Isolation of a Glucosidic β-Damascenone Precursor from Rose Petals

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The 9-*O*-β-D-glucopyranoside of 3-hydroxy-7,8-didehydro-β-ionol (**1**) has been isolated from a glycosidic XAD-2 extract obtained from rose petals. In addition to the β-damascenone-generating compound **1**, the following glycoconjugates have been isolated and characterized as peracetates: 3-hydroxy-7,8-dihydro-β-ionol 9-*O*-β-D-glucopyranoside (**2**), 3-hydroxy-7,8-dihydro-β-ionol 3-*O*-β-D-glucopyranoside (**3**), 2-phenylethyl-*O*-β-D-glucopyranoside (**4**), 2-phenylethyl-*O*-β-D-galactopyranoside (**5**), benzyl-*O*-β-D-glucopyranoside (**6**), (2*E*)-2,6-dimethyl-6-hydroxyocta-2,7-dienyl-*O*-β-D-glucopyranoside (**7**), (2*Z*)-2,6-dimethyl-6-hydroxyocta-2,7-dienyl-*O*-β-D-glucopyranoside (**8**), and (2*E*,6*E*)-2,6-dimethyl-1-hydroxyocta-2,6-dien-8-yl-*O*-β-D-glucopyranoside (**9**).

Keywords: *Rosa damascena; Rosaceae; petals; aroma precursors; glycosides; β-damascenone; 3-hydroxy-7,8-didehydro-β-ionol 9-O-β-D-glucopyranoside; 3-hydroxy-7,8-dihydro-β-ionol 3-O-β-D-glucopyranoside; 3-hydroxy-7,8-dihydro-β-ionol 9-O-β-D-glucopyranoside; 2-phenylethyl-O-β-D-glucopyranoside; 2-phenylethyl-O-β-D-galactopyranoside; benzyl-O-β-D-glucopyranoside; (2E)-2,6-dimethyl-6-hydroxyocta-2,7-dienyl-O-β-D-glucopyranoside; (2Z)-2,6-dimethyl-6-hydroxyocta-2,7-dienyl-O-β-D-glucopyranoside; (2E,6E)-2,6-dimethyl-1-hydroxyocta-2,6-dien-8-yl-O-β-D-glucopyranoside*

INTRODUCTION

Since the first report of monoterpene glucosides in rose petals in 1969 by Francis and Allcock, the knowledge about the distribution of glycosidically bound volatiles in the plant kingdom has dramatically increased (Stahl-Biskup et al., 1993; Winterhalter and Skouroumounis, 1997). The growing interest in these structures in recent years is mainly due to their role as flavor precursors (Schreier and Winterhalter, 1993; Teranishi et al., 1992). Glycosides of aroma compounds have been recognized as an important source of recoverable aroma, since upon enzymatic and/or acid hydrolysis the aroma active substances are readily liberated (Williams, 1993). Although rose petals have been the first substrate for terpenoid aroma precursors to be detected, still little information is available today about the presence of additional glycosidic aroma progenitors in roses (Ackermann et al., 1989; Burgorskii et al., 1979). Especially for the key aroma compounds of rose essential oil, i.e. the intensely odorous β-damascenone as well as isomeric rose oxides (Ohloff and Demole, 1987), the genuine progenitors remain to be elucidated. In this paper, we report the isolation and characterization of a glucosidic precursor of β-damascenone and the identification of additional glycoconjugates from the petals of *Rosa damascena*.

EXPERIMENTAL PROCEDURES

Plant Material. Rose flowers (*Rosa damascena bulgaria*, 7 kg) were harvested at their full bloom stage in the Shizuoka prefecture, Shizuoka, Japan.

Preparation of Glycosidic Extracts. Rose flower volatiles were first removed by steam distillation. The remaining aqueous residue was subjected to adsorption chromatography on an Amberlite XAD-2 column (Günata et al., 1985). After a rinse of the column with water, the glycosides were eluted with MeOH. The so-obtained isolate was fractionated by ODS column chromatography (ODS-A, 60-200/60, YMC Co. Ltd., Koyto, Japan; MeCN/H_2O gradient). A major fraction (7 g) that eluted with 20% MeCN was further purified with the aid of multilayer coil countercurrent chromatography (MLCCC).

