Free and Bound C_{13} Norisoprenoids in Quince (*Cydonia oblonga*, Mill.) Fruit

Peter Winterhalter and Peter Schreier*

The constituents of quince fruit (*Cydonia oblonga*, Mill.) juice were isolated by solvent extraction (pentane–dichloromethane, 2:1). In the polar fractions obtained by liquid chromatography of the extract on silica gel, capillary gas chromatography (HRGC) and capillary gas chromatography–mass spectrometry (HRGC–MS) revealed the occurrence of C_{13} norisoprenoids identified in quince fruit for the first time: 4-hydroxy-β-ionol, 3-hydroxy-β-ionol, 4-hydroxy-β-ionone, 4-oxo-β-ionol, 3-hydroxy-β-ionone, 5,6-dihydroxy-β-ionone, and dehydrovomifoliol. Enzymatic hydrolysis of a glycosidic extract obtained from quince fruit juice by adsorption on Amberlite XAD-2 resin and subsequent methanol elution led to the identification of 3-hydroxy-β-ionol as major product. Additionally, the following aglycons were found: 3-hydroxy-β-ionone, 3-hydroxy-7,8-dihydro-β-ionol, vomifoliol, 3-oxo-α-ionol, and 7,8-dihydrovomifoliol. On the basis of these results, the potential precursors of industrially attractive quince fruit constituents such as vitispiranes, bicyclo[4.3.0]nonane derivatives, 3,4-didehydro-β-ionol, megastigma-4,6,8-trien-3-ones, and theaspirones are discussed.

Norisoprenoids are known to originate from carotenoids (Enzell, 1985). Preferable cleavage of 6,7, 7,8, 8,9, and 9,10 bonds leads to flavor components with 9, 10, 11, and 13 carbon atoms, respectively. In the intact plant, carotenoid degradation is likely to be effected by oxygenase systems and by photooxygenations and other nonenzymatic oxidations (Enzell, 1981). However, our knowledge about the immediate precursors of the norisoprenoid compounds and the reactions by which they are formed is rather scarce.

In the past, carotenoid degradation has been particularly studied in plants in which norisoprenoids are considered to represent essential flavor constituents such as, e.g., tobacco (Enzell et al., 1977) and tea (Yamanishi, 1981). However, there are also other plants in which norisoprenoids contribute to the overall flavor impression. One of these is quince fruit (*Cydonia oblonga*, Mill.). In steam-distilled quince fruit oil, Tsuneya et al. (1983) and Ishihara et al. (1986) have already identified a number of C_{13} norisoprenoids: (i) the isomeric theaspiranes and vitispiranes; (ii) 2,2,6,7-tetramethylbicyclo[4.3.0]nona-4,7,9(1)-triene, 2,2,6,7-tetramethylbicyclo[4.3.0]nona-4,9-(1)-dien-8-ol, and 3,4-didehydro-β-ionol; (iii) the isomeric megastigma-4,6,8-trien-3-ones; (iv) the theaspirones. In this paper, the results of our studies on the precursors of these industrially attractive flavor compounds are represented.

EXPERIMENTAL SECTION

Fruits. Fresh ripe quince fruits (*C. oblonga*, Mill.) were available from the local market.

Isolation of Free C_{13} Norisoprenoids. The isolation was carried out as previously described for the theaspirane precursor 1 using solvent extraction and liquid chromatographic preseparation on silica gel (Winterhalter and Schreier, 1988).

Isolation of Bound C_{13} Norisoprenoids. To 1 kg of fruit (cut, seeds removed) were added 500 mL of 0.2 M phosphate buffer (pH 7.0) and 35 g of glucono-δ-lactone. After homogenizing (Braun blender) and pressing (Hafico press), a clear juice (1.2 L) was obtained. The isolation of bound C_{13} compounds was performed on Amberlite XAD-2 resin according to the method of Gunata et al. (1985). Methanol was used as eluting solvent. Half of the methanol eluate was concentrated and subjected to SDE (pH 3.7) as described below.

