(*S*)-3,7-Dimethyl-5-octene-1,7-diol and Related Oxygenated Monoterpenoids from Petals of *Rosa damascena* Mill.

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The methanolic extract obtained from rose flowers was subjected to XAD-2 adsorption chromatography. Prefractionation of the methanolic eluate using multilayer coil countercurrent chromatography (MLCCC) yielded five subfractions. From the least polar subfraction V, a major amount of the key odorants of rose oil, that is, isomeric rose oxides **1a/b**, was liberated upon heat treatment at pH 2.5. Further chromatographic workup of fraction V led, for the first time, to the identification of the genuine rose oxide precursor (*S*)-3,7-dimethyl-5-octene-1,7-diol (**2**). In addition to diol **2**, the following monoterpene diols have been identified: 3,7-dimethyl-7-octene-1,6-diol (**3**), 2,6-dimethyl-1,7-octadiene-3,6-diol (**4**), (2*E*,5*E*)-3,7-dimethyl-2,5-octadiene-1,7-diol (**5**), (2*E*)-3,7-dimethyl-2,7-octadiene-1,6-diol (**6**), (2*Z*,5*E*)-3,7-dimethyl-2,5-octadiene-1,7-diol (**7**), (2*Z*)-3,7-dimethyl-2,7-octadiene-1,6-diol (**8**), (*Z*)-2,6-dimethyl-2-octene-1,8-diol (**9**), (*E*)-2,6-dimethyl-2-octene-1,8-diol (**10**), (*Z*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**11**), (*E*)-2,6-dimethyl-2,7-octadiene-1,6-diol (**12**), (2*E*,6*E*)-2,6-dimethyl-2,6-octadiene-1,8-diol (**13**), (2*E*,6*Z*)-2,6-dimethyl-2,6-octadiene-1,8-diol (**14**), 2,6-dimethyloctane-1,8-diol (**15**), 2,6-dimethyl-7-octene-1,6-diol (**16**), (*E*)-3,7-dimethyl-2-octene-1,8-diol (**17**), (*Z*)-3,7-dimethyl-2-octene-1,8-diol (**18**), 3,7-dimethyloctane-1,7-diol (**19**), 2,6-dimethyl-7-octene-2,6-diol (**20**), 3,7-dimethyl-6-octene-1,3-diol (**21**) and (2*E*)-3,7-dimethyl-2,6-octadiene-1,4-diol (**22**).

Keywords: *(S)-3,7-Dimethyl-5-octene-1,7-diol; monoterpene diols; rose oxides; aroma precursors; multilayer coil countercurrent chromatography; rose petals; Rosa damascena Mill.*

INTRODUCTION

The C_{13}-norisoprenoid ketone, β-damascenone, and the isomeric monoterpene ethers, rose oxides **1a/b**, are major aroma contributors of Bulgarian rose oil (Ohloff and Demole, 1987, and references cited therein). Recent results of Surburg et al. (1993) have indicated the presence of labile precursors for both of the above-mentioned key aroma compounds in rose petals. By using a gentle isolation technique, that is, vacuum headspace concentration, the authors reported that neither β-damascenone nor the isomeric rose oxides **1a/b** could be detected in the aroma isolate of rose flowers. Consequently, both aroma compounds appear to be rearrangement products that are formed during the steam distillation process from extremely labile progenitors. Whereas in a most recent study (Straubinger et al., 1997a) an immediate precursor of β-damascenone has been isolated from rose flowers, the formation of isomeric rose oxides **1a/b** remained obscure.

In this paper, we report the isolation and structural elucidation of the labile monoterpene diol **2**, which was found to be the major genuine precursor for isomeric rose oxides **1a/b** in rose flowers.

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EXPERIMENTAL PROCEDURES

Plant Material. Rose flowers (*Rosa damascena* Mill.) were harvested at their full bloom stage in the Shizuoka prefecture, Japan.

Extraction of Rose Flowers and Preparation of an XAD-2 Extract. Rose flowers (10 kg) were homogenized in ice-cooled 80% aqueous MeOH. After filtration, the organic solvent was concentrated in vacuo. Freeze-drying of the aqueous residue yielded 206 g of a crude extract. This extract was subjected to XAD-2 column chromatography (700 × 55 mm i.d., 1 kg XAD) in portions of 26 g (Günata et al., 1985). The column was rinsed with water. Subsequent elution of the retained material with MeOH and concentration under reduced pressure yielded ≈40 g of an aroma precursor concentrate.

Multilayer Coil Countercurrent Chromatography (MLCCC) Separation. For the initial fractionation of the residue, MLCCC (Ito, 1986) was used (multilayer coil separator−extractor, P. C. Inc., Potomac, MD; equipped with an 85 m × 2.6 mm i.d. PTFE tubing; solvent system of $CHCl_3$/MeOH/H_2O 7:13:8; injection volume of 2.5 g of extract dissolved in 5 mL of aqueous phase). To facilitate the screening of aroma precursors, sequential MLCCC fractions were pooled into five groups, that is, combined MLCCC fractions I−V.

Isolation of Polyols 2, 12, 13, and 21. A screening of fractions I−V for rose oxide generating progenitors was carried out by acid hydrolysis (SDE, pH 2.5, 1 h). The generated compounds from these hydrolyses were then determined by GC/MS. The diethyl ether extract of fraction V was further separated by MLCCC (*n*-BuOH/MeOH/H_2O 10:1:10), and the major compounds were finally purified by flash chromatography and normal phase HPLC using hexane/MTBE gradients (Straubinger et al., 1997b).