Isolation of Glycoconjugates. The purification was guided by the detection of volatile compounds released after enzymatic (Rohapect D5L, Röhm, Darmstadt, Germany; citrate−phosphate buffer, pH 5) or acid hydrolyses (simultaneous distillation−extraction, pH 2.5). Analytical MLCCC separations of glycosidic subfractions have been carried out with an Ito multilayer coil separator−extractor (P.C. Inc., Potomac, MD) equipped with a 160 m × 1.6 mm i.d. PTFE tubing: solvent system, ethyl acetate−*n*-butanol−water (3:2:5); flow rate, 1.5 mL/min; elution mode, head to tail; rotational speed, 800 rpm (Ito, 1986; Roscher and Winterhalter, 1993). Separated fractions were acetylated (Ac_2O/pyridine) and after flash chromatography (SiO_2 60, 0.032−0.063 mm; pentane−diethyl ether gradient) purified by HPLC on Eurospher 100-C18 5 μm columns (Knauer Säulentechnik, Berlin, 250 mm × 16 mm i.d. and 250 mm × 4 mm i.d.) using MeCN/H_2O gradients.

Spectroscopic Data. The following instruments were used: UV, Perkin-Elmer Lambda 5; IR, Perkin-Elmer 1740; NMR, Bruker AM 360, Jeol EX-270, and Lambda-500 ($CDCl_3$, chemical shifts in ppm, relative to TMS); desorption chemical ionization (DCI)-MS, Finnigan TSQ 70 (reactant gas: ammonia). Details of sugar analysis using either β-glucosidase or β-galactosidase as cleaving enzyme have been reported earlier (Skouroumounis and Winterhalter, 1994).

3-Hydroxy-7,8-didehydro-β-ionol 9-O-β-D-glucopyranoside (**1**) was isolated as its pentaacetate (**1a**): 1.8 mg; UV (MeOH) λ_{max} 229 nm; IR (NaCl) ν 2921, 2362, 2214, 1757, 1368, 1230, 1039 cm^{-1}; DCI-MS (reactant gas: NH_3) pseudo-molecular ion at m/z 598, indicating a molecular mass of 580 ($C_{29}H_{40}O_{12}$); ^1H NMR (360 MHz, $CDCl_3$, ppm, J in Hz) δ 1.14 and 1.17 (2 × 3H, 2s, $2CH_3$-C1), 1.51 (3H, d, J = 6.5, CH_3-C9), 1.55 (1H, dd, J = 12.5, 3.0, H_aC2), 1.82 (1H, ddd, J = 12.5, 3.5, 2.0, H_bC2), 1.88 (3H, br s, CH_3-C5), 2.01−2.06 (5 × 3H, 5s, five acetates), 2.11 (1H, dd, J = 17.5, 3.0, H_aC4), 2.47 (1H, ddd, J = 17.5, 5.5, 2.0, H_bC4), 3.71 (1H, ddd, J = 10.0, 5.0, 2.5, HC5′), 4.09

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(1H, dd, J = 12.0, 2.5, H_aC6′), 4.25 (1H, dd, J = 12.0, 5.0, H_b-C6′), 4.74 (1H, q, J = 6.5, HC9), 4.86 (1H, d, J = 8.0, HC1′), 5.00 (1H, m, HC3), 5.03 (1H, dd, J = 9.5, 8.0, HC2′), 5.10 (1H, dd, J = 10.0, 9.5, HC4′), 5.21 (1H, dd, J = 9.5, 9.5, HC3′); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 22.3 (CH_3-C5) 23.1 (CH_3-C9), 28.5 and 30.1 ($2CH_3$-C1), 35.9 (C1), 37.3 (C4), 42.1 (C2), 62.0 (C6′), 67.5 (C9), 67.8 (C3), 68.4 (C4′), 71.8 (C2′), 71.9 (C5′), 73.0 (C3′), 84.0 (C7), 91.9 (C8), 98.9 (C1′), 123.2 (C6), 137.9 (C5), 20.6−21.4 and 169.3−170.7 (five acetates). Signals were assigned by ^{1}H−^{1}H-COSY and HSQC (^{1}H−^{13}C-COSY) as well as HMBC experiments.