Enzymatic Hydrolysis. The other half of the methanol fraction was carefully concentrated in vacuo to dryness and dissolved in 100 mL of 0.2 M phosphate buffer (pH 5.0). The solution was extracted with diethyl ether to ensure removal of any volatiles prior to enzymatic hydrolysis. Almond β-glucosidase (20 mg) was added and incubated for 72 h at 40 °C. Liberated aglycons were extracted with diethyl ether and subjected to HRGC and HRGC–MS analysis.

Simultaneous Distillation Extraction (SDE). SDE was performed with pentane–diethyl ether (1:1, v/v) over 2 h using the SDE head described by Schultz et al. (1977). SDE of 3-hydroxy-β-ionol (**4**): Five milligrams of **4** (prepared by the method of Isoe et al. (1971)) was dissolved in 250 mL of water (pH 3.7) and subjected to SDE. The extract was dried over anhydrous sodium sulfate and carefully concentrated to 1 mL on a Vigreux column.

High-Vacuum Distillation of Triol 11 and Hydroxytheaspirane (13). Five milligrams of **11** (prepared by the method of Strauss et al. (1986)) in 1 L of water (pH 3.5) was high-vacuum distilled at 40–50 °C (Idstein and Schreier, 1985) and the aqueous distillate as well as the distillation residue were each extracted with pentane–dichloromethane (2:1, v/v) over 24 h (Drawert and Rapp, 1968). The extracts were dried over anhydrous sodium sulfate and carefully concentrated to 1 mL on a Vigreux column (45 °C). Five milligrams of **13** was treated analogously.

Capillary Gas Chromatography (HRGC) and Coupled HRGC Techniques (HRGC–MS; HRGC–FTIR). HRGC, HRGC–MS, and HRGC–FTIR were carried out on a J&W fused silica DB-5 capillary column (30 m × 0.259 mm (i.d.), df = 0.25 μm). Conditions and instrumentation used were as described previously (Winterhalter and Schreier, 1988).

Nuclear Magnetic Resonance Spectroscopy. ^1H NMR spectra were recorded at 200 MHz on a Bruker AC-200 instrument, with $CDCl_3$ as solvent and Me_4Si as reference standard.

Reference Compounds. **3**, **5**, **6**, and **24** were donated samples. Preparation of 3-hydroxy-β-ionol (**4**) was performed by hydroboration of 3,4-didehydro-β-ionyl acetate (Isoe et al., 1971). 3,4-Didehydro-β-ionol (**16**) was prepared

Lehrstuhl für Lebensmittelchemie, Universität Würzburg, Am Hubland, D-8700 Würzburg, West Germany.

