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Glycosides and Phenylpropanoid Glycerol in *Vitis vinifera* Cv. Gewurztraminer Wine

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Eight glycosides and a phenylpropanoid glycerol were isolated from *Vitis vinifera* cv. Gewurztraminer wine, and their structures were elucidated by MS and NMR spectroscopies. *cis*-1-(5-Ethenyl-5-methyltetrahydrofuran-2-yl)-1-methylethyl *O*-β-D-apiofuranosyl-(1→6)-*O*-β-D-glucopyranoside, (*E*)-3,6,9-trihydroxymegastigm-7-ene 9-*O*-β-D-glucopyranoside, 2-phenylethyl *O*-β-D-apiofuranosyl-(1→6)-*O*-β-D-glucopyranoside, and 2-[4-(3-hydroxypropyl)-2-methoxyphenoxy]propane-1,3-diol are reported for the first time as wine components.

Keywords: *Vitis vinifera; Gewurztraminer wine; mono- and diglycosides; cis-furan linalool oxide; (E)-3,6,9-trihydroxymegastigm-7-ene; benzyl alcohol; phenylethanol; isolariciresinol; phenylpropanoid glycerol*

INTRODUCTION

Increasing interest has been devoted in the past years to the study of glycosidically bound volatile compounds occurring in *Vitis vinifera* grape and wine, in relation with their potential organoleptic role. Sugars involved in these glycoconjugates are mono- and disaccharides, mainly β-D-glucopyranose, α-L-arabinofuranosyl-(1→6)-*O*-β-D-glucopyranose, α-L-rhamnnopyranosyl-(1→6)-*O*-β-D-glucopyranose (Williams et al., 1982, 1983), and β-D-apiofuranosyl-(1→6)-*O*-β-D-glucopyranose (Voirin et al., 1992b). Many aglycons have been identified as monoterpenoids with various oxidation states, norisoprenoids with 13 carbon atoms, and shikimate-derived compounds (Winterhalter et al., 1990). As most of these products are volatile and show interesting sensory properties, their flavorless glycosidic counterparts, often by far more abundant than the free aglycons, may represent an important potential source of aroma. Glycosides are especially abundant in aromatic grape varieties, in particular in those growing in Alsace (France) (Günata et al., 1985; Voirin et al., 1992b).

In our previous publications on the nonvolatile aroma precursors aiming to investigate the relationships between wine molecular markers and grape varieties, we reported on the isolation and characterization of new megastigmane (**1**−**4**) (Baltenweck-Guyot et al., 1996) and hemiterpene (**5** and **6**) (Baltenweck-Guyot et al., 1997) glycosides (Figure 1) occurring in an Alsatian Gewurztraminer white wine. We have now obtained, from the same source, eight additional glycosides and a phenylpropanoid glycerol. This paper deals with their structural elucidation and gives detailed or revised NMR data. Among these products, four are reported for the first time as wine components.

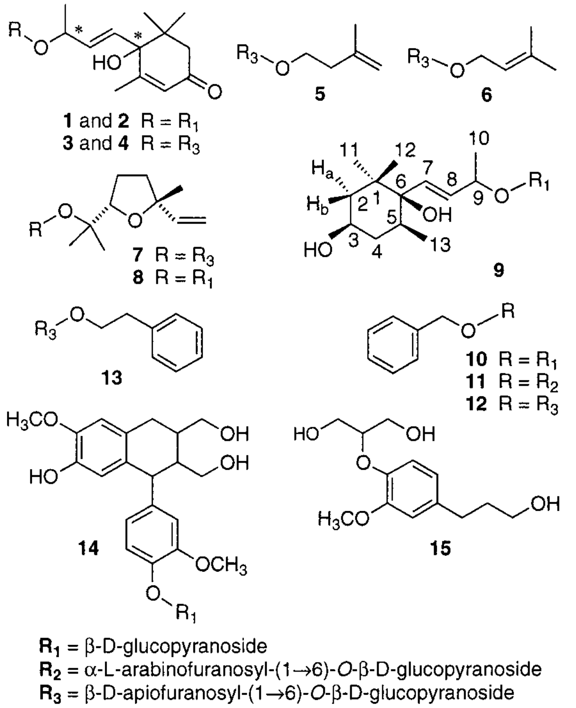

Figure 1. Structures of compounds **1**−**15**. Configurations shown for compounds **7**−**9** are relative.

MATERIALS AND METHODS

Spectroscopy. *NMR.* ^{1}H, ^{1}H−^{1}H COSY, NOESY, HSQC, and HMBC spectra were obtained at 500 and 125 MHz for ^{1}H and ^{13}C, respectively, on a Bruker ARX 500 spectrometer using the standard Bruker software package. The ^{13}C signal and the residual ^{1}H signal of the solvent ($CDCl_3$) were used as secondary references (δ 77.0 and 7.26 from TMS, respectively). ^{13}C data were taken from HMBC and HSQC spectra.

LRMS. Spectra were recorded on a Finnigan MAT TSQ 700 spectrometer.

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CIMS. NH_3 was used as reagent gas, source pressure = 40 mbar, source temperature = 150 °C, 70 eV.