*3-Hydroxy-7,8-dihydro-β-ionol 9-O-β-D-glucopyranoside (**2**) and 3-hydroxy-7,8-dihydro-β-ionol 3-O-β-D-glucopyranoside* (**3**) were isolated as their respective peracetates (**2a** and **3a**). Spectral data for **2a** (1.2 mg): UV (MeOH) λ_{max} 209 nm; IR (NaCl) ν 2918, 2850, 1757, 1448, 1366, 1224, 1036 cm^{-1}; DCI-MS (reactant gas: NH_3) pseudo-molecular ion at m/z 602, indicating a molecular mass of 584 ($C_{29}H_{44}O_{12}$); ^{1}H NMR (360 MHz, $CDCl_3$, ppm, J in Hz) δ 1.04 and 1.05 (2 × 3H, 2s, $2CH_3$-C1), 1.14 (3H, d, J = 6.5, CH_3-C9), 1.49 (1H, dd, J = 12.0, 2.0, H_aC2), 1.52 (2H, m, H_2C8), 1.59 (3H, s, CH_3-C5), 1.70 (1H, ddd, J = 12.0, 3.5, 2.0, H_bC2), 1.93 (1H, dd, J = 12.5, 6.5, H_aC7), 1.98 (1H, dd, J = 17.0, 2.5, H_aC4), 2.00−2.07 (5 × 3H, 5s, five acetates), 2.07 (1H, dd, J = 12.5, 5.5, H_bC7), 2.28 (1H, ddd, J = 17.0, 5.5, 2.0, H_bC4), 3.67 (1H, ddd, J = 10.0, 5.0, 2.5, HC5′), 3.75 (1H, m, HC9), 4.12 (1H, dd, J = 12.5, 2.5, H_aC6′), 4.23 (1H, dd, J = 12.5, 5.0, H_bC6′), 4.55 (1H, d, J = 8.0, HC1′), 4.96 (1H, dd, J = 9.5, 8.0, HC2′), 4.98 (1H, m, HC3), 5.09 (1H, dd, J = 10.0, 9.5, HC4′), 5.21 (1H, dd, J = 9.5, 9.5, HC3′); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 19.5 (CH_3-C5), 19.6 (CH_3-C9) 23.7 (C7), 28.3 and 29.4 ($2CH_3$-C1), 37.2 (C8), 37.3 (C1), 38.1 (C4), 44.2 (C2), 62.1 (C6′), 68.6 (C4′), 68.7 (C3), 71.5 (C2′/C5′), 72.9 (C3′), 76.4 (C9), 99.2 (C1′), 123.5 (C5), 137.1 (C6), 20.6−21.5 and 169.3−170.9 (five acetates).

Spectral data for **3a**: UV (MeOH) λ_{max} 216 nm; IR (NaCl): ν 2960, 2936, 1752, 1434, 1373, 1229, 1040 cm^{-1}; DCI-MS (reactant gas: NH_3) pseudo-molecular ion at m/z 602, indicating a molecular mass of 584 ($C_{29}H_{44}O_{12}$); ^{1}H NMR (360 MHz, $CDCl_3$, ppm, J in Hz) δ 1.00 and 1.03 (2 × 3H, 2s, $2CH_3$-C1), 1.23 (3H, d, J = 6.5, H_3C-C9), 1.47 (1H, dd, J = 12.5, 2.0, H_a-C2), 1.54 (2H, m, H_2C8), 1.60 (3H, s, H_3C-C5), 1.76 (1H, ddd, J = 12.5, 3.5, 2.0, H_bC2), 1.92 (1H, dd, J = 16.0, 2.5, H_aC4), 1.95 (1H, dd, J = 12.5, 6.5, H_aC7), 2.00−2.07 (5 × 3H, 5s, five acetates), 2.05 (1H, dd, J = 12.5, 5.5, H_bC7), 2.15 (1H, ddd, J = 16.0, 5.5, 2.0 Hz, H_bC4), 3.70 (1H, ddd, J = 10.0, 5.0, 2.5, HC5′), 3.90 (1H, m, HC3), 4.11 (1H, dd, J = 12.5, 2.5, H_aC6′), 4.24 (1H, dd, J = 12.5, 5.0, H_bC6′), 4.63 (1H, d, J = 8.0, HC1′), 4.87 (1H, m, HC9), 4.95 (1H, dd, J = 9.5, 8.0, HC2′), 5.07 (1H, dd, J = 10.0, 9.5, HC4′), 5.21 (1H, dd, J = 9.5, 9.5, HC3′); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 19.6 (CH_3-C5), 19.8 (CH_3-C9), 23.9 (C7), 28.4 and 29.5 ($2CH_3$-C1), 36.2 (C8), 37.6 (C1), 38.6 (C4), 45.8 (C2), 62.1 (C6′), 68.5 (C4′), 71.3 (C9), 71.4 (C2′), 71.7 (C5′), 72.8 (C3′), 73.4 (C3), 99.6 (C1′), 123.6 (C5), 137.0 (C6), 20.6−21.3 and 169.2−170.8 (five acetates).