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by the method of Henbest (1951) and showed the following data: R_t 1413; MS m/z (%) 43 (40), 77 (9), 91 (20), 105 (11), 119 (100), 121 (20), 134 (10), 144 (6), 159 (18), 174 (5), 177 (3), 192 (24); FTIR (vapor phase; ν, cm^{-1}) 3648 (OH), 3042, 2965, 2924, 2874, 2824, 1465, 1380 and 1364 (*gem*-dimethyl), 1246, 1134, 1080, 1039, 969 (–CH=CH–, tr), 717 (–CH=CH–, cis); ^1H NMR (δ, TMS) 0.98 and 0.99 (2 × 3 H, 2 s, 2 CH_3 C1), 1.33 (3 H, d, J = 6.5 Hz, CH_3 C9), 1.81 (3 H, s, CH_3 C5), 2.0 (1 H, br, s, OH), 2.05 (2 H, d, J = 4.5 Hz, 2 H C2), 4.39 (1 H, quint, J = 6.5 Hz, H C9), 5.62 (1 H, dd, J = 16, 6.5 Hz, H C8), 5.7 (1 H, dt, J = 9.5, 4.5 Hz, H C3), 5.80 (1 H, d, J = 9.5 Hz, H C4), 6.05 (1 H, d, J = 16 Hz, H C7). Acetylation with acetic anhydride–pyridine afforded the acetate derivative of **16**: R_t 1531; MS, m/z (%) 43 (100), 55 (10), 71 (10), 91 (13), 105 (15), 119 (15), 131 (11), 133 (11), 144 (12), 159 (57), 174 (8), 192 (2), 234 (10); FTIR (vapor phase; ν, cm^{-1}) 3039, 2964, 2930, 2872, 2828, 1758, 1462, 1373, 1235, 1049, 969, 717. Hydroboration of acetylated **16** was performed according to the method of Kienzle and Minder (1975). After deacetylation at room temperature with dilute $NaOCH_3$ in methanol, crude diol **4** was obtained which was purified by liquid chromatography on silica gel using a pentane–diethyl ether gradient: R_t 1639; MS, m/z (%) 43 (100), 55 (36), 69 (25), 77 (31), 91 (50), 105 (44), 119 (58), 121 (44), 133 (33), 144 (14) 159 (44), 174 (8), 177 (5), 192 (1), 210 (3); FTIR (vapor phase; ν, cm^{-1}) 3652 (sec OH), 2977, 2931, 2870, 1464, 1373, 1247, 1126, 1047, 971 (–CH=CH–, tr); ^1H NMR (δ, TMS) 1.04 (6 H, 2 s, 2 CH_3 C1), 1.32 (3 H, d, J = 6.8 Hz, CH_3 C9), 1.70 (3 H, s, CH_3 C5), 1.9 (2 H, br, s, OH), 4.0 (1 H, m, H C3), 4.36 (1 H, quint, J = 6.8 Hz, H C9), 5.51 (1 H, dd, J = 16, 6,8 Hz, H C8), 6.02 (1 H, d, J = 16 Hz, H C7).

Oxidation of **4** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in dioxane (Mori, 1973) gave 3-hydroxy-β-ionone (**7**): R_t 1701; MS, m/z (%) 43 (100), 55 (6), 65 (6), 79 (8), 91 (12), 105 (11), 131 (7), 147 (11), 157 (5), 175 (30), 190 (4), 193 (47), 208 (4); FTIR (vapor phase; ν, cm^{-1}) 3651 (sec OH), 2969, 2929, 1691 (C=O), 1612 (C=C), 1459, 1366, 1242, 1041 (C—O), 979 (–CH=CH–, tr).

Hydrogenation of 4. To a solution of 40 mg of **4** in 5 mL of methanol was added 10 mg of Pd on $BaSO_4$ (5%) and the resultant mixture hydrogenated at room temperature and atmospheric pressure for 20 min. Filtration of the catalyst and liquid chromatographic purification on silica gel (pentane–diethyl ether gradient) yielded **22**: R_t 1669; MS, m/z (%) 41 (51), 43 (76), 45 (25), 55 (34), 67 (28), 69 (32), 77 (13), 79 (21), 81 (29), 91 (19), 93 (45), 95 (26), 105 (29), 107 (19), 109 (20), 119 (67), 121 (100), 123 (14), 136 (40), 137 (29), 153 (11), 154 (7), 161 (29), 176 (2), 179 (7), 194 (4), 212 (6); FTIR (vapor phase; ν, cm^{-1}) 3654 (sec OH), 2969, 2926, 1471, 1378 (*gem*-dimethyl), 1238, 1119, 1042.