GC-EIMS. The column used was a DB5 J&W (60 m × 0.25 mm i.d. × 0.1 μm film thickness), He at 2 mL min^{-1}; 38 °C (1 min), 38−220 °C at 10 °C min^{-1}, 220−300 °C at 3 °C min^{-1}, 300 °C (30 min); source temperature = 200 °C, 70 eV.

HRMS. Measurements on $(M + Na)^+$ ions of the peracetylated compounds were performed on a Micromass Autospec spectrometer in positive LSIMS mode using a mixture of 3-nitrobenzyl alcohol, TFA (1%), and NaI as the matrix.

Wine. The Gewurztraminer wine from year 1993 was obtained from the cave vinicole of Ribeauvillé (Alsace, France).

Solvents and Reagents. Usual solvents (CH_2Cl_2, MeOH, Me_2CO, and EtOAc) were distilled twice. Acetic anhydride (Prolabo), iso-PrOH (Carlo Erba), and pyridine (Prolabo, distilled over CaH_2 and stored over 4 Å molecular sieves) were of analytical grade. MeCN (Aldrich) was of HPLC grade. H_2O was distilled and deionized.

Isolation of Compounds. The crude glycosidic extract (500 mg) obtained from the wine (5 L) was subjected to HPLC gross separation, affording 10 fractions A1−A10 (Baltenweck-Guyot et al., 1996, 1997). Further fractionation of A5 (60 mg) and A6 (40 mg) by analytical HPLC (Du Pont Zorbax ODS, 250 × 4.6 mm, H_2O/MeCN 9:1 for A5, H_2O/Me_2CO 9:1 for A6, 1 mL min^{-1}) furnished in each case 10 subfractions B1−B10 and C1−C10, respectively. Final purification of compounds from B6 (**5** and **6**), B7 (**10**, 1 mg; and **11**, 0.8 mg), B9 (**1** and **2**), B10 (**3**, **4**, and **14**, 0.5 mg), C3 (**9**, 0.6 mg; and **15**, 1.6 mg), C6 (**13**, 1 mg), and C10 (**7**, 0.7 mg; and **8**, 0.3 mg) was achieved by analytical HPLC [Astec cyclobond I acetylated β-cyclodextrin, 250 × 4.6 mm, H_2O (H_2O/MeCN 95:5 for C10), 0.8−1 mL min^{-1}]. Glycoside **12** (3.5 mg) was purified by TLC (silica gel 60 F_{254} Merck, EtOAc/iso-PrOH/H_2O 60:30:10) from B8. Owing to possible loss of product during the isolation procedure, weights indicated for the investigated compounds may be underestimated with regard to their true concentrations in the wine.

Acetylation of Compounds. Compounds were acetylated in a mixture of acetic anhydride and anhydrous pyridine for 3 days at room temperature.

*(Z)-1-(5-Ethenyl-5-methyltetrahydrofuran-2-yl)-1-methylethyl O-β-D-Apiofuranosyl-(1→6)-O-β-D-glucopyranoside (**7**), Hexaacetate:* ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (3H, s, H-10), 1.21 (3H, s, H-9), 1.26 (3H, s, H-8), 1.71 (1H, m, Hb-4), 1.76 (1H, m, Hb-3), 1.79 (1H, m, Ha-4), 1.92 (1H, m, Ha-3), 1.99, 2.01, 2.02, 2.03, 2.08, 2.11 (18H, 6s, H of acetate CH_3), 3.54 (1H, dd, *J* = 6.9, 11.1 Hz, Glc-H-6), 3.64 (1H, ddd, *J* = 2.3, 6.9, 9.5 Hz, Glc-H-5), 3.68 (1H, dd, *J* = 2.3, 11.1 Hz, Glc-H-6), 3.92 (1H, t, *J* = 6.8 Hz, H-2), 4.14 (1H, d, *J* = 10.6 Hz, Api-Ha-4), 4.21 (1H, d, *J* = 10.6 Hz, Api-Hb-4), 4.49 (1H, d, *J* = 12.3 Hz, Api-H-5), 4.80 (1H, d, *J* = 12.3 Hz, Api-H-5), 4.81 (1H, d, *J* = 8.0 Hz, Glc-H-1), 4.90 (1H, dd, *J* = 8.0, 9.5 Hz, Glc-H-2), 4.90 (1H, dd, *J* = 9.5, 9.5 Hz, Glc-H-4), 4.96 (1H, dd, *J* = 1.5, 10.8 Hz, Ha-7), 5.01 (1H, d, *J* = 0.4 Hz, Api-H-1), 5.15 (1H, dd, *J* = 1.5, 17.4 Hz, Hb-7), 5.19 (1H, dd, *J* = 9.5, 9.5 Hz, Glc-H-3), 5.32 (1H, d, *J* = 0.4 Hz, Api-H-2), 5.92 (1H, dd, *J* = 10.8, 17.4 Hz, H-6); ^{13}C NMR (125 MHz) δ 20.6−21.9 (acetate CH_3), 21.8 (C-10), 24.2 (C-9), 25.5 (C-8), 26.9 (C-3), 37.5 (C-4), 63.0 (Api-C-5), 66.7 (Glc-C-6), 69.3 (Glc-C-4), 71.6 (Glc-C-2), 72.4 (Api-C-4), 72.8 (Glc-C-5), 73.2 (Glc-C-3), 76.5 (Api-C-2), 79.6 (C-1), 83.0 (C-5), 84.0 (Api-C-3), 84.2 (C-2), 95.3 (Glc-C-1), 105.9 (Api-C-1), 111.3 (C-7), 144.3 (C-6), 169.5−171.0 (acetate C=O); GC-EIMS 70 eV, *m/z* (rel int) 547 (1), 317 (4), 260 (10), 259 (100), 169 (6), 154 (5), 153 (86), 139 (58), 135 (11), 129 (8), 127 (6), 111 (7), 109 (9), 97 (10), 93 (7), 71 (13); HRMS, *m/z* 739.2794 (calcd for $C_{33}H_{48}O_{17}Na$, 739.2789).