*2-Phenylethyl-O-β-D-glucopyranoside (**4**), 2-Phenylethyl-O-β-D-galactoside (**5**), and Benzyl-O-β-D-glucopyranoside (**6**).* Spectral data for peracetylated glucosides **4a** (170 mg) and **6a** (1 mg): Williams et al., 1983; Voirin et al., 1990; Yano et al., 1991. In order to confirm the structure of the novel peracetylated galactoside **5a** (1.3 mg) an authentic specimen was synthesized by reacting 2-phenylethanol with tetra-O-acetyl-α-bromogalactose in the presence of Ag_2CO_3. The spectral data of the synthetic product were identical with those for the natural peracetate **5a**: UV (MeOH) λ_{max} 258 nm; IR ($CHCl_3$) ν 3005, 2875, 1757, 1368, 1195, 1111, 1042 cm^{-1}; DCI-MS (reactant gas: NH_3) pseudo-molecular ion at m/z 470, indicating a molecular mass of 452 ($C_{22}H_{28}O_{10}$); ^{1}H NMR (360 MHz, $CDCl_3$, ppm, J in Hz) δ 1.89−2.16 (4 × 3H, 4s, four acetates), 2.88−2.93 (2H, m, H_2C2), 3.68 (1H, m, H_aC1), 3.89 (1H, ddd, J = 7.0, 6.5, 1.0, HC5′), 4.13 (1H, dd, J = 11.0, 7.0, H_aC6′), 4.14 (1H, m, H_bC1), 4.19 (1H, dd, J = 11.0, 6.5, H_bC6′), 4.45 (1H, d, J = 8.0, HC1′), 4.98 (1H, dd, J = 10.5, 3.5, HC3′), 5.21 (1H, dd, J = 10.5, 8.0, HC2′), 5.38 (1H, dd, J = 3.5, 1.0, HC4′), 7.18−7.30 (5H, m, aromatic protons); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 36.0 (C2), 61.3 (C6′), 67.1 (C4′), 68.7 (C2′), 70.7 (C1 and C5′), 70.9 (C3′), 101.3 (C1′), 126.3 (C6), 128.4 (C4/C8), 129.0 (C5/C7), 138.5 (C3), 20.6−20.7 and 169.4−170.4 (four acetates).

*(2E)-2,6-Dimethyl-6-hydroxyocta-2,7-dienyl-O-β-D-glucopyranoside (**7**) and (2Z)-2,6-dimethyl-6-hydroxyocta-2,7-dienyl-O-β-D-glucopyranoside (**8**)* were isolated as tetraacetates **7a** (1.6 mg) and **8a** (1.2 mg). The known diol glucosides (Tschesche et al., 1977; Strauss et al., 1988; Schwab et al., 1990) were identified on the basis of the ^{1}H NMR spectral data. **7a**: DCI-MS (reactant gas: NH_3) pseudo-molecular ion at m/z 518, indicating a molecular mass of 500 ($C_{24}H_{36}O_{11}$); ^{1}H NMR (360 MHz, $CDCl_3$, ppm, J in Hz) δ 1.30 (3H, s, CH_3-C6), 1.60 (3H, br s, CH_3-C2), 1.60 (2H, m, H_2C5), 1.89 (1H, s, −OH), 2.01−2.09 (4 × 3H, 4s, four acetates), 2.09 (2H, m, H_2C4), 3.65 (1H, ddd, J = 10.0, 5.0, 2.5, HC5′), 3.97 (1H, br d, J = 12.0, H_aC1), 4.14 (1H, dd, J = 12.0, 2.5, H_aC6′), 4.16 (1H, br d, J = 12.0, H_bC1), 4.26 (1H, dd, J = 12.0, 5.0, H_bC6′), 4.48 (1H, d, J = 8.0, HC1′), 5.01 (1H, dd, J = 9.5, 8.0, HC2′), 5.08 (1H, dd, J = 10.0, 9.5, HC4′), 5.09 (1H, dd, J = 11.0, 1.5, H_aC8), 5.20 (1H, dd, J = 9.5, 9.5, HC3′), 5.23 (1H, dd, J = 17.5, 1.5, H_bC8), 5.41 (1H, dt, J = 7.5, 1.0, HC3), 5.92 (1H, dd, J = 17.5, 11.0, HC7).

