Structures of Two New Ionone Glycosides from Quince Fruit (*Cydonia oblonga* Mill.)

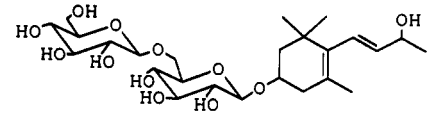
Alexandra Güldner and Peter Winterhalter*

Lehrstuhl für Lebensmittelchemie, Universität Würzburg, Am Hubland, 8700 Würzburg, Germany

The β-D-gentiobioside [β-D-glucopyranosyl(1→6) β-D-glucopyranoside] and the β-D-glucopyranoside of (3*R*)-3-hydroxy-β-ionone have been isolated and characterized in quince (*Cydonia oblonga* Mill.) fruit through spectral (NMR, MS) and chemical studies. Model experiments (SDE, pH 3.5) carried out with the aglycon 3-hydroxy-β-ionone revealed a formation of a number of volatile C_{13} norisoprenoid degradation products, including (*E*)-3,4-didehydro-β-ionone and 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN).

INTRODUCTION

During the past decade the powerful and characteristic odor of quince fruit has attracted considerable research interest (Schreyen et al., 1979; Tsuneya et al., 1980, 1983; Ishihara et al., 1986; Umano et al., 1986; Näf et al., 1990, 1991). Studies provided by our group (Winterhalter et al., 1987) revealed that most of the C_{13} norisoprenoids and monoterpenoids identified in quince essential oil are not original volatiles of quince fruit but are formed during technological processes, e.g., heating, by degradation of acid-labile, nonvolatile precursor compounds (Winterhalter and Schreier, 1988a,b). Examples are the formation of bicyclo[4.3.0]nonane derivatives **2** and **3**, which —together with 3,4-didehydro-β-ionol (**4**)—are generated upon heat treatment of quince juice in a collective concentration of approximately 10 ppm. Compounds **2–4** have recently been found to be degradation products of



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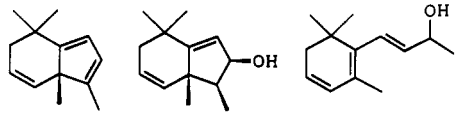

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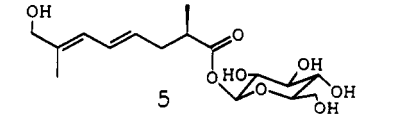

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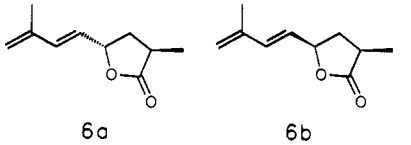

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glycosidically bound 3-hydroxy-β-ionol, the latter occurring in quince fruit mainly in form of the β-D-gentiobioside (**1**) (Winterhalter et al., 1991a). Another example for secondary flavor formation in quince is the acid-catalyzed degradation of glucoside **5**, giving rise to the formation of isomeric marmelo lactones **6a/b** (Winterhalter et al., 1991b), which have been reported as important contributors to the overall flavor impression of quince (Tsuneya et al., 1980).

A further bound constituent of quince fruit is the C_{13} norisoprenoid hydroxyketone **7** (Winterhalter and Schreier, 1988b). In the present paper, the isolation and structural elucidation of glycosidic conjugates of **7** from quince juice are reported and the role of **7** as flavor precursor is examined.

EXPERIMENTAL PROCEDURES

General. NMR spectra were taken on a Fourier transform Bruker AC 200 (200 MHz) and WM 400 (400 MHz) spectrometer. For flash chromatography (Still et al., 1978) Merck silica gel 60 (0.032–0.063 mm) was used. All solvents were of the highest purity obtainable commercially and were redistilled before use.

Plant Material. Fresh ripe quince fruit (*C. oblonga* Mill.) was available from the local market.

Isolation of Glycosides. After the seeds were removed from 10 kg of quince fruits and the fruits were cut into small pieces, the fruits were submerged in 5 L of 0.2 M phosphate buffer (pH 7.0), containing 0.2 M glucono-δ-lactone as glycosidase inhibitor (Heyworth and Walker, 1962). The fruits were homogenized with a Braun blender and pressed with a Hafico press. The clear juice so obtained was passed through a column (50 cm × 5 cm i.d.) of Amberlite XAD-2 resin (Günata et al., 1985). After the column was rinsed with 2 L of distilled water, the glycosidic fraction was eluted with 2 L of MeOH. Careful concentration of the MeOH eluate in vacuo, followed by Et_2O extraction to ensure removal of any volatiles, gave approximately 5 g of a dark brown residue, which was subjected to a prefractionation using rotation locular countercurrent chromatography (RLCC).