*(Z)-1-(5-Methyl-5-vinyltetrahydrofuran-2-yl)-1-methylethyl O-β-D-Glucopyranoside (**8**), Tetraacetate:* ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (3H, s, H-10), 1.22 (3H, s, H-9), 1.27 (3H, s, H-8), 1.79 (2H, m, H-4), 1.85 (2H, m, H-3), 2.00, 2.02, 2.04, 2.06 (12H, 4s, H of acetate CH_3), 3.67 (1H, m, Glc-H-5), 3.74 (1H, t, *J* = 6.4 Hz, H-2), 4.10 (1H, m, Glc-H-6), 4.21 (1H, dd, *J* = 10.6, 12.4 Hz, H-6), 4.85 (1H, d, *J* = 7.7 Hz, Glc-H-1), 4.95 (1H, dd, *J* = 7.7, 9.5 Hz, Glc-H-2), 4.98 (1H, dd, *J* = 1.7, 10.4 Hz, Ha-7), 5.03 (1H, dd, *J* = 9.5, 9.5 Hz, Glc-H-4), 5.18 (1H, dd, *J* = 1.7, 17.0 Hz, Hb-7), 5.21 (1H, dd, *J* = 9.5, 9.5 Hz, Glc-H-3), 5.83 (1H, dd, *J* = 10.4, 17.0 Hz, H-6); GC-EIMS 70 eV, in agreement with literature data (Winterhalter et al., 1990); HRMS, *m/z* 523.2159 (calcd for $C_{24}H_{36}O_{11}Na$, 523.2155).

*3,6,9-Trihydroxymegastigm-7-ene 9-O-β-D-Glucopyranoside (**9**), Pentaacetate:* ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77 (3H, d, *J* = 6.7 Hz, H-13), 0.88 (3H, s, H-12), 1.02 (3H, s, H-11), 1.25 (H-10, multiplicity obscured due to partial overlapping with signals of impurities), 1.48 (3H, m, Ha-2 and H-4), 1.77 (1H, m, Hb-2), 1.96 (1H, m, H-5), 2.00−2.15 (15H, 5s, H of acetate CH_3), 3.61 (1H, ddd, *J* = 2.5, 4.5, 9.6 Hz, Glc-H-5), 4.13 (1H, dd, *J* = 4.5, 12.4 Hz, Glc-H-6), 4.18 (1H, dd, *J* = 2.5, 12.4 Hz, Glc-H-6), 4.25 (1H, m, H-9), 4.55 (1H, d, *J* = 8.0 Hz, Glc-H-1), 4.94 (1H, m, H-3), 4.98 (1H, dd, *J* = 8.0, 9.6 Hz, Glc-H-2), 5.08 (1H, dd, *J* = 9.6, 9.6 Hz, Glc-H-4), 5.18 (1H, dd, *J* = 9.6, 9.6 Hz, Glc-H-3), 5.58 (1H, d, *J* = 15.8 Hz, H-7), 5.73 (1H, dd, *J* = 6.6, 15.8 Hz, H-8); ^{13}C NMR (125 MHz) δ 15.8 (C-13), 20.4−21.2 (acetate CH_3), 24.5 (C-11), 25.1 (C-12), 34.0 (C-5), 34.8 (C-4), 39.5 (C-1), 40.7 (C-2), 62.0 (Glc-C-6), 68.3 (Glc-C-4), 69.9 (C-3), 71.5 (Glc-C-2), 71.8 (Glc-C-5), 73.0 (Glc-C-3), 77.0 (C-6), 77.8 (C-9), 99.5 (Glc-C-1), 131.9 (C-8), 134.7 (C-7), 169.5−171.0 (acetate C=O), C-10 not determined; GC-EIMS 70 eV, *m/z* (rel int) 540 (2), 331 (30), 271 (13), 253 (13), 252 (9), 211 (6), 193 (23), 192 (78), 169 (100), 149 (21), 135 (18), 127 (15), 109 (54), 97 (13), 82 (15); HRMS, *m/z* 623.2678 (calcd for $C_{29}H_{44}O_{13}Na$, 623.2680).