8a: DCI-MS (reactant gas: NH_3) pseudo-molecular ion at m/z 518, indicating a molecular mass of 500 ($C_{24}H_{36}O_{11}$); ^{1}H NMR (360 MHz, $CDCl_3$, ppm, J in Hz) δ 1.29 (3H, s, CH_3-C6), 1.61 (2H, m, H_2C5), 1.69 (3H, br s, CH_3-C2), 1.77 (1H, br s, −OH), 2.00−2.09 (4 × 3H, four acetates), 2.13 (2H, m, H_2C4), 3.66 (1H, ddd, J = 9.5, 4.0, 2.5, HC5′), 4.14 (1H, br d, J = 12.0, H_aC1), 4.18 (1H, dd, J = 12.0, 2.5, H_aC6′), 4.28 (1H, br d, J = 12.0, H_bC1), 4.29 (1H, dd, J = 12.0, 4.0, H_bC6′), 4.46 (1H, d, J = 8.0, HC1′), 5.01 (1H, dd, J = 9.5, 8.0, HC2′), 5.07 (1H, dd, J = 11.0, 1.5, H_aC8), 5.12 (1H, dd, J = 9.5, 9.5, HC4′), 5.19 (1H, dd, J = 9.5, 9.5, HC3′), 5.21 (1H, dd, J = 17.5, 1.5, H_bC8), 5.44 (1H, dt, J = 7.5, 1.0, HC3), 5.89 (1H, dd, J = 17.5, 11.0, HC7).

*(2E,6E)-2,6-Dimethyl-1-hydroxyocta-2,6-dien-8-yl-O-β-D-glucopyranoside (**9**)* was isolated as its pentaacetate (**9a**) (2 mg): UV (MeOH) λ_{max} 210 nm; IR (NaCl) ν 2922, 1747, 1435, 1374, 1224, 1039, 907 cm^{-1}; DCI-MS (reactant gas: NH_3) pseudo-molecular ion at m/z 560, indicating a molecular mass of 542 ($C_{26}H_{38}O_{12}$); ^{1}H NMR (360 MHz, $CDCl_3$, ppm, J in Hz) δ 1.66 (3H, br s, CH_3-C2), 1.67 (3H, br s, CH_3-C6), 2.00−2.09 (5 × 3H, 5s, five acetates), 2.10 (2H, m, H_2C5), 2.17 (2H, m, H_2C4), 3.67 (1H, ddd, J = 10.0, 5.0, 2.5, HC5′), 4.16 (1H, dd, J = 12.0, 2.5, H_aC6′), 4.22 (1H, m, H_aC8), 4.25 (1H, dd, J = 12.0, 5.0, H_bC6′), 4.26 (1H, m, H_bC8), 4.46 (2H, br s, H_2C1), 4.54 (1H, d, J = 8.0, HC1′), 4.99 (1H, dd, J = 9.5, 8.0, HC2′), 5.09 (1H, dd, J = 10.0, 9.5, HC4′), 5.21 (1H, dd, J = 9.5, 9.5, HC3′), 5.27 (1H, m, HC7), 5.44 (1H, m, HC3); ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 14.0 (CH_3-C2), 16.4 (CH_3-C6), 26.0 (C4), 38.9 (C5), 62.0 (C6′), 65.3 (C8), 68.5 (C4′), 70.1 (C1), 71.3 (C2′), 71.8 (C5′), 72.9 (C3′), 98.9 (C1′), 119.5 (C7), 128.8 (C3), 130.5 (C2), 141.5 (C6), 20.6−21.0 and 169.4−171.0 (five acetates).