13 (4 isomers) was prepared by reduction of 100 mg of theaspirone (**28**) and showed the following data: R_t 1518; MS, m/z (%) 43 (100), 55 (61), 69 (51), 77 (31), 93 (57), 98 (37), 107 (22), 121 (35), 125 (20), 136 (27), 154 (73), 177 (24), 192 (M – H_2O, 38) (isomer I). R_t 1526; MS m/z (%) 43 (100), 55 (55), 69 (44), 77 (25), 93 (47), 98 (35), 107 (17), 121 (22), 125 (18), 135 (18), 154 (58), 177 (12), 192 (M – H_2O, 21) (isomer II). R_t 1529; MS, m/z (%) 43 (93), 55 (53), 69 (52), 77 (27), 93 (58), 98 (39), 107 (21), 121 (31), 125 (24), 135 (26), 154 (100), 177 (23), 192 (M – H_2O, 48) (isomer III). R_t 1545; MS, m/z (%) 43 (83), 55 (49), 69 (47), 93 (51), 98 (34), 107 (20), 121 (29), 125 (26), 135 (24), 154 (100), 177 (24), 192 (M – H_2O, 44) (isomer IV).

5,6-Dihydroxy-β-ionone (**8**) (Endo et al., 1979), dehydrovomifoliol (**9**) (Lehmann et al., 1973), megastigma-5,7,9-trien-3-ol (**17**) (Bütikofer and Eugster, 1983), isomeric megastigma-4,6,8-trien-3-ols (**18**) (Rowland, 1966), vomifoliol (**23**), and 7,8-dihydrovomifoliol (**25**) (Heckman and Roberts, 1969) were prepared by methods cited. **8**: R_t 1736; MS, m/z (%) 43 (100), 55 (26), 69 (28), 71 (17), 97 (16), 98 (18), 109 (34), 123 (38), 135 (8), 139 (7), 165 (7), 208 (M – H_2O, 4). **9**: R_t 1800; MS, m/z (%) 41 (24), 43 (91), 55 (18), 69 (12), 95 (12), 124 (100), 149 (6), 166 (M – 56, 15). **17**: R_t 1439; MS m/z (%) 41 (73), 43 (40), 57 (28), 65 (21), 79 (33), 91 (79), 105 (71), 117 (50), 121 (19), 131 (35), 133 (100), 144 (11), 159 (41), 174 (4), 177 (1), 192 (31). **18**: R_t 1509, 1512, 1534, 1537, (four isomers with identical MS data); MS m/z (%) 41 (36), 55 (24), 65 (17), 77 (28), 91 (41), 105 (33), 117 (29), 119 (29), 128 (26), 129 (35), 131 (36), 144 (35), 159 (100), 174 (33), 177 (9), 192 (10). **23**: R_t 1801; MS, m/z (%) 43 (54), 55 (13), 69 (6), 79 (16), 94 (6), 107 (5), 111 (5), 124 (100), 135 (8), 150 (10), 168 (6), 206 (3), 224 (0.5). **25**: R_t 1866; MS, m/z (%) 43 (71), 55 (40), 68 (42), 72 (28), 96 (34), 110 (100), 111 (66), 125 (25), 152 (60), 153 (27), 170 (31), 183 (1), 218 (1), 226 (0.5).

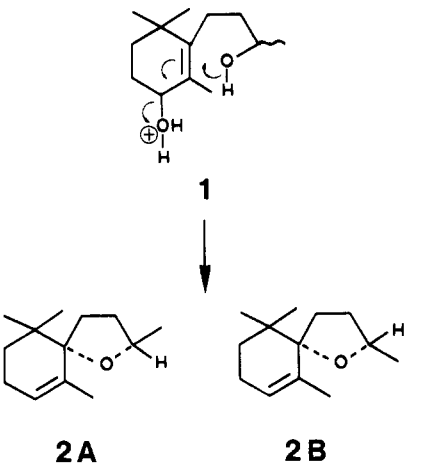

Figure 1. Proposed mechanism of theaspirane **2A/2B** formation from 4-hydroxy-7,8-dihydro-β-ionol (**1**) as prototropic dehydration according to Ohloff et al. (1964).