*Phenylmethyl O-β-D-Glucopyranoside (**10**), Tetraacetate:* ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99−2.12 (12H, 4s, H of acetate CH_3), 3.67 (1H, ddd, *J* = 2.3, 4.5, 9.4 Hz, Glc-H-5), 4.16 (1H, dd, *J* = 2.3, 12.2 Hz, Glc-H-6), 4.28 (1H, dd, *J* = 4.5, 12.2 Hz, Glc-H-6), 4.54 (1H, d, *J* = 7.9 Hz, Glc-H-1), 4.62 (1H, d, *J* = 12.4 Hz, H-1), 4.90 (1H, d, *J* = 12.4 Hz, H-1), 5.07 (1H, dd, *J* = 7.9, 9.4 Hz, Glc-H-2), 5.11 (1H, dd, *J* = 9.4, 9.4 Hz, Glc-H-4), 5.16 (1H, dd, *J* = 9.4, 9.4 Hz, Glc-H-3), 7.28 (2H, m, H-2aro and H-6aro), 7.28−7.35 (1H, m, H-4aro), 7.31−7.37 (2H, m, H-3aro and H-5aro); ^{13}C NMR (125 MHz) δ 20.5−21.2 (acetate CH_3), 62.0 (Glc-C-6), 68.0 (Glc-C-4), 70.5 (C-1), 71.1 (Glc-C-2), 71.8 (Glc-C-5), 72.8 (Glc-C-3), 99.0 (Glc-C-1), 127.8 (C-2aro and C-6aro), 128.2 (C-4aro), 128.5 (C-3aro and C-5aro), 136.5 (C-1aro), 169.0−171.0 (acetate C=O); GC-EIMS 70 eV, in agreement with literature data (Williams et al., 1983); HRMS, *m/z* 461.1426 (calcd for $C_{21}H_{26}O_{10}Na$, 461.1424).

*Phenylmethyl O-α-L-Arabinofuranosyl-(1→6)-O-β-D-glucopyranoside (**11**), Hexaacetate:* ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99−2.13 (18H, 6s, H of acetate CH_3), 3.66 (1H, dd, *J* = 1.0, 10.2 Hz, Glc-H-6), 3.68 (1H, m, Glc-H-5), 3.78 (1H, m, Glc-H-6), 4.22 (1H, dd, *J* = 5.8, 11.9 Hz, Ara-Hb-5), 4.30 (1H, ddd, *J* = 3.3, 5.2, 5.8 Hz, Ara-H-4), 4.41 (1H, dd, *J* = 3.3, 11.9 Hz, Ara-Ha-5), 4.53 (1H, d, *J* = 8.0 Hz, Glc-H-1), 4.62 (1H, d, *J* = 12.4 Hz, H-1), 4.87 (1H, d, *J* = 12.4 Hz, H-1), 4.99 (1H, dd, *J* = 1.5, 5.2 Hz, Ara-H-3), 5.02 (1H, dd, *J* = 8.0, 9.5 Hz, Glc-H-2), 5.04 (1H, dd, *J* = 9.5, 9.5 Hz, Glc-H-4), 5.08 (1H, d, *J* = 1.5 Hz, Ara-H-2), 5.10 (1H, s, Ara-H-1), 5.14 (1H, dd, *J* = 9.5, 9.5 Hz, Glc-H-3), 7.26−7.32 (1H, m, H-4aro), 7.28 (2H, m, H-2aro and H-6aro), 7.34 (2H, m, H-3aro and H-5aro); ^{13}C NMR (125 MHz) δ 20.0−21.0 (acetate CH_3), 63.3 (Ara-C-5), 65.8 (Glc-C-6), 69.0 (Glc-C-4), 70.2 (C-1), 71.3 (Glc-C-2), 72.9 (Glc-C-3), 73.1 (Glc-C-5), 77.0 (Ara-C-3), 80.3 (Ara-C-4), 81.2 (Ara-C-2), 99.0 (Glc-C-1), 105.9 (Ara-C-1), 127.8 (C-2aro and C-6aro), 128.0 (C-4aro), 128.2 (C-3aro and C-5aro), 136.8 (C-1aro), 169.6−170.2 (acetate C=O); GC-EIMS 70 eV, in agreement with literature data (Williams et al., 1983); HRMS, *m/z* 677.2067 (calcd for $C_{30}H_{38}O_{16}Na$, 677.2058).