RESULTS AND DISCUSSION

The aqueous residue left after steam distillation of rose petals (7 kg) was passed through a column of XAD-2. The glycosidic isolate obtained after MeOH elution was fractionated by ODS column chromatography. The glycosidic subfraction that eluted with 20% MeCN was separated by MLCCC. Enzymatic hydrolyses of MLCCC fractions liberated 3-hydroxy-7,8-didehydro-β-ionol, 3-hydroxy-β-damascone, phenylethanol, benzyl alcohol, and a series of oxygenated monoterpenyl alcohols. In order to isolate the intact glycoconjugates, each glycosidic fraction was acetylated and after flash chromatography purified by HPLC. In this way, nine glycosidic compounds **1**−**9** were obtained as their respective acetates **1a**−**9a** (cf. Figure 1).

The molecular mass 580 for compound **1a** was determined by means of DCI-MS. From the ^{1}H NMR spectrum the presence of a peracetylated β-glucose moiety was apparent ($J_{1',2'}$ = 8 Hz). For the aglycon moiety three methyl singlets (δ 1.14, 1.17, 1.88) and one

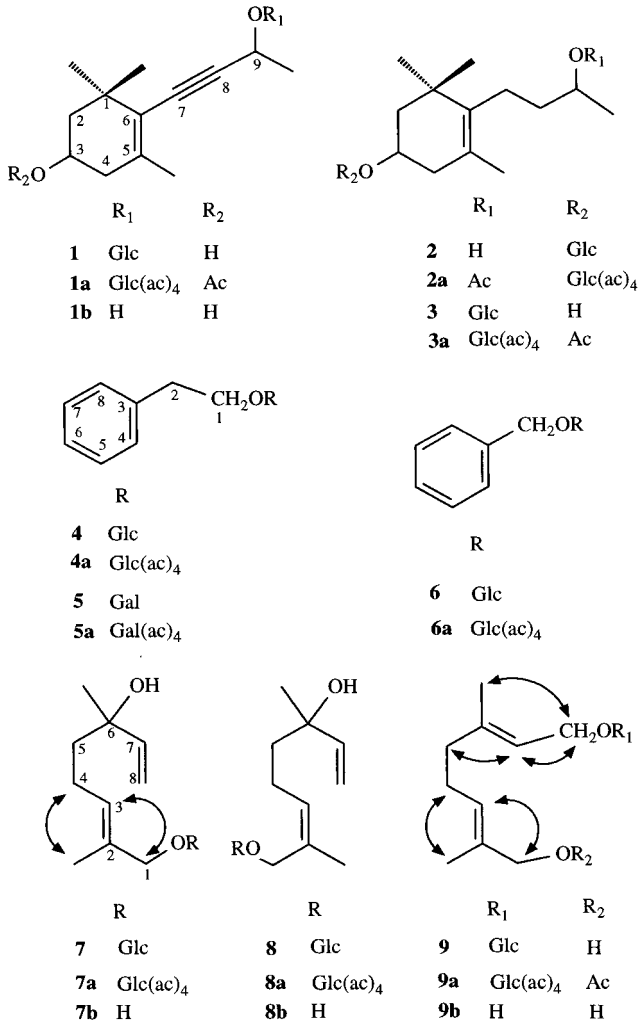

Figure 1. Structures of glycoconjugates **1**−**9** isolated from rose petals (arrows indicate NOEs).

methyl doublet (δ 1.51) indicated a C_{13}-norisoprenoid, i.e. ionol-type, carbon skeleton. Since five acetoxy groups were detected, with four of them located at the sugar moiety, the aglycon was considered to be a C_{13}-norisoprenoid diol. In the FTIR spectrum, a weak absorption band at 2214 cm^{-1}, characteristic for an acetylenic bond (Winterhalter et al., 1991), was observed. Each set of cross peaks on HMBC (e.g. from Me-9 to C-9 and C-8; H-9 to C-7, C-8, and Me-9; Me_2-1 to C-1, C-2, and C-6; and Me-5 to C-4, C-5, and C-6, as well as from H_2-4 to C-2, C-3, C-5, and C-6), together with the data from the $^1H-^1H$-COSY measurement, revealed the aglycon moiety to be 3-hydroxy-7,8-didehydro-β-ionol. The connection of the glucose moiety at C-9 was clarified by the cross peaks H-9 to C-1′ and H-1′ to C-9. Hence, the remaining acetyl group has to be attached to C-3. Low-field shift of H-3 (δ 5.00) also supported the elaborated connectivity. The spectral data obtained for **1a** are in good agreement with those published for a synthetic diastereomeric mixture of peracetylated 3-hydroxy-7,8-didehydro-β-ionol 9-*O*-β-D-glucoside (Skouroumounis et al., 1995). After deacetylation and enzymatic hydrolysis (almond emulsin), 3-hydroxy-7,8-didehydro-β-ionol was liberated as aglycon.