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Spectral Data for Isolated Monoterpene Diols 2, 12, 13, and 21. ***2***: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.89 (3H, d, J = 6.5 Hz, Me-C3), 1.30 (6H, s, 2Me-C7), 1.35 (1H, m, $H2_a$), 1.59 (1H, m, $H2_b$), 1.67 (1H, m, H3), 1.91 (1H, m, $H4_a$), 2.01 (1H, m, $H4_b$), 3.60 (1H, ddd, J = 12.0, 7.0, 2.0 Hz, $H1_a$), 3.67 (1H, ddd, J = 12.0, 7.0, 3.0 Hz, $H1_b$), 5.56 (1H, ddd, J = 15.0, 5.5, 1.0 Hz, H5), 5.61 (1H, d, J = 15.0 Hz, H6); ^{13}C NMR (91 MHz, $CDCl_3$) δ 19.5 (Me-C3), 29.6 (2Me-C7), 29.7 (C3), 38.9 (C2), 39.5 (C4), 60.5 (C1), 70.5 (C7), 125.1 (C5), 139.4 (C6).

12: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.30 (3H, s, Me-C6), 1.59 (2H, m, H_25), 1.65 (3H, d, J = 1.0 Hz, Me-C2), 2.08 (2H, m, H_24), 3.98 (2H, s, H_21), 5.07 (1H, dd, J = 11.0, 1.5 Hz, $H8_a$), 5.22 (1H, dd, J = 17.5, 1.5 Hz, $H8_b$), 5.41 (1H, tq, J = 7.0, 1.0 Hz, H3), 5.91 (1H, dd, J = 17.5, 11.0 Hz, H7); ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.6 (Me-C2), 22.3 (C4), 27.8 (Me-C6), 41.7 (C5), 68.7 (C1), 73.3 (C6), 111.8 (C8), 125.8 (C3), 135.9 (C2), 144.8 (C7).

13: R_i (DB-Wax) 2635; R_i (DB-5) 1522; UV (MeOH) λ_{max} 209 nm; IR (NaCl) ν (cm^{-1}) 3336 (OH), 2965, 2919, 2861, 1669 (C=C), 1442, 1384, 1236, 1065, 1007, 843 (>C=CH−); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.64 (3H, d, J = 1.0 Hz, Me-C2), 1.66 (3H, d, J = 1.0 Hz, Me-C6), 2.02−2.23 (4H, m, H_24, H_25), 2.88 (2H, br s, OH), 3.95 (2H, s, H_21), 4.11 (2H, d, J = 7.0 Hz, H_28), 5.37 (1H, tq, J = 7.0, 1.0 Hz, H3), 5.38 (1H, tq, J = 7.0, 1.0 Hz, H7); ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.6 (Me-C2), 16.0 (Me-C6), 25.4 (C4), 38.9 (C5), 58.9 (C8), 68.3 (C1), 123.8 (C7), 125.0 (C3), 134.9 (C2), 138.3 (C6).

21: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.26 (3H, s, Me-C3), 1.56 (2H, m, H_24), 1.63 (3H, d, J = 1.0 Hz, Me-C7), 1.67 (1H, ddd, J = 14.5, 6.5, 4.5 Hz, $H2_a$), 1.69 (3H, d, J = 1.0 Hz, Me-C7), 1.81 (1H, ddd, J = 14.5, 7.5, 4.5 Hz, $H2_b$), 2.06 (2H, m, H_25), 3.86 (1H, ddd, J = 11.0, 6.5, 4.5 Hz, $H1_a$), 3.92 (1H, ddd, J = 11.0, 7.5, 4.5 Hz, $H1_b$), 5.15 (1H, tqq, J = 7.0, 1.0, 1.0 Hz, H6); ^{13}C NMR (91 MHz, $CDCl_3$) δ 17.7 (Me-C7), 22.7 (C5), 25.7 (Me-C7), 26.7 (Me-C3), 41.7 (C2), 42.4 (C4), 59.9 (C1), 74.0 (C3), 124.1 (C6), 132.1 (C7).

GC/MS Identification of Minor Constituents. The diols **3**−**11** and **14**−**20** were identified by GC/MS analyses through comparison with authentic reference compounds (Winterhalter et al., 1998). Compounds **2**−**12** and **14**−**21** were prepared according to published procedures. Diol **22** was donated, and diol **13** was commercially obtained (Aldrich, Steinheim, Germany).

Preparation of Reference Compounds. *(i) Photooxidation (Tietze and Eicher, 1981).* A solution of 0.5 g of the monoterpene alcohol and 70 mg of Rose Bengal in MeOH (25 mL) was irradiated with an UV lamp at 25 °C in an oxygen atmosphere (10 h). Na_2SO_3 reduction (25 °C, 1 h), filtration, evaporation of the solvent in vacuo and flash chromatographic purification yielded the diols **2**−**8**.

*(3S)-(E)-3,7-Dimethyl-5-octene-1,7-diol (**2**) and (3S,6RS)-3,7-Dimethyl-7-octene-1,6-diol (**3**) from (S)-(−)-Citronellol.* ***2***: R_i (DB-Wax) 2220; R_i (DB-5) 1346; UV (MeOH) λ_{max} 203 nm; IR (NaCl) ν (cm^{-1}) 3358 (OH), 2969, 2927, 1459, 1377, 1232, 1152, 1058, 972 (C=C, trans); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.89 (3H, d, J = 6.5 Hz, Me-C3), 1.30 (6H, s, 2Me-C7), 1.35 (1H, m, $H2_a$), 1.59 (1H, m, $H2_b$), 1.67 (1H, m, H3), 1.91 (1H, m, $H4_a$), 2.01 (1H, m, $H4_b$), 2.60 (1H, br s, OH), 2.87 (1H, br s, OH), 3.60 (1H, ddd, J = 12.0, 7.0, 2.0 Hz, $H1_a$), 3.67 (1H, ddd, J = 12.0, 7.0, 3.0 Hz, $H1_b$), 5.56 (1H, ddd, J = 15.0, 5.5, 1.0 Hz, H5), 5.61 (1H, d, J = 15.0 Hz, H6); ^{13}C NMR (91 MHz, $CDCl_3$) δ 19.5 (Me-C3), 29.6 (2Me-C7), 29.7 (C3), 38.9 (C2), 39.5 (C4), 60.5 (C1), 70.5 (C7), 125.1 (C5), 139.4 (C6). ***3***: R_i (DB-Wax) 2369; R_i (DB-5) 1414; UV (MeOH) λ_{max} 203 nm; IR (NaCl) ν (cm^{-1}) 3355 (OH), 2934, 2871, 1650 (C=C), 1451, 1377, 1108, 1059, 898 (>C=CH$_2$); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.91 (3H, d, J = 6.0 Hz, Me-C3), 1.24−1.63 (7H, m, H_22, H3, H_24, H_25), 1.72 (3H, s, Me-C7), 3.64 (1H, ddd, J = 11.0, 7.5, 2.5 Hz, $H1_a$), 3.71 (1H, ddd, J = 11.0, 7.0, 2.5 Hz, $H1_b$), 4.03 (1H, t, J = 6.5 Hz, H6), 4.82 (1H, d, J = 1.0 Hz, $H8_a$), 4.92 (1H, d, J = 1.0 Hz, $H8_b$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.4/17.5 (Me-C7), 19.6 (Me-C3), 29.3/29.5 (C3), 32.2 (C5), 32.6/32.7 (C4), 39.8 (C2), 61.0 (C1), 76.0/76.3 (C6), 110.9/111.1 (C8), 147.5/147.6 (C7).