*Phenylmethyl O-β-D-Apiofuranosyl-(1→6)-O-β-D-glucopyranoside (**12**), Hexaacetate:* ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.00−2.15 (18H, 6s, H of acetate CH_3), 3.57 (1H, dd, *J* = 5.5, 11.0 Hz, Glc-H-6), 3.62 (1H, m, Glc-H-5), 3.68 (1H, dd, *J* = 3.0, 11.0 Hz, Glc-H-6), 4.11 (1H, d, *J* = 10.5 Hz, Api-H-4), 4.20 (1H, d, *J* = 10.5 Hz, Api-H-4), 4.51 (1H, d, *J* = 7.9 Hz, Glc-H-1), 4.56 (1H, d, *J* = 12.2 Hz, Api-H-5), 4.57 (1H, d, *J* = 12.3 Hz, H-1), 4.72 (1H, d, *J* = 12.2 Hz, Api-H-5), 4.82 (1H, d, *J* = 12.3 Hz, H-1), 4.90 (1H, dd, *J* = 9.5, 9.5 Hz, Glc-H-4), 4.97 (1H, dd, *J* = 7.9, 9.5 Hz, Glc-H-2), 5.02 (1H, s, Api-H-1), 5.12 (1H, dd, *J* = 9.5, 9.5 Hz, Glc-H-3), 5.32 (1H, s, Api-H-2), 7.28 (2H, m, H-2aro and H-6aro), 7.28−7.34 (1H, m, H-4aro), 7.34 (2H, m, H-3aro and H-5aro); ^{13}C NMR (125 MHz) δ 20.5−21.2 (acetate CH$_3$), 63.2 (Api-C-5), 66.7 (Glc-C-6), 69.3 (Glc-C-4), 70.7 (C-1), 71.4 (Glc-C-2), 72.6 (Api-C-4), 72.8 (Glc-C-3), 73.3 (Glc-C-5), 76.1 (Api-C-2), 84.0 (Api-C-3), 99.3 (Glc-C-1), 106.2 (Api-C-1), 127.8 (C-2aro and C-6aro), 128.0 (C-4aro), 128.2 (C-3aro and C-5aro), 137.0 (C-1aro), 169.1−170.3 (acetate C=O); GC-EIMS 70 eV, *m/z* (rel int) 317 (2), 289 (7), 260 (5), 259 (48), 245 (7), 217 (9), 189 (4), 169 (4), 145 (9), 140 (8), 139 (82), 109 (13), 97 (18), 91 (100); HRMS, *m/z* 677.2070 (calcd for $C_{30}H_{38}O_{16}Na$, 677.2058).

*2-Phenylethyl O-β-D-Apiofuranosyl-(1→6)-O-β-D-glucopyranoside (**13**), Hexaacetate:* ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.00−2.15 (18H, 6s, H of acetate CH$_3$), 2.80 (2H, m, H-2), 3.59 (1H, dd, $J = 6.5$, 11.1 Hz, Glc-H-6), 3.65 (1H, m, Ha-1), 3.67 (1H, m, Glc-H-5), 3.70 (1H, m, Glc-H-6), 4.11 (1H, m, Hb-1), 4.14 (1H, d, $J = 10.7$ Hz, Api-Ha-4), 4.21 (1H, d, $J = 10.7$ Hz, Api-Hb-4), 4.46 (1H, d, $J = 8.0$ Hz, Glc-H-1), 4.56 (1H, d, $J = 12.3$ Hz, Api-Ha-5), 4.74 (1H, d, $J = 12.3$ Hz, Api-Hb-5), 4.92 (1H, dd, $J = 9.5$, 9.5 Hz, Glc-H-4), 4.95 (1H, dd, $J = 8.0$, 9.5 Hz, Glc-H-2), 5.03 (1H, s, Api-H-1), 5.17 (1H, dd, $J = 9.5$, 9.5 Hz, Glc-H-3), 5.33 (1H, s, Api-H-2), 7.19 (2H, m, H-2aro and H-6aro), 7.26−7.30 (signals obscured due to overlapping with residual protons of the solvent, 3H, m, H-3aro, H-4aro and H-5aro); ^{13}C NMR (125 MHz) δ 20.5−21.2 (acetate CH$_3$), 36.0 (C-2), 63.3 (Api-C-5), 66.5 (Glc-C-6), 69.3 (Glc-C-4), 70.5 (C-1), 72.7 (Glc-C-2), 72.7 (Api-C-4), 73.0 (Glc-C-3), 73.3 (Glc-C-5), 76.1 (Api-C-2), 100.7 (Glc-C-1), 106.0 (Api-C-1), 128.2−128.8 (C-3aro, C-4aro and C-5aro), 129.0 (C-2aro and C-6aro), 169.3−170.2 (acetate C=O); GC-EIMS 70 eV, *m/z* (rel int) 317 (2), 289 (2), 260 (7), 259 (100), 217 (12), 169 (5), 145 (4), 139 (77), 127 (7), 109 (4), 105 (81), 104 (31), 97 (7), 91 (7), 65 (2); HRMS, *m/z* 691.2225 (calcd for $C_{31}H_{40}O_{16}Na$, 691.2214).