RESULTS AND DISCUSSION

Theaspirane Precursor and Related Norisoprenoids. In our recent study of quince fruit volatiles, 4-hydroxy-7,8-dihydro-β-ionol (**1**) (Figure 1) was identified as precursor of the isomeric spiro ethers **2A/2B** (Winterhalter and Schreier, 1988) The mechanism of theaspirane formation from the natural precursor **1** has been explained as prototropic dehydration of an allyl 1,6-diol (Ohloff et al., 1964). Diol **1** had been isolated from quince fruit pulp by solvent extraction. With use of this isolation technique and subsequent preseparation by liquid chromatography on silica gel, additionally, the C_{13} norisoprenoids outlined in Figure 2 were identified by HRGC and HRGC–MS in the polar silica gel fractions. As shown from Figure 2, 4-hydroxy-β-ionol (**3**), 3-hydroxy-β-ionol (**4**), 4-hydroxy-β-ionone (**5**), 4-oxo-β-ionol (**6**), 3-hydroxy-β-ionone (**7**), 5,6-dihydroxy-β-ionone (**8**), and dehydrovomifoliol (**9**) were found in quince fruit for the first time. Among them, compounds **3** and **4** were determined as major constituents (100–200 μg/kg), whereas for all the other C_{13} norisoprenoids amounts of 10–30 μg/kg were estimated. In the group of norisoprenoids, two components **A** and **B** were isolated whose structures could not be elucidated. They showed the following mass spectral data (m/z, %): 43 (100), 138 (92), 82 (63), 96 (49), 41 (46), 55 (41), 109 (27), 119 (26) (A); 43 (100), 119 (53), 121 (41), 41 (27), 107 (27), 93 (26), 136 (23), 152 (18) (B).

The norisoprenoids newly identified in quince fruit have been rarely identified in nature. Compounds **3**, **5**, and **6**

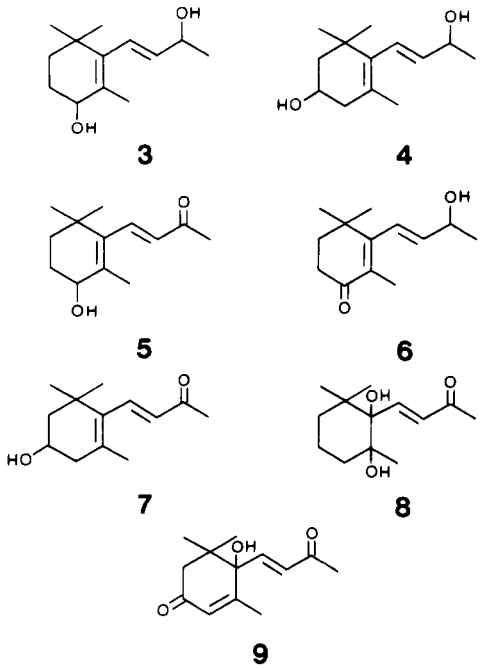

Figure 2. Structures of C_{13} norisoprenoids identified in quince fruit for the first time.

have been detected in *Osmanthus absolue* (Kaiser et al., 1978); diol **3** has been additionally found in tobacco (Weeks and Seltmann, 1986). Diol **4** has only been detected in tobacco (Fujimori et al., 1975; Weeks and Seltmann, 1986), whereas compound **7** has been previously characterized from tobacco (Fujimori et al., 1975), *Lycium chinense* (Sannai et al., 1983), and *Pueraria lobata* (Shibata et al., 1978) The identification of free **8** has been performed from tea (Sannai et al., 1983), and glycosidically bound **9** has been detected in *Aeginetia indica* (Endo et al., 1979) and *Rehmannia glutinosa* roots (Yoshikawa et al., 1986). Dehydrovomifoliol (**9**) has been found in kidney bean roots (Takasugi et al., (1973), tea (Etoh et al., 1980), and, recently, grapes (Strauss et al., 1987).