*(3RS,6RS)-2,6-Dimethyl-1,7-octadiene-3,6-diol (**4**) from (±)-Linalool*: R_i (DB-Wax) 2135; R_i (DB-5) 1277; UV (MeOH) λ_{max} 203, 225, 271 nm; IR (NaCl) ν (cm^{-1}) 3375 (OH), 3087, 2973, 2949, 1651, 1449, 1412, 1372, 1151, 1115, 1058, 997, 920 (−CH=CH$_2$), 900 (>C=CH$_2$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.28 (3H, s, Me-C6), 1.61 (4H, m, H_24, H_25), 1.71 (3H, d, J = 1.0 Hz, Me-C2), 4.03 (1H, tdd, J = 5.0, 1.0, 1.0 Hz, H3), 4.82 (1H, dd, J = 1.5, 1.0, Hz, $H1_a$), 4.94 (1H, ddq, J = 1.5, 1.0, 1.0 Hz, $H1_b$), 5.04 (1H, dd, J = 11.0, 1.5 Hz, $H8_a$), 5.21 (1H, dd, J = 18.0, 1.5 Hz, $H8_b$), 5.88 (1H, dd, J = 18.0, 11.0 Hz, H7); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.7/17.8 (Me-C2), 27.8/28.2 (Me-C6), 29.1/29.3 (C4), 37.6/38.2 (C5), 72.9 (C6), 75.5/76.0 (C3), 110.8 (C1), 111.7/111.9 (C8), 144.8/145.0 (C7), 147.3/147.5 (C2).

*(2E,5E)-3,7-Dimethyl-2,5-octadiene-1,7-diol (**5**) and (6RS)-(E)-3,7-Dimethyl-2,7-octadiene-1,6-diol (**6**) from Geraniol.* ***5***: R_i (DB-Wax) 2345; R_i (DB-5) 1388; UV (MeOH) λ_{max} 204, 237 nm; IR (NaCl) ν (cm^{-1}) 3357 (OH), 2973, 2928, 1665 (C=C), 1440, 1378, 1233, 1150, 1094, 1045, 974 (C=C trans), 846 (>C=CH−); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.31 (6H, s, 2Me-C7), 1.65 (3H, d, J = 1.0 Hz, Me-C3), 2.71 (2H, d, J = 6.0 Hz, H_24), 4.14 (2H, d, J = 7.0 Hz, H_21), 5.41 (1H, tq, J = 7.0, 1.0 Hz, H2), 5.58 (1H, dt, J = 16.0, 6.0 Hz, H5), 5.65 (1H, d, J = 16.0 Hz, H6); ^{13}C NMR (63 MHz, $CDCl_3$) δ 16.3 (Me-C3), 29.6 (2Me-C7), 42.0 (C4), 59.1 (C1), 70.6 (C7), 124.2 (C2), 124.2 (C5), 137.4 (C3), 139.9 (C6). ***6***: R_i (DB-Wax) 2472; R_i (DB-5) 1437; UV (MeOH) λ_{max} 208 nm; IR (NaCl) ν (cm^{-1}) 3341 (OH), 3074, 2971, 2941, 1668 and 1651 (C=C), 1444, 1381, 1308, 1239, 1181, 1100, 1062, 1002, 899 (>C=CH$_2$), 756; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.58 (2H, m, H_25), 1.59 (3H, d, J = 1.0 Hz, Me-C3), 1.65 (3H, d, J = 1.0 Hz, Me-C7), 1.98 (2H, m, H_24), 3.95 (1H, td, J = 6.5, 1.0 Hz, H6), 4.04 (2H, d, J = 7.0 Hz, H_21), 4.76 (1H, dd, J = 1.5, 1.0 Hz, $H8_a$), 4.86 (1H, dq, J = 1.5, 1.0 Hz, $H8_b$), 5.34 (1H, tq, J = 7.0, 1.0 Hz, H2); ^{13}C NMR (63 MHz, $CDCl_3$) δ 16.0 (Me-C3), 17.4 (Me-C7), 32.6 (C5), 35.3 (C4), 58.8 (C1), 75.0 (C6), 110.8 (C8), 123.6 (C2), 138.5 (C3), 147.2 (C7).