*Isolariciresinol 4-O-β-D-Glucopyranoside (**14**), Heptaacetate:* ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.00, 2.01, 2.04, 2.07, 2.29, 2.62, 2.62 (21H, 7s, H of acetate CH$_3$), 2.04 (1H, m overlapping with acetate signals, H-8), 2.29 (1H, m overlapping with acetate signals, H-8′), 2.84 (2H, m, H-7′), 3.44 (1H, ddd, $J = 2.4$, 2.7, 9.4 Hz, Glc-H-5), 3.78 (3H, s, CH$_3$−O−C-3′), 3.79 (3H, s, CH$_3$−O−C-3), 3.81 (1H, dd, $J = 2.4$, 12.6 Hz, Glc-H-6), 3.91 (1H, d broad $J = 10.8$ Hz, H-7), 3.98 (1H, dd, $J = 3.4$, 11.6 Hz, H-9′), 4.09 (1H, m, H-9), 4.10 (1H, m, H-9′), 4.16 (1H, dd, $J = 2.7$, 12.6 Hz, Glc-H-6), 4.23 (1H, dd, $J = 4.2$, 11.1 Hz, H-9), 4.52 (1H, m, Glc-H-1), 5.12−5.20 (3H, m, Glc-H-2, Glc-H-3 and Glc-H-4), 6.47 (1H, s broad, H-5′), 6.61 (1H, s broad, H-2′), 6.66 (1H, dd, $J = 1.7$, 8.0 Hz, H-6), 6.71 (1H, d, $J = 1.7$ Hz, H-2), 6.96 (1H, d, $J = 8.0$ Hz, H-5); GC-EIMS 70 eV, *m/z* (rel int) 486 (1), 426 (11), 395 (1), 366 (6), 331 (17), 289 (4), 271 (9), 224 (10), 211 (5), 170 (6), 169 (100), 164 (10), 149 (6), 137 (11), 127 (9), 109 (37), 103 (11), 97 (7); HRMS, *m/z* 839.2776 (calcd for $C_{40}H_{48}O_{18}Na$, 839.2738).

*2-[4-(3-Hydroxypropyl)-2-methoxyphenoxy]propane-1,3-diol (**15**), Triacetate:* ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.93 (2H, m, H-8′), 1.96 (3H, s, CH$_3$ of acetate at C-9′), 1.98 (6H, 2s, CH$_3$ of acetates at C-1 and C-3), 2.63 (2H, t broad, $J = 8.1$ Hz, H-7′), 3.82 (3H, s, H$_3$C−O−C-2′), 4.08 (2H, t broad, $J = 6.6$ Hz, H-9′), 4.43 (4H, d, $J = 5.1$ Hz, H-1 and H-3), 4.49 (1H, q, $J = 5.1$ Hz, H-2), 6.69 (1H, dd, $J = 1.5$, 8.1 Hz, H-5′), 6.71 (1H, d, $J = 1.5$ Hz, H-3′), 6.93 (1H, d, $J = 8.1$ Hz, H-6′); ^{13}C NMR (125 MHz) δ 21.8 (2 × acetate CH$_3$ at C-1 and C-3), 22.2 (acetate CH$_3$ at C-9′), 30.4 (C-8′), 33.1 (C-7′), 57.4 (H$_3$C−O−C-2′), 63.1 (C-1 and C-3), 63.9 (C-9′), 76.1 (C-2), 112.6 (C-3′), 120.5 (C-5′), 120.9 (C-6′), 137.0 (C-4′), 144.8 (C-1′), 150.9 (C-2′), 170.8 (2 × acetate C=O at C-1 and C-3), 171.2 (acetate C=O at C-9′); GC-EIMS 70 eV, *m/z* (rel int) 382 (7), 224 (1), 164 (7), 160 (8), 159 (100), 139 (5), 137 (7), 117 (2), 103 (3), 99 (10), 57 (4); HRMS, *m/z* 405.1526 (calcd for $C_{21}H_{25}O_8Na$, 405.1549).

RESULTS AND DISCUSSION

The investigated compounds **7**−**15** were obtained from the glycosidic extract of the wine according to the procedure described under Materials and Methods. The products were acetylated before their examination by GC-MS and by NMR.

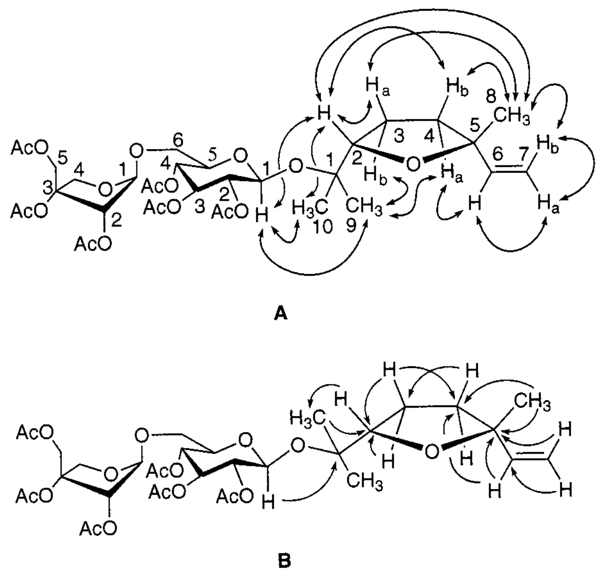


Figure 2. Most relevant NOESY connectivities (A) and HMBC connectivities (B) observed for the aglycon moiety of the peracetylated compound **7**. Configurations shown for the aglycon residue are relative.