Vitispirane Precursor. In Figure 3, the results previously obtained on vitispirane formation by Strauss et al. (1984, 1986) are outlined. Heat treatment of triol **10** in acidic solution has given rise to various degradation products. As major product, the rearranged, more stable triol **11** has been isolated. Additionally to the reactions outlined in Figure 3, it has to be pointed out that heating triol **11** under acidic conditions gave the same composition of degradation products as obtained from triol **10**. Since in grapes, as studied by the authors, only vitispiranes **12A/12B** could be identified as major products, the occurrence of a free triol seemed to be unlikely. Indeed, triol **11** has been found only after enzymatic hydrolysis of a glycosidic extract from grapes. Furthermore, it is important to know that chemical hydrolysis of bound **11** has been achieved only under strong acidic conditions, i.e. at pH 1.0 and not at native pH 3.0. Thus, triol **11** did not seem to be the natural precursor of **12A/12B**.

Apart from triol **11** hydroxytheaspirane (**13**) has been also found as an aglycon after enzymatic treatment of the glycosidic fraction. Acid hydrolysis of **13** under mild conditions yielded **12A/12B** as the only significant products. Thus, in the opinion of Strauss et al. (1984, 1986), the most probable structure for the precursor of vitispiranes is the glycoside of spiro ether **13**.

In analogy to the above suggested theaspirane formation, it was our aim to elucidate the generation of hydroxytheaspirane (**13**) from the synthesized triol **11** (Figure 4). Under mild conditions the cyclization of **11** to spiro ethers **13** as the preferable reaction was expected. Therefore, high-vacuum distillation at pH 3.5 (40 °C) with subsequent extraction (HVD/SE) of **11** was performed. Unfortunately, **13** was found to be not steam-distillable; consequently, the distillation residue was studied. However, under the mild HVD conditions no significant degradation of triol **11** occurred. The stabilitiy of **11** was also shown during its storage at pH 3.5 over 6 days; again, no significant formation of **13** was observed. Summarizing, it has to be stressed that the analogy to theaspirane formation was not given for vitispirane because of the different chemical reactivity of triol **11**. At present, the pathway shown in Figure 5 seems to be logical for vitispirane formation: There is a bound form of triol **11** in which—as demonstrated by Strauss et al. (1984, 1986)—the glycosidic bonding is resistant to heating in dilute acidic medium. The only reaction that might occur is, in analogy to theaspirane formation, the cyclization to the spiro ether. In this new glycoside, the allylic bond facilitates removal of the sugar moiety, and at least vitispiranes **12A/12B** are formed as sole products.

Precursors of Bicyclo[4.3.0]nonanes and 3,4-Didehydro-β-ionol. The formation of compounds **14–16** under simultaneous distillation-extraction conditions (Schultz et al., 1977) of quince fruit juice has been recently reported (Winterhalter et al., 1987). In smaller amounts, several isomers of **14** as well as an isomer of **15** have been