*(2Z,5E)-3,7-Dimethyl-2,5-octadiene-1,7-diol (**7**) and (6RS)-(Z)-3,7-Dimethyl-2,7-octadiene-1,6-diol (**8**) from Nerol.* ***7***: R_i (DB-Wax) 2287; R_i (DB-5) 1355; UV (MeOH) λ_{max} 207, 236 nm; IR (NaCl) ν (cm^{-1}) 3357 (OH), 2971, 2929, 1665 (C=C), 1441, 1376, 1234, 1151, 1090, 1050, 972 (C=C trans), 895; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.31 (6H, s, 2Me-C7), 1.73 (3H, dt, J = 1.0, 1.0 Hz, Me-C3), 2.79 (2H, d, J = 6.0 Hz, H_24), 4.14 (2H, dd, J = 7.0, 1.0 Hz, H_21), 5.49 (1H, tq, J = 7.0, 1.0 Hz, H2), 5.55 (1H, dt, J = 15.0, 6.0 Hz, H5), 5.66 (1H, d, J = 15.0 Hz, H6); ^{13}C NMR (63 MHz, $CDCl_3$) δ 23.5 (Me-C3), 29.8 (2Me-C7), 34.8 (C4), 59.1 (C1), 70.6 (C7), 124.2 (C2/6), 124.9 (C2/6), 138.3 (C3), 139.3 (C5). ***8***: R_i (DB-Wax) 2423; R_i (DB-5) 1415; UV (MeOH) λ_{max} 203 nm; IR (NaCl) ν (cm^{-1}) 3349 (OH), 2969, 2937, 2872, 1652 (C=C), 1445, 1377, 1322, 1150, 1100, 1053, 997, 900 (>C=CH$_2$), 837 (>C=CH−); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.58 (1H, dddd, J = 12.5, 9.0, 8.0, 5.0 Hz, $H5_a$), 1.66 (1H, dddd, J = 12.5, 8.5, 8.0, 4.0 Hz, $H5_b$), 1.69 (3H, s, Me-C7), 1.70 (3H, d, J = 1.0 Hz, Me-C3), 2.02 (1H, ddd, J = 13.5, 8.0, 5.0 Hz, $H4_a$), 2.34 (1H, ddd, J = 13.5, 8.5, 8.0 Hz, $H4_b$), 3.94 (1H, ddd, J = 9.0, 4.0, 1.0 Hz, H6), 3.98 (1H, dd, J = 12.5, 7.0 Hz, $H1_a$), 4.14 (1H, dd, J = 12.5, 7.0 Hz, $H1_b$), 4.79 (1H, dd, J = 1.5, 1.0 Hz, $H8_a$), 4.91 (1H, d, J = 1.5 Hz, $H8_b$), 5.49 (1H, ddq, J = 7.0, 7.0, 1.0 Hz, H2); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.9 (Me-C7), 22.9 (Me-C3), 27.4 (C4), 32.7 (C5), 58.1 (C1), 73.9 (C6), 110.5 (C8), 124.6 (C2), 140.0 (C3), 147.5 (C7).

*(ii) Preparation of (3RS)-(Z)-2,6-Dimethyl-2-octene-1,8-diol (**9**) from Isopulegol (Waddell and Ross, 1987):* R_i (DB-Wax) 2382; R_i (DB-5) 1482; UV (MeOH) λ_{max} 202 nm; IR (NaCl) ν (cm^{-1}) 3333 (OH), 2951, 2924, 1455, 1052, 846 (>C=CH−); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.85 (3H, d, J = 6.5 Hz, Me-C6), 1.25−1.70 (5H, m, H_25, H6, H_27), 1.74 (3H, d, J = 1.0 Hz, Me-C2), 2.09 (2H, m, H_24), 3.43 (1H, ddd, J = 10.0, 6.5, 3.0 Hz, $H8_a$), 3.48 (1H, ddd, J = 10.0, 6.0, 3.5 Hz, $H8_b$), 4.10 (2H, d, J = 1.0 Hz, H_21), 5.21 (1H, ttq, J = 7.0, 1.0, 1.0 Hz, H3); ^{13}C NMR (91 MHz, $CDCl_3$) δ 19.6 (Me-C6), 21.2 (Me-C2), 24.8 (C4), 28.3 (C6), 37.0 (C5), 38.9 (C7), 60.4 (C8), 60.9 (C1), 128.3 (C3), 134.2 (C2).

(iii) ω-Hydroxylation. Synthesis of diols **10**−**12** and **14** was accomplished by SeO_2 oxidation of the monoterpene alcohols, followed by $LiAlH_4$ reduction of the resulting aldehyde and liquid chromatographic purification (Behr et al., 1978).

(6RS)-(E)-2,6-Dimethyl-2-octene-1,8-diol (***10***) *from (±)-Citronellol*: R_i (DB-Wax) 2550; R_i (DB-5) 1496; UV (MeOH) λ_{max} 203 nm; IR (NaCl) ν (cm^{-1}) 3408 (OH), 2959, 2924, 1644 (C═C), 1455, 1377, 1057, 1011, 835 (>C═CH−); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.92 (3H, d, J = 6.5 Hz, Me-C6), 1.18−1.70 (5H, m, $H_2$5, H6, $H_2$7), 1.67 (3H, br s, Me-C2), 2.06 (2H, m, $H_2$4), 3.68 (1H, ddd, J = 10.5, 6.5, 3.0 Hz, $H8_a$), 3.69 (1H, ddd, J = 10.5, 6.0, 3.5 Hz, $H8_b$), 4.00 (2H, s, $H_2$1), 5.40 (1H, tq, J = 7.0, 1.0 Hz, H3); ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.6 (Me-C2), 19.5 (Me-C6), 25.0 (C4), 29.1 (C6), 36.7 (C5), 39.8 (C7), 61.1 (C8), 69.0 (C1), 126.4 (C3), 134.6 (C2).