***cis*-Furan Linalool Oxide Glycosides 7 and 8.** The CI(NH$_3$) mass spectrum of the nonderivatized diglycoside **7** displays a pseudomolecular $[M + NH_4]^+$ ion at *m/z* 482, whereas the GC-EI mass spectrum of peracetylated **7** shows the typical fragments of a tri-*O*-acetylpentafuranose (*m/z* 259 and 139) and a tri-*O*-acetylhexapyranose (*m/z* 169 and 109) together with ions at *m/z* 153, 111, and 93 arising from the aglycon moiety, all data consistent with the proposed structure. NMR data, including NOESY and HMBC spectra, allowed the nature and the assemblage of the sugars to be determined as a β-D-apiofuranosyl-(1→6)-*O*-β-D-glucopyranoside, as previously described for diglycosides **3**−**6** (Baltenweck-Guyot et al., 1996, 1997). Concerning the aglycon residue, ^{1}H and ^{1}H−^{1}H COSY spectra reveal the presence of three olefinic protons H-6 and H-7 belonging to a vinyl group, of three methyl singlets, and one proton H-2 coupling with two geminal protons H-3, which in turn are coupled with the protons H-4. These data support the structure of a linalyl furanic oxide moiety. This proposal was fully confirmed by analysis of the connectivity networks of NOESY and HMBC spectra (Figure 2), allowing in particular the glycosidic linkage and the cis configuration of the aglycon to be determined. Consequently, the structure of **7** was established as being *cis*-1-(5-ethenyl-5-methyltetrahydrofuran-2-yl)-1-methylethyl O-β-D-apiofuranosyl-(1→6)-*O*-β-D-glucopyranoside. Chemical shift values of the aglycon are in agreement with those obtained by Strauss et al. (1987) for an arabinosyl-glucoside of *cis*-furan linalool oxide isolated from a Riesling grape juice. Although Baumes et al. (1993) have reported the isolation from grape of a mixture of the cis and trans isomers bound to the apiosyl-glucosyl residue, we nevertheless present here the first unambiguous characterization of compound **7** in a wine. In a similar manner, from both MS and NMR (^{1}H−^{1}H COSY and NOESY) studies, the structure of **8** was elucidated as being the β-D-glucopyranoside of *cis*-furan linalool oxide. This compound was previously identified by Winterhalter et al. (1990) in a Riesling wine. We report here its detailed ^{1}H NMR data.

Norisoprenoid glycoside 9. Mass spectral, ^{1}H NMR, and 2D NMR data for the derivatized component

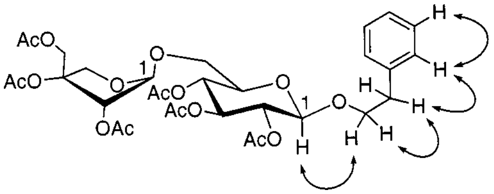


Figure 3. Most relevant NOESY connectivities observed for the aglycon moiety of the peracetylated compound **13**.

9 allowed its structure to be established as the (*E*)-3,6,9-trihydroxymegastigm-7-ene 9-*O*-*β*-D-glucopyranoside, already characterized by Lutz et al. (1993) from starfruit and by Otsuka et al. (1994) from leaves of *Alangium premnifolium*. The relative configurations at C-3, C-5, and C-6 shown in Figure 1 follow from NOE effects observed between H-11 and protons H-3, H-5, and H-7. As for megastigmane derivatives **1**−**4**, the configuration at C-9 remains undetermined. This glucoside has not been previously reported as a constituent of grape or wine, although the free aglycon was characterized in glycoside hydrolysates of various grape cultivars (Sefton et al., 1996).

Benzyl Alcohol and Phenylethanol Glycosides 10−**13.** The peracetylated components **10**−**12**, identified by mass spectral and NMR studies as benzyl alcohol glycosides, were previously characterized in various wines and grapes. Thus, the benzyl *O*-*β*-D-glucopyranoside **10** was isolated from Riesling and Muscat of Alexandria grapes by Williams et al. (1983), the benzyl *O*-α-L-arabinofuranosyl-(1→6)-*O*-*β*-D-glucopyranoside **11** was found by Williams et al. (1983) in the same grape varieties and by Voirin et al. (1992a,b) in Muscat of Alexandria, Muscat Frontignan, Muscat Hambourg, Muscat Ottonel, and Gewurztraminer grapes, and the apiosyl glucoside **12** was identified in a Muscat Frontignan grape by Baumes et al. (1993). Except for H-1 and H-2 of the apiose moiety, the assignments of which should be reversed on the basis of the NOESY, HMBC, and HSQC correlations observed, NMR data of **12** are very similar to that of the compound obtained by synthesis by Suzuki et al. (1988) and Mbaïraroua et al. (1994). The GC-EI mass spectrum of the diglycoside **13** comprises, in addition to the usual fragments corresponding to an apiosyl- or arabinosyl-glucoside, ions at *m*/*z* 91 and 105, which may arise from a phenylethyl unit. The pseudomolecular $[M + NH_4]^+$ ion at *m*/*z* 434 obtained by CIMS further supports the hypothesis of such a diglycoside of phenylethanol. NMR spectra of the peracetylated compound **13** reveal the presence of the same sugar moiety as for the diglycoside **12**, that is, a peracetyl *β*-D-apiofuranosyl-*β*-D-glucopyranoside, and for the aglycon part, a 2-phenylethyl unit linked at C-1 to the sugars, as shown in particular by NOE effects observed (Figure 3). Hence, the structure of **13** is that of the 2-phenylethyl *O*-*β*-D-apiofuranosyl-(1→6)-*O*-*β*-D-glucopyranoside. Again except for H-1 and H-2 of the apiose moiety, our NMR data are similar to those of Mbaïrouara et al. (1994) for the same compound obtained by a synthetic way. However, it is the first time that the glycoside **13** has been identified in a wine, although several authors have attempted to characterize it, especially by MS (Voirin et al., 1992b).

