Hydroxy-1,8-cineole turned out to be very stable under high-temperature acidic conditions as no peak but that of the starting material was detected either by flame ionization detection or by the conventional sniffing technique.

The second set of experiments involved fermentation of both an actual Grenache Blanc must (defined as a neutral variety with regard to its aroma components) and a synthetic must previously spiked with 2-*exo*-hydroxy-1,8-cineole. Comparative analyses, after fermentation, showed no difference between the samples containing the hydroxycineole component and the control samples, whatever the original culture medium investigated.

These results account for the high stability of 2-*exo*-hydroxy-1,8-cineole, should it be chemical or biological.

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LITERATURE CITED

Baldwin, J. E. Rules for Ring Closure. *J. Chem. Soc., Chem. Commun.* **1976**, 734–6.

Banthorpe, D. V.; Bucknall, G. A.; Gutowski, J. A.; Rowan, M. G. Terpene Biosynthesis. Part 18. Epoxidation and Hydration of Phenyl Pyrophosphates by Plant Extracts. *Phytochemistry* **1977**, *16*, 355–8.

Baumes, R.; Bayonove, C.; Barillère, J.-M.; Escudier, J.-L.; Cordonnier, R. La macération pelliculaire dans la vinification en blanc. Incidence sur la composante volatile des moûts. *Conn. Vigne Vin* **1988**, *22*, 209–23.

Bitteur, S.; Rosset, R. Use of an Octadecyl-Bonded Silica and a Styrene-Divinylbenzene Copolymer for the Recovery of Blackcurrant Aroma Compounds from a Food Plant Waste Water. *J. Food Sci.* **1988**, *53*, 141–7.

Carman, R. M.; MacRae, I. C.; Perkins, M. V. The Oxidation of 1,8-Cineole by *Pseudomonas flava*. *Aust. J. Chem.* **1986**, *39*, 1739–46.

Colonge, J.; Crabalona, J. Action of Formaldehyde on the Monocyclic Terpenic Hydrocarbons. I. *p*-8-Menthene. *Bull. Soc. Chim. Fr.* **1959**, 1505–11.

Cordonnier, R. E.; Günata, Y. Z.; Baumes, R. L.; Bayonove, C. L. Recherche d'un Matériel Enzymatique Adapté à l'Hydrolyse des Précurseurs d'Arôme de Nature Glycosidique du Raisin. *J. Int. Sci. Vigne Vin* **1989**, in press.

Gandini, A.; Bondavalli, F.; Schenone, P.; Bignardi, G. Stereochemistry of 1,8-Cineole Derivatives. II: 2-Cineolylols. *Ann. Chim. (Rome)* **1972**, *62*, 188–99.

Günata, Y. Z.; Bayonove, C. L.; Baumes, R. L.; Cordonnier, R. E. The Aroma of Grapes. 1. Extraction and Determination of Free and Glycosidically Bound Fractions of some Grape Aroma Components. *J. Chromatogr.* **1985**, *331*, 83–90.

Günata, Z.; Bitteur, S.; Brillouet, J.-M.; Bayonove, C.; Cordonnier, R. Sequential Enzymic Hydrolysis of Potentially Aromatic Glycosides from Grape. *Carbohydr. Res.* **1988**, *184*, 139–49.

Hammer, F. E.; Scott, D. L'Oxydation des Boissons Rafraîchissantes. Description et Moyens de Lutte. *Bios* **1982**, *13*, 5–13.

Jennings, W.; Shibamoto, T. Appendix IV. In *Qualitative analysis of flavor and flagrance volatiles by glass capillary gas chromatography*; Academic Press: New York, 1980; p 367.

Kopperman, H. L.; Hallcher, R. C.; Riehl, A., Sr.; Carlson, R. M.; Caple, R. Aqueous Chlorination of α-Terpineol. *Tetrahedron* **1976**, *32*, 1621–6.

Maarse, H.; Visscher, C. A. Qualitative Data. Suppt. 3. In *Volatile Compounds in Food*; TNO-CIVO: Zeist, The Netherlands, 1986.

MacRae, I. C.; Alberts, V.; Carman, R.; Shaw, M. Products of 1,8-Cineole Oxidation by a Pseudomonad. *Aust. J. Chem.* **1979**, *32*, 917–22.

Miyazawa, M.; Kameoka, H.; Morinaga, R.; Negoro, K.; Mura, N. Hydroxycineole: Four New Metabolites of 1,8-Cineole in Rabbits. *J. Agric. Food Chem.* **1989**, *37*, 222–6.

Nishimura, H.; Noma, Y.; Mizutani, J. *Eucalyptus* as biomass. Novel Compounds from Microbial Conversion of 1,8-Cineole. *Agric. Biol. Chem.* **1982**, *46*, 2601–4.

Ohloff, G. Singlet Oxygen: a Reagent in Organic Synthesis. *Pure Appl. Chem.* **1975**, *43*, 481–502.

Sablayrolles, J.-M.; Barre, P. Effect of anisothermal conditions on the kinetics of alcoholic fermentation by *Saccharomyces cerevisiae*. *Bioprocess Eng.* **1989**, *4*, 139–43.

Strauss, C. R.; Wilson, B.; Williams, P. J. Novel Monoterpene Diols and Diol Glycosides in *Vitis Vinifera* Grapes. *J. Agric. Food Chem.* **1988**, *36*, 569–73.

Thomas, A. F.; Willhalm, B.; Müller, R. Mass Spectrometry and Organic Analysis. XIII - The Mass Spectra of Doubly Unsaturated Carbonyl Compounds. *Org. Mass Spectrom.* **1969**, *2*, 223–39.

Versini, G.; Dalla Serra, A.; Dell'Eva, M.; Scienza, A.; Rapp, A. Evidence of some glycosidically bound new monoterpenes and norisoprenoids in grapes. *Bioflavour'87*; W. de Gruyter: Berlin, New York, 1988a; pp 161–70.

Versini, G.; Scienza, A.; Dell'Eva, M.; Dalla Serra, A.; Romano, F. Presenza ed Interesse di Sostanze Monoterpeniche e Norisopreniche in Uve da Cloni Chardonnay e Sauvignon Bianci nel Trentino. *Atti Acad. Ital. Vite Vino* **1988b**, *XL*, 121–34.

Williams, A. A. *Fruit Juices Res. Technol. Symp. Proc.* **1972**, *XII*, 21–42.

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