(6RS)-(Z)-2,6-Dimethyl-2,7-octadiene-1,6-diol (***11***) *and (6RS)-(E)-2,6-Dimethyl-2,7-octadiene-1,6-diol* (***12***) *from (±)-Linalyl Acetate.* ***11***: R_i (DB-Wax) 2254; R_i (DB-5) 1346; UV (MeOH) λ_{max} 205 nm; IR (NaCl) ν (cm^{-1}) 3357, 3087, 2969, 2925, 1718, 1160, 999 and 918 (−CH═CH_2), 816 (>C═CH−); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.29 (3H, s, Me-C6), 1.59 (2H, m, $H_2$5), 1.79 (3H, d, J = 1.0 Hz, Me-C2), 2.12 (2H, m, $H_2$4), 4.12 (2H, d, J = 1.0 Hz, $H_2$1), 5.07 (1H, dd, J = 11.0, 1.5 Hz, H_{8a}), 5.22 (1H, dd, J = 17.0, 1.5 Hz, H_{8b}), 5.31 (1H, ttq, J = 7.5, 1.0, 1.0 Hz, H3), 5.91 (1H, dd, J = 17.0, 11.0 Hz, H7); ^{13}C NMR (91 MHz, $CDCl_3$) δ 21.4 (Me-C2), 22.4 (C4), 28.1 (Me-C6), 42.1 (C5), 61.6 (C1), 73.5 (C6), 111.9 (C8), 128.5 (C3), 134.6 (C2), 144.9 (C7). ***12***: R_i (DB-Wax) 2324; R_i (DB-5) 1362; UV (MeOH) λ_{max} 203, 222 nm; IR (NaCl) ν (cm^{-1}) 3357 (OH), 3087, 2972, 2925, 1641 (C═C), 1454, 1412, 1371, 1159, 1114, 1079, 1065, 1001 and 921 (−CH═CH_2), 851, 808 (>C═CH−); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.30 (3H, s, Me-C6), 1.59 (2H, m, $H_2$5), 1.65 (3H, d, J = 1.0 Hz, Me-C2), 2.08 (2H, m, $H_2$4), 3.98 (2H, s, $H_2$1), 5.07 (1H, dd, J = 11.0, 1.5 Hz, $H8_a$), 5.22 (1H, dd, J = 17.5, 1.5 Hz, $H8_b$), 5.41 (1H, tq, J = 7.0, 1.0 Hz, H3), 5.91 (1H, dd, J = 17.5, 11.0 Hz, H7); ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.6 (Me-C2), 22.3 (C4), 27.8 (Me-C6), 41.7 (C5), 68.7 (C1), 73.3 (C6), 111.8 (C8), 125.8 (C3), 135.0 (C2), 144.8 (C7).

(2E,6Z)-2,6-Dimethyl-2,6-octadiene-1,8-diol (***14***) *from Nerol:* R_i (DB-Wax) 2597; R_i (DB-5) 1503; UV (MeOH) λ_{max} 203 nm; IR (NaCl) ν (cm^{-1}) 3904 (OH), 2965, 2918, 1668, 1445, 1377, 1053 (C−O prim.), 1006, 839 (>C═CH−); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.64 (3H, d, J = 1.0 Hz, Me-C2), 1.75 (3H, d, J = 1.0 Hz, Me-C6), 2.15 (4H, m, $H_2$4, $H_2$5), 3.97 (2H, s, $H_2$1), 4.06 (2H, d, J = 7.5 Hz, $H_2$8), 5.40 (1H, m, H3), 5.42 (1H, tq, J = 7.5, 1.0 Hz, H7); ^{13}C NMR (63 MHz, $CDCl_3$) δ 13.7 (Me-C2), 23.2 (Me-C6), 25.2 (C4), 31.3 (C5), 58.8 (C8), 68.4 (C1), 124.8 (C2), 124.9 (C6), 135.6 (C7), 138.3 (C3).

(iv) Preparation of Diols **15**−**18** *Using Baker's Yeast Reduction of SeO_2 Oxidation Products according to the Method of Gramatica et al. (1985). Preparation of (2RS,6RS)-2,6-Dimethyloctane-1,8-diol* (***15***) *from (RS)-2,6-Dimethyl-2-octenal:* R_i (DB-Wax) 2455; R_i (DB-5) 1468; UV (MeOH) λ_{max} 203 nm; IR (NaCl) ν (cm^{-1}) 3336 (OH), 2952, 2926, 1462, 1378, 1122, 1054, 906, 847; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.90 (3H, d, J = 6.5 Hz, Me-C6), 0.92 (3H, d, J = 6.5 Hz, Me-C2), 1.03−1.70 (10H, m, H2, $H_2$3, $H_2$4, $H_2$5, H6, $H_2$7), 3.41 (1H, dd, J = 10.5, 6.0 Hz, $H1_a$), 3.51 (1H, dd, J = 10.5, 6.0 Hz, $H1_b$), 3.64 (1H, ddd, J = 10.5, 6.5, 6.5 Hz, $H8_a$), 3.70 (1H, ddd, J = 10.5, 7.0, 7.0 Hz, $H8_b$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 16.5/16.6 (Me-C2), 19.6/19.7 (Me-C6), 24.2 (C4), 29.3/29.4 (C6), 33.2/33.3 (C3), 35.7/35.7 (C2), 37.2/37.3 (C5), 39.8/39.9 (C7), 61.1 (C8), 68.3 (C1).

(2RS,6RS)-2,6-Dimethyl-7-octene-1,6-diol (***16***) *from (RS)-6-Acetoxy-2,6-dimethylocta-2,7-dienal:* R_i (DB-Wax) 2227; R_i (DB-5) 1346; UV (MeOH) λ_{max} 204 nm; IR (NaCl) ν (cm^{-1}) 3360 (OH), 3086, 2934, 1463, 1411, 1371, 1154, 1038, 996 and 919 (−CH═CH_2); ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.91 (3H, d, J = 7.0 Hz, Me-C2), 1.10−1.66 (7H, m, H2, $H_2$3, $H_2$4, $H_2$5), 1.28 (3H, s, Me-C6), 3.42 (1H, dd, J = 10.5, 6.0 Hz, $H1_a$), 3.49 (1H, dd, J = 10.5, 6.0 Hz, $H1_b$), 5.04 (1H, dd, J = 11.0, 1.0 Hz, $H8_a$), 5.20 (1H, dd, J = 18.0, 1.0 Hz, $H8_b$), 5.91 (1H, dd, J = 11.0, 18.0 Hz, H7); ^{13}C NMR (63 MHz, $CDCl_3$) δ 16.6 (Me-C2), 21.2 (C4), 27.7/27.8 (Me-C6), 33.5 (C3), 35.7 (C2), 42.5 (C5), 68.2 (C1), 73.2 (C6), 111.6 (C8), 145.1/145.2 (C7).