The RLCC apparatus (Eyela RLCC UP-60, Tokyo Rikakikai Co.) was operated in the ascending mode, employing a solvent system made up from the two phases produced by mixing $CHCl_3$–MeOH–H_2O (7:13:8) with the more dense, less polar layer used as the stationary phase. The flow rate was 1 mL/min, rotation speed 80 rpm, and slope 30°. Fifty fractions (each 10 mL) were collected. For the workup of the glycosidic isolate five RLCC separations (each 1 g) were carried out.

Screening of RLCC Fractions. For the monitoring of glycosidically bound compounds in separated RLCC fractions, closely spaced fractions were pooled, the solvent was evaporated, and an enzymatic hydrolysis (16 h, pH 5.2) with a nonselective pectinase (Rohapect D5L, Röhm, Darmstadt, Germany) was carried out on aliquots from these fractions. Phenyl β-D-glucopyranoside (100 μg) was used as internal standard. The liberated aglycons were extracted with Et_2O, dried (Na_2SO_4), carefully concentrated, and analyzed by HRGC and HRGC–MS.

Derivatization and Purification of Peracetylated Glycosides. Combined RLCC fractions 31–40 were acetylated (24 h) with Ac_2O–pyridine at room temperature, and the peracetylated glycosides were further separated by flash chromatography on SiO_2 (pentane–Et_2O 2:8). From combined flash fractions

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Table I. ^1H NMR Spectral Data (400 MHz, $CDCl_3$) of Acetylated Disaccharide Glycoside 8a (δ Relative to TMS; J in Hertz)

δ	signal	assignment
1.10, 1.13	2 × 3 H, 2s	H_3C11, H_3C12
1.56	1 H, dd; J = 12.5, 12	H_aC2
1.75	3 H, s	H_3C13
1.85	1 H, ddd; J = 12.5, 3.5, 1.9	H_bC2
1.98–2.09	21 H, 7s	7 × CO–CH_3
2.03	1 H, m (obscured)	H_a–C4
2.29	3 H, s	H_3C10
2.38	1 H, dd; J = 17.3, 5.4	H_b–C4
3.65–3.85	4 H, m	HC5′, HC5″, H_2C6'
4.02	1 H, dddd; J = 12, 7.5, 5.4, 3.5	HC3
4.12	1 H, dd; J = 12.3, 2.3	H_aC6''
4.25	1 H, dd; J = 12.3, 5.0	H_bC6''
4.58 and	1 H, d; J = 8.0	HC1′, HC1″
4.62	1 H, d; J = 8.0	
4.90	1 H, dd; J = 9.6, 9.5	HC4′
4.92 and	1 H, dd; J = 9.6, 8.0	HC2′, HC2″
4.96	1 H, dd; J = 9.6, 8.0	
5.04	1 H, dd; J = 9.9, 9.4	HC4″
5.16 and	1 H, dd; J = 9.5, 9.4	HC3′, HC3″
5.19	1 H, dd; J = 9.6, 9.5	
6.08	1 H, d; J = 16.4	HC8
7.18	1 H, d; J = 16.4	HC7

Table II. ^1H NMR Spectral Data (400 MHz, $CDCl_3$) of Acetylated Glucoside 9a (δ Relative to TMS; J in Hertz)

δ	signal	assignment
1.09, 1.10	2 × 3 H, 2s	H_3C11, H_3C12
1.56	1 H, dd; J = 12.5, 12	H_aC2
1.75	3 H, s	H_3C13
1.88	1 H, ddd; J = 12.5, 3.5, 1.9	H_bC2
2.01–2.06	12 H, 4s	4 × CO–CH_3
	1 H, m (obscured)	H_a–C4
2.29	3 H, s	H_3C10
2.38	1 H, dd; J = 17.3, 5.4	H_b–C4
3.71	1 H, ddd; J = 9.6, 5.3, 2.4	HC5′
3.97	1 H, dddd; J = 12, 7.5, 5.4, 3.5	HC3
4.13	1 H, dd; J = 12.2, 2.4	H_aC6'
4.25	1 H, dd; J = 12.2, 5.3	H_bC6'
4.64	1 H, d; J = 8.0	HC1′
4.97	1 H, dd; J = 9.5, 8.0	HC2′
5.07	1 H, dd; J = 9.6, 9.5	HC4′
5.21	1 H, dd; J = 9.5, 9.5	HC3′
6.08	1 H, d; J = 16.4	HC8
7.18	1 H, d; J = 16.4	HC7

20–26 pure disaccharide glycoside 8a was obtained in the form of a white powder (60 mg): ^1H NMR, see Table I; ^{13}C NMR, see Table III; thermospray MS, m/z 844 $(M + NH_4)^+$, indicating a molecular mass of 826 ($C_{39}H_{54}O_{19}$).