Isolariciresinol 4-*O*-*β*-D-Glucopyranoside 14. ^1H NMR data of the peracetylated compound **14** (Figure 4) are similar to those of peracetylated isolariciresinol 4-*O*-*β*-D-glucopyranoside already identified by Marinos et al. (1992) in a Riesling wine. Assignment of H-2′ and H-5′ chemical shifts, obtained in our case on the basis of NOE effects, should, however, be reversed.

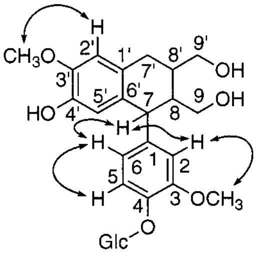
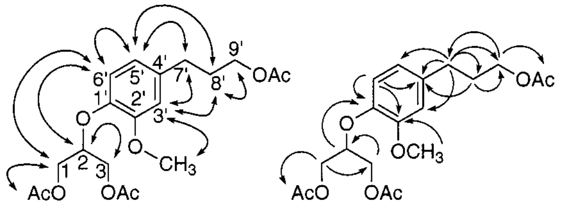


Figure 4. Most relevant NOESY connectivities observed for the aglycon moiety of the peracetylated compound **14**.



A B

Figure 5. Most relevant NOESY connectivities (A) and HMBC connectivities (B) observed for the peracetylated compound **15**.

Phenylpropanoid Glycerol 15. The CIMS (NH_3) of the nonderivatized compound **15** shows a pseudomolecular $[M + NH_4]^+$ ion at *m*/*z* 274, shifted to *m*/*z* 400 for its peracetylated counterpart, which indicates the presence of three derivatizable groups. The GC-EI mass spectrum of acetylated **15** displays, besides the molecular ion $M^+ = 382$, a major fragment at *m*/*z* 159 $[(AcOCH_2)_2C]^+$ and ions at *m*/*z* 175 $[AcOCH_2)_2CH - O]^+$, 117 $[159 - CH_2CO]^+$, and 99 $[159 - CH_3COOH]^+$, which can be issued from a diacetyl glyceryl unit. Additional ions at *m*/*z* 224 $[M - (AcOCH_2)_2C]^+$ and 164 $[224 - CH_3COOH]^+$ clearly arise from the second part of the molecule, which bears one acetylated hydroxyl group, as confirmed by MS/MS studies showing that fragments at *m*/*z* 224 and 159 belong to two different subunits of **15**. ^1H and $^1H-^1H$ COSY NMR spectra exhibit downfield signals of three aromatic protons, two of which are vicinal, at δ 6.69 ($J = 1.5$, 8.1 Hz, H-5′), 6.71 ($J = 1.5$ Hz, H-3′), and 6.93 ($J = 8.1$ Hz, H-6′), thus indicating the presence of a trisubstituted aromatic ring. These spectra also include a methyl singlet at δ 3.82 ascribable to a methoxy group, a proton quintuplet at δ 4.49 (H-2) coupled with four protons appearing as a doublet at δ 4.33 (H-1 and H-3), these five protons characteristic of an acetylated glycerol subunit linked by its C-2 hydroxy group, and a sequence of three methylene groups at δ 4.08 (H-9′), 2.83 (H-7′), and 1.93 (H-8′) typical of a phenylpropanol side chain. The arrangement of these three substituent groups on the aromatic ring easily follows from the NOESY and HMBC spectra correlations as pictured in Figure 5. Thus, the structure of compound **15** was identified as 2-[4-(3-hydroxypropyl)-2-methoxyphenoxy]propane-1,3-diol. Our NMR data are in good agreement with those obtained by Marinos et al. (1992) for the glucosidic derivative of **15** isolated by these authors from a Riesling wine. However, the free aglycon **15**, which has a marked butter and caramel smell as also noted by Marinos et al. (1992), has not been previously reported as a wine component.

Besides glycosides **1**−**6** previously characterized in an Alsatian Gewurztraminer wine, we have reported here the unambiguous identification, based on MS and 2D-NMR data, of nine additional compounds isolated from the same wine. Four of them are reported for the first time as wine components, and most of the others, the NMR data of which have been revised or made more precise, have not been recorded before from the Gewurztraminer cultivar. A more extensive study of glycosides of Gewurztraminer and other Alsatian white wines, with regard to their role as aroma precursors and their use as markers of wine variety, is under way and will be reported later.

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