(7RS)-(2E)-3,7-Dimethyl-2-octene-1,8-diol (***17***) *from (2E,6E)-2,6-Dimethyl-8-hydroxyocta-2,6-dienal:* R_i (DB-Wax) 2555; R_i (DB-5) 1518; UV (MeOH) λ_{max} 203 nm; IR (NaCl) ν 3347 (OH), 2952, 2929, 2872, 1668 (C═C), 1462, 1379, 1216, 1030, 757, 665; ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.85 (3H, d, J = 6.5 Hz, Me-C7), 1.26−1.58 (5H, m, $H_2$5, $H_2$6, H7), 1.60 (3H, s, Me-C3), 1.92−2.10 (2H, m, $H_2$4), 3.36 (1H, dd, J = 10.5, 6.5 Hz, $H8_a$), 3.43 (1H, dd, J = 10.5, 6.5 Hz, $H8_b$), 4.08 (2H, d, J = 7.0 Hz, $H_2$1), 5.35 (1H, t, J = 7.0 Hz, H2); ^{13}C NMR (63 MHz, $CDCl_3$) δ 16.1 (Me-C3), 16.5 (Me-C7), 24.9 (C5), 32.6 (C6), 35.6 (C7), 39.7 (C4), 59.4 (C1), 68.3 (C8), 123.4 (C2), 139.9 (C3).

(7RS)-(2Z)-3,7-Dimethyl-2-octene-1,8-diol (***18***) *from (2E,6Z)-2,6-Dimethyl-8-hydroxyocta-2,6-dienal:* R_i (DB-Wax) 2515; R_i (DB-5) 1492; UV (MeOH) λ_{max} 203 nm; IR (NaCl) ν (cm^{-1}) 3347 (OH), 2952, 2929, 2872, 1668 (C═C), 1462, 1379, 1216, 1030, 757, 665; ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.84 (3H, d, J = 6.5 Hz, Me-C7), 1.26−1.58 (5H, m, $H_2$5, $H_2$6, H7), 1.67 (3H, d, J = 1.0 Hz, Me-C3), 1.92−2.10 (2H, m, $H_2$4), 3.36 (1H, dd, J = 10.5, 6.5 Hz, $H8_a$), 3.43 (1H, dd, J = 10.5, 6.5 Hz, $H8_b$), 4.08 (2H, d, J = 7.0 Hz, $H_2$1), 5.35 (1H, tq, J = 7.0, 1.0 Hz, H2); ^{13}C NMR (63 MHz, $CDCl_3$) δ 16.5 (Me-C7), 23.4 (Me-C3), 25.2 (C5), 31.8 (C4), 32.6 (C6), 35.4 (C7), 59.0 (C1), 68.3 (C8), 124.3 (C2), 140.1 (C3).

(v) Diols **19**−**21** *Prepared by Epoxidation (MCPB) and Subsequent $LiAlH_4$ Reduction according to the Method of Williams et al. (1980). (3RS)-3,7-Dimethyloctane-1,7-diol* (***19***) *from (±)-Citronellol*: R_i (DB-Wax) 2215; R_i (DB-5) 1364; UV (MeOH) λ_{max} 204 nm; IR (NaCl) ν (cm^{-1}) 3357 (OH), 2965, 2935 (C−H), 1644, 1464, 1379, 1218, 1157, 1058, 937, 910, 759; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.89 (3H, d, J = 6.5 Hz, Me-C3), 1.20 (6H, s, 2 Me-C7), 1.25−1.68 (9H, m, $H_2$2, H3, $H_2$4, $H_2$5, $H_2$6), 3.62 (1H, ddd, J = 11.0, 7.0, 6.5 Hz, $H1_a$), 3.68 (1H, ddd, J = 11.0, 7.5, 6.0 Hz, $H1_b$); ^{13}C NMR (63 MHz, $CDCl_3$) δ 19.5 (Me-C3), 21.4 (C5), 28.9 (C3), 29.1 (Me-C7), 29.2 (Me-C7), 37.4 (C4), 39.5 (C2), 43.8 (C6), 60.5 (C1), 70.9 (C7).

(6RS)-2,6-Dimethyl-7-octene-2,6-diol (***20***) *from (±)-Linalyl Acetate*: R_i (DB-Wax) 1988; R_i (DB-5) 1233; UV (MeOH) λ_{max} 208 nm; IR (NaCl) ν (cm^{-1}) 3399 (OH), 3087, 2969, 2911, 1643 (C═C), 1468, 1371, 1163, 997 and 920 (−CH═CH_2), 756; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.20 (6H, s, 2Me-C2), 1.28 (3H, s, Me-C6), 1.47 (6H, m, $H_2$3, $H_2$4, $H_2$5), 5.03 (1H, dd, J = 11.0, 1.5 Hz, $H8_a$), 5.20 (1H, dd, J = 17.5, 1.5 Hz, $H8_b$), 5.91 (1H, dd, J = 17.5, 11.0 Hz, H7); ^{13}C NMR (63 MHz, $CDCl_3$) δ 18.5 (C4), 27.6 (Me-C6), 29.1 (Me-C2), 29.1 (Me-C2), 42.6 (C5), 44.0 (C3), 70.9 (C2), 73.1 (C6), 111.5 (C8), 145.1 (C7).