The combined stationary phases of the RLCC separations were concentrated to dryness, acetylated, and also subjected to flash chromatography on SiO_2 (pentane–Et_2O gradient). Final purification of the major compound (flash fractions 14 and 15) by semipreparative HPLC [LiChrospher Si 100, 5-μm column, 250 × 16 mm; Knauer, Berlin; eluent; pentane–Et_2O (1:9); flow rate, 7 mL/min; UV detection, 280 nm] gave compound **9a** (19 mg) as a colorless syrup: ^1H NMR, see Table II; ^{13}C NMR, see Table III; thermospray MS m/z 556 $(M + NH_4)^+$, indicating a molecular mass of 538 ($C_{27}H_{38}O_{11}$); R_i (DB-5) 3086; EIMS (70 eV) m/z (%) 331 (1), 190 (14), 175 (19), 169 (9), 147 (10), 109 (10), 43 (100).

Deacetylation of Glycoside 8a. Deacetylation was carried out according to the method reported by Paulsen et al. (1985). To 30 mg of **8a** in 5 mL of MeOH was added 5 mL of 0.02 M NaOMe solution. After 12 h, the mixture was neutralized by adding 90 mg of Dowex 50 WX8 (H^+ form). After removal of the ion-exchange resin by filtration and rinsing with MeOH, the solvent was evaporated in vacuo and the deacetylated **8b** was taken up in 3 mL of H_2O.

Enzymatic Hydrolysis. To 2 mL of the solution of **8b** in 10 mL of 0.2 M citric acid—phosphate buffer (pH 5.2) was added 300 μL of Rohapect D5L. Incubation under N_2 was carried out over 16 h at 37 °C. The liberated aglycon 7 was extracted with Et_2O and subjected to HRGC and HRGC–MS analysis: R_i (DB-Wax) 2701; EIMS (70 eV) m/z (%) 208 (5), 193 (67), 175 (20), 157 (5), 147 (10), 131 (11), 121 (9), 105 (18), 91 (17), 77 (12), 65 (8), 55 (9), 43 (100). The specific rotation of 7 was determined to be $[\alpha]^{20}_D$ −77° ($CHCl_3$).

Table III. ^{13}C NMR Spectral Data (100 MHz, $CDCl_3$) of Acetylated Glycosides 8a and 9a as well as Reference Compounds

	isolated glycoside			ref compd	
	8a		**9a**	**7**[b]	A
position	δ[a]	DEPT	δ[a]	δ	δ
1	36.49	C	36.66	36.85	
2	45.62	CH_2	45.85	48.35	
3	72.84[d]	CH	72.80[f]	64.38	
4	39.15	CH_2	39.35	42.72	
5	130.67	C	131.02	132.37	
6	136.26	C	136.13	135.58	
7	132.64	CH	132.60	132.27	
8	142.02	CH	142.03	142.38	
9	198.30	C	198.34	198.59	
10	27.28	CH_3	27.31	27.24	
11[c]	28.72	CH_3	28.56	28.52	
12[c]	29.85	CH_3	29.91	30.03	
13	21.59	CH_3	21.58	21.54	
1′	98.81	CH	99.63		91.63
2′	71.54	CH	71.54		70.31
3′	72.78[d]	CH	72.87[f]		72.77[g]
4′	68.41[e]	CH	68.66		68.40[h]
5′	73.45	CH	71.84		73.95
6′	68.10	CH_2	62.29		67.52
1″	100.69	CH			100.64
2″	71.18	CH			70.95
3″	72.04[d]	CH			72.88[g]
4″	69.18[e]	CH			68.49[h]
5″	71.87[d]	CH			71.95
6″	61.93	CH_2			61.88
CO–CH_3	20.54–20.69	CH_3	20.60–20.73		20.53–20.75
*C*O–CH_3	169.10	C	169.20		168.77
	169.15	C	169.40		169.19
	169.37	C	170.31		169.37
	169.50	C	170.58		169.48
	170.09	C			170.05
	170.24	C			170.21
	170.52	C			170.60

[a] Chemical shifts were assigned on the basis of a DEPT experiment and comparison with reference substances: 7 [3-hydroxy-β-ionone. [b] (50 MHz spectrum, $CDCl_3$)]; A (β-D-gentiobiose octaacetate). [c–h] Interchangeable values in each column.