Also for acetylated glucosides **2a** and **3a**, ^1H NMR data suggested that both compounds were ionol-type glucosides. $^1H-^1H$-COSY, HSQC, and HMBC spectra of these compounds revealed in both cases the presence of 3-hydroxy-7,8-dihydro-β-ionol as aglycon moiety (Humpf and Schreier, 1992). By comparison of the chemical shifts of H-3 and H-9 of each of the aglycons, compounds **2a** and **3a** were found to be the peracetylated 9-*O*-β-D-glucoside and 3-*O*-β-D-glucoside, respectively, of 3-hydroxy-7,8-dihydro-β-ionol. The connectivity of each glucose moiety was confirmed by HMBC. Deacetylated compounds **2** and **3** yielded 3-hydroxy-7,8-dihydro-β-ionol after enzymatic hydrolysis. Of the aromatic alcohol glycosides **4**−**6**, the glucosides **4** and **6** are known constituents of rose flowers. For glycoconjugate **5**, NMR spectral data were suggesting that 2-phenylethanol is linked to β-galactose as glycon moiety. In order to confirm the proposed structure, peracetylated 2-phenylethyl-β-D-galactoside **5a** has been synthesized using a modified Königs−Knorr reaction (Krohn, 1987). All spectral data of the synthetic product were identical with those obtained for rose flower glycoside **5a**. The remaining glycoconjugates **7**−**9** were identified by MS and NMR data as (2*E*)-2,6-dimethyl-6-hydroxy-2,7-dienyl-*O*-β-D-glucopyranoside (**7**), (2*Z*)-2,6-dimethyl-6-hydroxyocta-2,7-dienyl-*O*-β-D-glucopyranoside (**8**), and (2*E*,6*E*)-2,6-dimethyl-1-hydroxyocta-2,6-dien-8-yl-*O*-β-D-glucopyranoside (**9**). The role of monoterpene diols **7b** and **8b** as potential flavor precursors has been studied by Strauss et al. (1988). Upon heating at pH 3, diol **7b** was found to be partly converted into the allylic rearrangement product **9b**. In addition, a formation of two dehydration products, i.e. the so-called dill ether (3,9-epoxy-*p*-menth-1-ene) as well as two diastereomers of *p*-menth-1-en-9-al, was observed. The latter aldehydes have earlier been recognized as part of the odoriferous principle of rose oil (Ohloff et al., 1969). By far more important, however, is the precursor role of the glucoconjugate of 3-hydroxy-7,8-didehydro-β-ionol (**1**). The acetylenic diol **1b** as well as its glucoconjugate **1** are known progenitors of the potent aroma compound β-damascenone. It is noteworthy, that glucoconjugate **1** was found to yield a higher portion of β-damascenone compared to the free aglycon (Skouroumounis et al., 1993). This finding has been explained by assuming a stabilization of the hydroxy group at C-9 through glycoconjugation, which obviously allows a forced dehydration at C-3. The acetylenic glucoside **1** has recently been isolated and characterized from Riesling wine (Baderschneider et al., 1997). Moreover, a disaccharidic conjugate of diol **1b** has been identified and partially characterized from apple fruit (Roberts et al., 1994). As immediate precursors of the acetylenic diol **1b**, allenic intermediates, i.e. the so-called grasshopper ketone and its reduction product, megastigma-6,7-diene-3,5,9-triol, have to be considered (Näf et al., 1990). The isolation of these presumed biogenetic precursors of acetylenic diol **1b** is part of ongoing studies.

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