(3RS)-3,7-Dimethyl-6-octene-1,3-diol (***21***) *from Geraniol:* R_i (DB-Wax) 2264; R_i (DB-5) 1393; UV (MeOH) λ_{max} 205 nm; IR (NaCl) ν (cm^{-1}) 3357, 2968, 2926, 1644 (C═C), 1453, 1376, 1162, 1119, 1060, 1029, 934, 835 (>C═CH−); ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.26 (3H, s, Me-C3), 1.56 (2H, m, $H_2$4), 1.63 (3H, br s, Me-C7), 1.67 (1H, ddd, J = 14.5, 6.5, 4.5 Hz, $H2_a$), 1.69 (3H, d, J = 1.0 Hz, Me-C7), 1.81 (1H, ddd, J = 14.5, 7.5, 4.5 Hz, $H2_b$), 2.06 (2H, m, $H_2$5), 3.86 (1H, ddd, J = 11.0, 6.5, 4.5 Hz, $H1_a$), 3.92 (1H, ddd, J = 11.0, 7.5, 4.5 Hz, $H1_b$), 5.15 (1H, tqq, J = 7.0, 1.0, 1.0 Hz, H6); ^{13}C NMR (63 MHz, $CDCl_3$) δ 17.6 (Me-C7), 22.7 (C5), 25.6 (Me-C7), 26.6 (Me-C3), 41.5 (C2), 42.3 (C4), 59.7 (C1), 73.8 (C3), 124.2 (C6), 131.9 (C7).

Multidimensional Gas Chromatography (MDGC). For MDGC two Carlo Erba GC 8000 coupled via an MCSS column switching device and a heated transfer line (200 °C) were applied. Split/splitless injector (splitless mode, 210 °C) and flame ionization detectors (FID) on each oven (240 °C) were used. The pressures for the detector gases were 0.5 bar of hydrogen and 1.5 bar of air. Hydrogen was used as carrier gas at a pressure of 1.5 bar for column 1 and 0.8 bar for column 2. Preseparation was achieved in oven 1 on an Innowax-20M fused silica capillary column (38 m × 0.25 mm i.d.; film thickness = 0.5 μm). The temperature was programmed from 50 °C (5 min isotherm) to 235 °C at 4 °C/min. An MCSS column switching device in oven 1 was used to perform effluent cuts onto the chiral column in oven 2 [6-(*tert*-butyldimethylsilyl)-2,3-dimethyl-β-cyclodextrin in SE 54; 30 m × 0.25 mm i.d., film thickness = 0.25 μm]. The temperature in oven 2 was 70 °C for 20 min; it was then increased to 130 °C at 2 °C/min and from 130 °C the rate was 10 °C/min up to 210 °C. One effluent cut from 18.6 to 19.9 min was carried out to transfer the *cis*- and *trans*-rose oxides **1a**/**b** onto the chiral column.

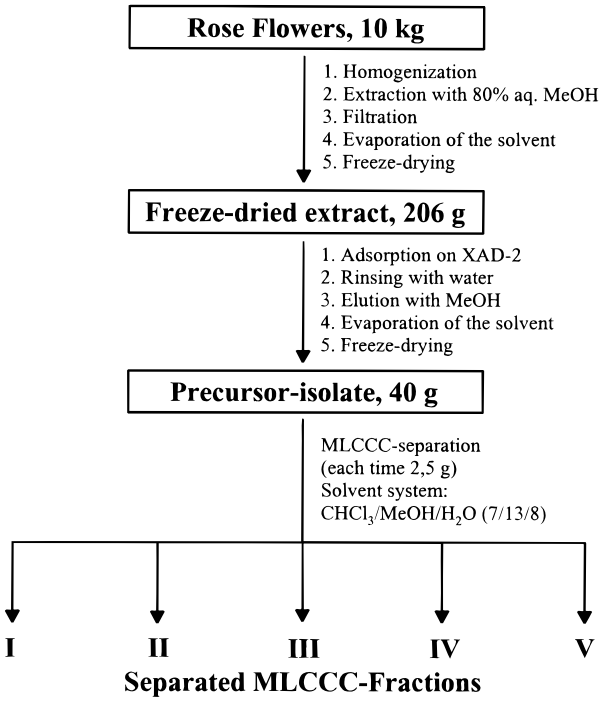

Figure 1. Protocol for the isolation and separation of aroma precursors from rose flowers.

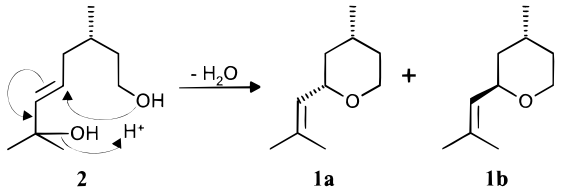

Figure 2. Acid-catalyzed conversion of (*S*)-3,7-dimethyl-5-octene-1,7-diol (**2**) into isomeric rose oxides **1a**/**b**.

Capillary Gas Chromatography/Mass Spectrometry (GC/MS). GC/MS was performed with a Hewlett-Packard GCD system equipped with a PTV injector (KAS system, Gerstel, Mülheim, Germany). The system was equipped with a J&W fused silica DB-5 capillary column (30 m × 0.25 mm i.d., film thickness = 0.25 μm). The temperature program was from 60 °C (2 min isothermal) to 300 °C at 5 °C/min. The flow rate of the carrier gas was 1.0 mL/min He. Other conditions were as follows: temperature of ion source, 180 °C; electron energy, 70 eV. The linear retention index (R_i) is based on a series of *n*-hydrocarbons.

Nuclear Magnetic Resonance (NMR). ^{1}H and ^{13}C NMR spectral data were recorded on Fourier transform Bruker AM 360 and AC 250 spectrometers with TMS as internal reference standard.