Partial Hydrolysis of 8b. To a further aliquot (1 mL) of the solution of **8b** were added 2 mL of H_2O and 50 mg of cation-exchange resin (Dowex 50WX, H^+ form). The sample was stirred under N_2 at 80 °C for 1 h. After filtration, the water phase was lyophilized, per-O-methylated according to the method of Finne et al. (1980), and subjected to HRGC and HRGC–MS analyses. These analyses revealed a main product possessing the same retention time and identical MS data as found for authentic per-O-methylated β-D-gentiobiose: R_i (DB-5) 2430 and 2473 (two anomers); EIMS (70 eV) m/z (%) 353 (3), 279 (11), 219 (12), 187 (7), 131 (5), 101 (36), 88 (100), 75 (55), 71 (22), 45 (20).

Degradation of 7 at Natural pH Conditions of Quince Fruit. Approximately 5 mg of aglycon 7 was diluted with 30 mL of 0.2 M citric acid—phosphate buffer (pH 3.5) and subjected to a simultaneous distillation–extraction (SDE) treatment, using the SDE head described by Schultz et al. (1977). The organic layer was dried over anhydrous Na_2SO_4 and carefully concentrated (Vigreux column) prior to HRGC and HRGC–MS analyses.

Reference Compounds. 3-Hydroxy-β-ionone (7) was prepared by DDQ oxidation of 3-hydroxy-β-ionol (Mori, 1974) and showed the following chromatographic and spectral data: HRGC R_i (DB-Wax) = 2701, R_i (DB-5) = 1701; UV λ_{max} 280 nm; EIMS (70 eV) identical with natural product 7; ^1H NMR (200 MHz, $CDCl_3$, J in Hz) δ 1.08 and 1.09 (6 H, 2s, H_3C11 and H_3C12), 1.46 (1 H, dd, J = 12.4, 12.0, H_a-C2), 1.75 (3 H, s, CH_3-C13), 1.78 (1

H, ddd, J = 12.4, 3.7, 2.0, H_b-C2), 2.0–2.2 (2 H, HO-C3 and partly obscured H_a-C4), 2.28 (3 H, s, H_3Cl0), 2.41 (1 H, dd, J = 17.2, 5.5, H_b-C4), 3.97 (1 H, m, H-C3), 6.08 (1 H, d, J = 16.4, H-C8), 7.19 (1 H, d, J = 16.4, H-C7); ^{13}C NMR, see Table III. The syntheses of (*E*)-3,4-didehydro-β-ionone (**10**) (Henbest, 1951) and 1,1,6-trimethyl-1,2-dihydronaphthalene (**11**) (Strauss et al., 1987) were carried out according to the methods cited.

Capillary Gas Chromatography (HRGC). For HRGC a Carlo Erba Fractovap 4160 as well as a Hewlett-Packard 5890 gas chromatograph equipped with FID was used. Two types of WCOT fused silica capillary columns were employed: (a) J&W DB-Wax (30 m × 0.25 mm i.d., film thickness 0.25 μm); (b) J&W DB-5 (30 m × 0.25 mm i.d., film thickness 0.25 μm). Split injection (1:20) was used. The temperature programs were 3 min isothermal at 50 °C and then increased at 4 °C/min to 240 °C (a) and 1 min isothermal at 60 °C and then increased at 5 °C/min to 300 °C (b). The flow rates for the carrier gas were 2.0 mL/min of He, for the makeup gas 30 mL/min N_2, and for the detector gases 30 mL/min of H_2 and 300 mL/min of air, respectively. The injector temperature was kept at 220 °C and the detector temperature at 250 (a) and 300 °C (b), respectively.

Capillary Gas Chromatography–Mass Spectrometry (HRGC–MS). A Varian Aerograph 1440 gas chromatograph equipped with a split injector was combined by direct coupling to a Finnigan MAT 44 mass spectrometer with PCDS data system. The same type of columns as mentioned above for HRGC analysis were used. The conditions were as follows: temperature programs, (a) from 40 to 240 °C at 4 °C/min, (b) from 50 to 300 °C at 5 °C/min; carrier gas flow rate 2.5 mL/min of He; temperature of ion source and all connection parts, 200 °C; electron energy, 70 eV; cathodic current, 0.7 mA.

Thermospray Mass Spectrometry. For thermospray analyses a Finnigan MAT 4500 mass spectrometer equipped with a thermospray–bypass interface jet 220 (0.05 M NH_4Ac) was used. Positive ions over a range m/z 123–900 were scanned.

RESULTS AND DISCUSSION

Isolation of Glycosides 8a and 9a. A glycosidic extract from quince fruit was isolated by passing neutralized quince juice through a column of XAD-2 resin (Günata et al., 1985). After elution with methanol, the glycosidic fraction was subjected to a prefractionation using rotation locular countercurrent chromatography (RLCC; Snyder et al., 1984). In the separated RLCC fractions the precursor compounds were screened by analysis of the enzymatically liberated aglycons. The target compound, 3-hydroxy-β-ionone (**7**), could be detected in combined RLCC fractions 31–40 (80%) and also in the stationary phase (20%), which was left in the RLCC apparatus after 50 fractions had been collected. For the further purification of the conjugates of **7**, combined RLCC fractions 31–40, as well as the material left in the stationary phase, were concentrated, acetylated with acetanhydride/pyridine, and subjected to flash chromatography on SiO_2. In the case of glucoside **9a** a final purification was achieved by preparative HPLC on SiO_2.

Characterization of Disaccharide Glycoside 8a. The characterization was made by MS as well as ^{1}H and ^{13}C NMR spectroscopy. Thermospray MS analysis yielded a strong pseudomolecular ion at m/z 844 ($M^+ + NH_4$, molecular mass 826, $C_{39}H_{54}O_{19}$), thus indicating a disaccharide as sugar moiety. From both ^{1}H (cf. Table I) and ^{13}C NMR data (cf. Table III) the presence of a disaccharide moiety was confirmed. The ^{1}H NMR spectrum exhibited two doublets at δ 4.58 (J = 8.0 Hz) and 4.62 (J = 8.0 Hz) for two anomeric protons, indicating the presence of two β-glycosidic linkages. Furthermore, from the ^{13}C NMR data obtained for the sugar moiety, a coincidence with data published for per-O-acetylated β-gentiobiose (Bock et al., 1984) was evident. Authentic β-gentiobiose was therefore acetylated, and the ^{13}C NMR data for the reference (cf. Table III) were in good agreement with the

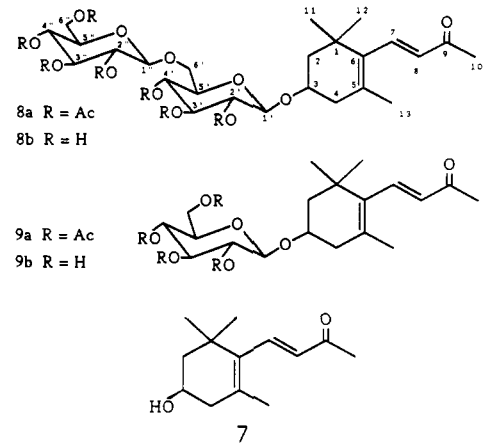

Figure 1. Structures of the newly identified ionone glycosides **8** and **9**, as well as the enzymatically liberated aglycon (*R*)-3-hydroxy-β-ionone (**7**).

data obtained for the unknown sugar moiety. The presence of β-D-gentiobiose was finally proved by a partial hydrolysis of the deacetylated glycoside **8b** under mild conditions according to the method described by Shipchandler and Soine (1968); i.e., gentle hydrolysis with a cation-exchange resin in the acid cycle afforded, after lyophilization and per-O-methylation (Finne et al., 1980), two anomers of permethylated β-D-gentiobiose as major compounds.

Finally, an enzymatic hydrolysis of **8b** was carried out. This treatment liberated 3-hydroxy-β-ionone (**7**) as sole product. Due to the specific rotaton of $[\alpha]^{20}_D$ −77°, **7** was assigned as the *R* enantiomer (Mori, 1973). With regard to the configuration of the hydroxy group, natural hydroxyketone **7** has the same configuration as can be found in a series of ubiqitous carotenoids, such as zeaxanthine. This finding supports the assumption that **7** is formed by an oxidative degradation of carotenoids (Enzell, 1985). Compound **7** has previously been reported as free aroma constituent of tobacco (Fujimori et al., 1974), kudzu oil (Shibata et al., 1978), and *Lycium chinense* (Sannai et al., 1983, 1984). In the latter case the authors described the odor of **7** as being "oily, dry, powdery, woody" (recognition threshold 1×10^{-4}). Besides these identifications as a free volatile constituent, bound forms of **7** have recently been detected in raspberry (Pabst et al., 1991) and several *Prunus* species (Krammer et al., 1991).