RESULTS AND DISCUSSION

An aroma precursor isolate has been obtained from rose flowers by MeOH extraction and subsequent XAD-2 adsorption chromatography (see Figure 1). Elution with methanol yielded 40 g of a precursor concentrate, which was prefractionated by MLCCC. Sequential fractions from the MLCCC separation were pooled into five groups. Aliquots of these grouped fractions I−V were then subjected to SDE (pH 2.5). Upon SDE, the major portion of rose oxide (80% of total) was observed from the least polar fraction V; the remaining 20% were produced upon heating of MLCCC fraction III. Extraction of fraction V with diethyl ether and subsequent GC/MS analysis revealed that this fraction contains polyhydroxylated monoterpenoids, so-called "polyols". In an effort to further separate the diethyl ether extract, an additional MLCCC fractionation with *n*-BuOH/MeOH/H_2O (10:1:10) as solvent system was carried out. Due to the complexity of the Et_2O isolate (≈50 different compounds), further workup by flash chromatography and purification by HPLC were necessary. In this way, four oxygenated monoterpenes (**2**, **12**, **13**, and **21**) could be isolated, and their structures were elucidated by NMR spectroscopy. Importantly, the isolated compounds included 3,7-dimethyl-5-octene-1,7-diol (**2**), the known synthetic precursor of isomeric rose oxides **1a/b** (Ohloff et al., 1961). The configuration at the stereogenic center C-3 of rose oxide precursor **2**, which has for the first time been isolated from a natural source, was determined by acid-catalyzed conversion of diol **2** into isomeric rose oxides **1a**/**b**. Since chiral MDGC analysis [Innowax-20M/6-(*tert*-butyldimethylsilyl)-2,3-dimethyl-β-cyclodextrin] revealed 2*S*,4*R* and 2*R*,4*R*

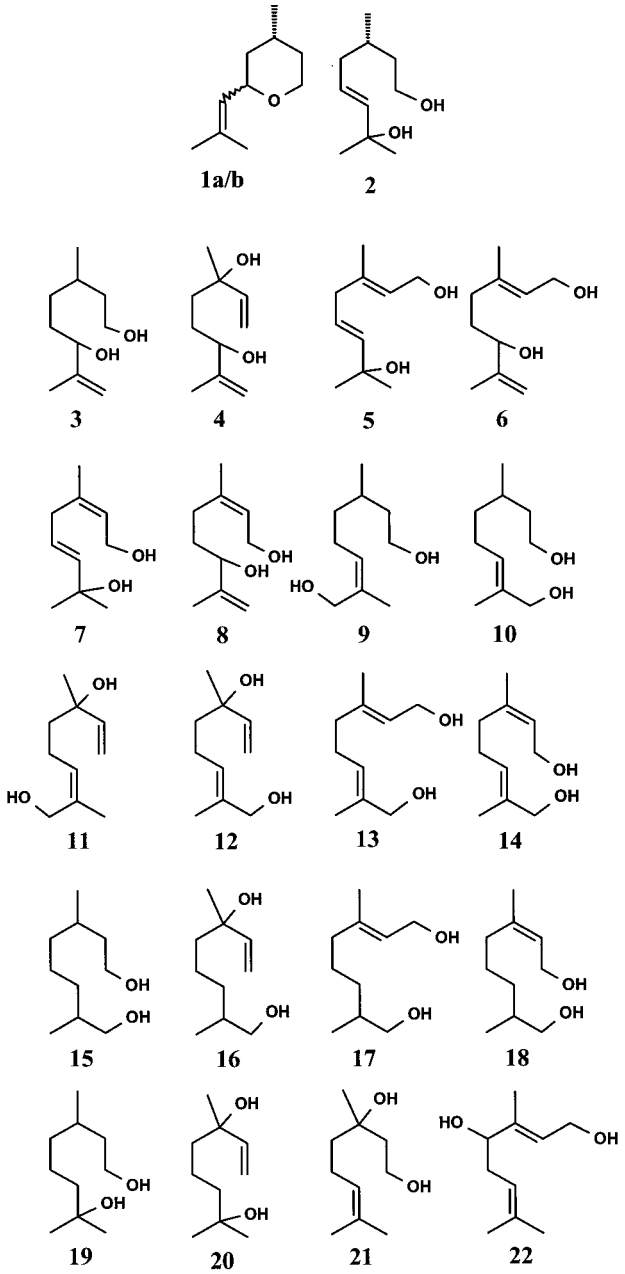

Figure 3. Structures of monoterpene diols **2**−**22** identified in a polar extract of rose flowers.

configurations for cyclic ethers **1a/b**, the configuration of precursor diol **2** was assigned as *S* (Figure 2).

In addition to isolated diols **2**, **12**, **13**, and **21**, 17 structurally related compounds could be identified by GC/MS analyses and comparison of the mass spectral data with those of authentic references (see Figure 3). With regard to the odor contribution of these diols, the precursor role of diol **7** must also be stressed. Under acidic conditions cyclization gives rise to isomeric nerol oxides, which are known odoriferous constituents of rose essential oil (Ohloff and Demole, 1987).

Precursor Function of Monoterpene Diols. Polyhydroxylated terpenoids (polyols) together with the well-known terpene glycoconjugates (Winterhalter and Skouroumounis, 1997) have been found to be involved in the generation of volatile compounds. The specific role of polyols in the acid-catalyzed production of volatiles in fruits and wine has been the subject of several reviews (Rapp et al., 1984; Williams et al., 1985; Strauss et al., 1986). With regard to rose polyols, only the identification of diols **3** and **21** has so far been reported (Ohloff et al., 1980, 1985). The remaining 19 diols are to the best of our knowledge reported in rose flowers for the first time. It is furthermore noteworthy that the structures of five additional diols remain to be elucidated. In view of the reactivity of terpene diols and the well-recognized aroma properties of the volatiles formed, their contribution to rose odor has obviously been underestimated. Concerning the formation of rose oxides in rose essential oil, it can be concluded that a major portion of isomeric ethers **1a/b** is chemically formed from the acid labile progenitor **2** during the steam distillation process. The isolation and structure elucidation of the additional precursor of cyclic ethers **1a/b** from MLCCC fraction III is the subject of ongoing research.

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