Characterization of Glucoside 9a. The second conjugate of ketone **7** did not elute under conditions used for the RLCC separation and was therefore recovered from the stationary phase. Acetylation and subsequent liquid chromatographic purification (flash chromatography/HPLC) provided pure **9a**. Thermospray MS analysis indicated a molecular mass of 538, which led to the assumption that **9a** was a monosaccharide glycoside. From ^{1}H and ^{13}C NMR spectral interpretation **9a** was then identified as the β-D-glucopyranoside of 3-hydroxy-β-ionone. Like the corresponding disaccharide **8**, this glucoside of **7** is reported as a natural product for the first time. The structures of both glycosides are outlined in Figure 1.

Biomimetic Degradation Studies. In a further series of experiments the enzymatically liberated aglycon **7** was subjected to an atmospheric SDE at natural pH conditions (pH 3.5) of quince juice. Besides a number of still unknown trace components, HRGC and HRGC–MS analyses (cf. Figure 2) revealed the formation of three major products, i.e., (*E*)-3,4-didehydro-β-ionone (**10**), 1,1,6-trimethyl-1,2-dihydronaphthalene (**12**), and (*Z*)-3,4-didehydro-β-ionone (**11**) (tentative). The latter compound gave an almost

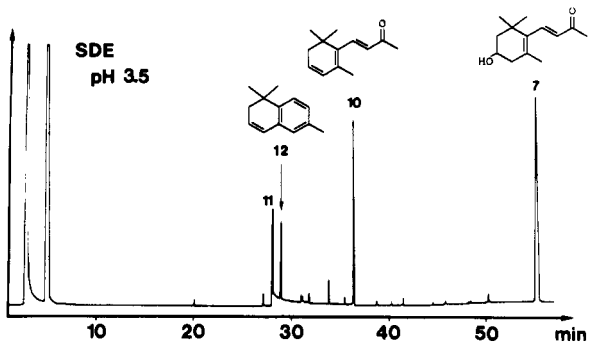

Figure 2. HRGC separation (J&W DB-Wax, 30 m × 0.25 mm i.d., film thickness 0.25 μm) of steam volatile products obtained by SDE treatment (1 h, pH 3.5) of aglycon 7.

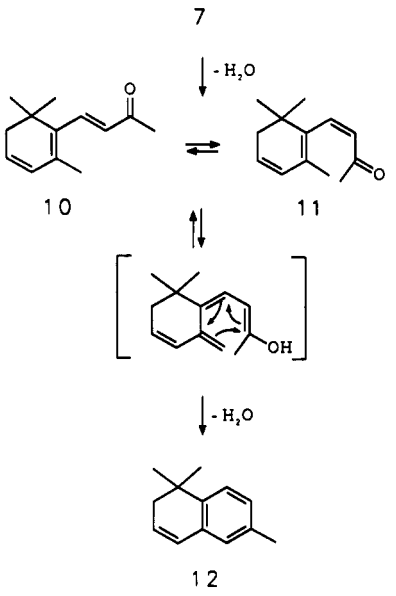

Figure 3. Proposed pathway for TDN (12) formation from 3-hydroxy-β-ionone (7).

identical MS spectrum as obtained for the *E* isomer **10**. A proposed pathway for TDN (**12**) formation from hydroxyketone **7** is outlined in Figure 3. Confirmation of the structure of **11** and the identification of the minor degradation products of **7** will remain the subject for continuing research.

CONCLUSIONS

From the early work of Williams et al. (1982) it is known that monoterpenoid flavor compounds exist in different glycosidically bound forms in grape juice and wine. Also for the C_{13} norterpenoid volatiles in wine a generation from multiple bound precursor forms was recently observed (Winterhalter et al., 1990). The same situation is now apparent for quince fruit, where at least two different sugar moieties, i.e. β-D-gentiobiose and β-D-glucose, are implicated in conjugating C_{13} norterpenoid flavor compounds. Such glycosides often constitute an important reserve of covered flavor. However, in the case of 3-hydroxy-β-ionone conjugates **8** and **9**, heat treatment at natural pH conditions may result in a negative flavor impression, due to the formation of the known off-flavor-causing hydrocarbon 1,1,6-trimethyl-1,2-dihydronaphthalene (**12**) (Simpson, 1978).

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