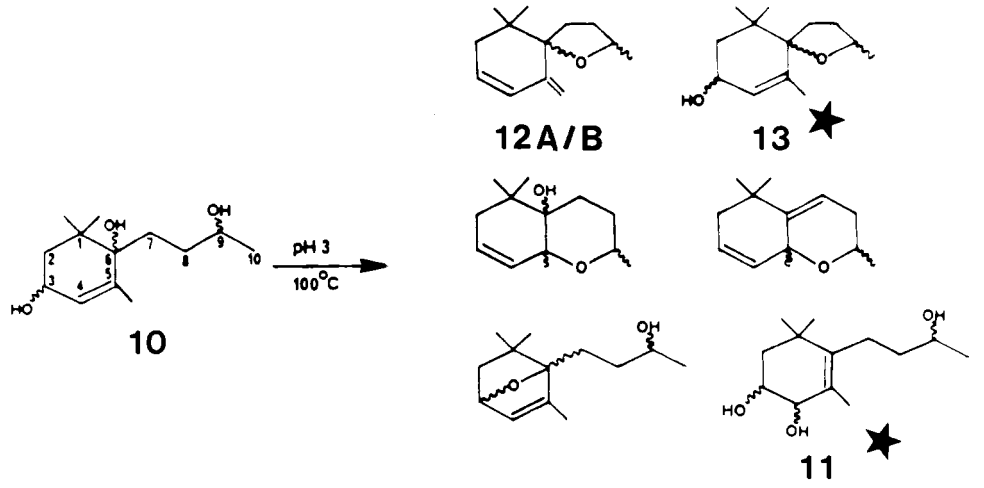

Figure 3. Results previously obtained on vitispirane **12A/12B** formation (scheme modified according to Strauss et al. (1984, 1986)). Glycosidically bound compounds indicated by stars.

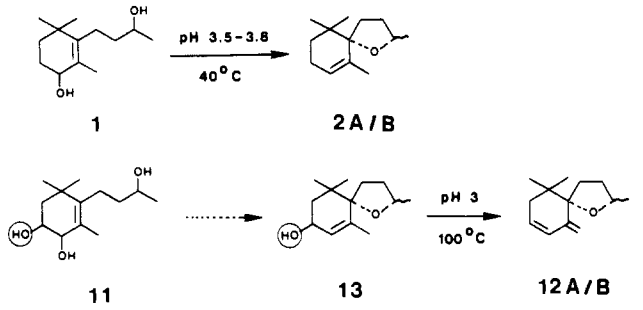

Figure 4. Suggested generation of vitispiranes 12A/12B from triol 11 in analogy to theaspirane 2A/2B formation from diol 1.

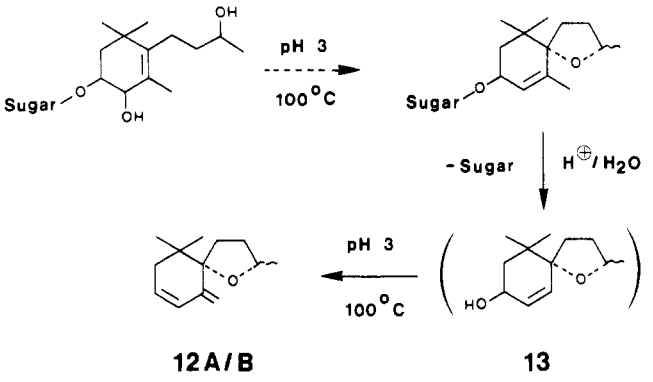

Figure 5. Proposed pathway for vitispirane 12A/12B formation based on the results of Strauss et al. (1984, 1986) and findings obtained in the present study.

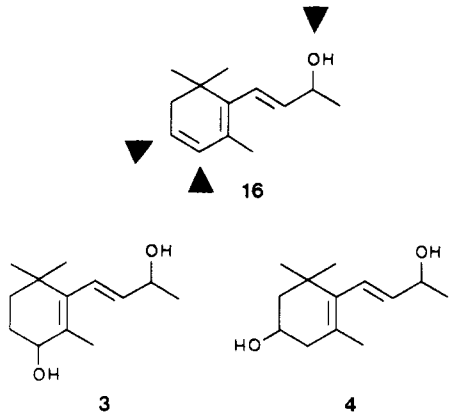

Figure 6. Potential precursors of 16; glycoside of 16 as well as diols 3 and 4. Positions preferably derivatized are marked by arrows.

also detected. At the same time, it could be demonstrated that 16 has a key role as flavor intermediate originating from a still unknown precursor. Our reflections on the structure of this precursor are shown in Figure 6. First of all, the OH group of 16 might be glycosidically bound. Futhermore, the 3- and 4-hydroxylated β-ionol derivatives 3 and 4 have to be considered. Theoretically, simple dehydration leads to the double bond in the 3,4-position.

With both 3 and 4, model reactions were carried out. First of all, 3 was subjected to SDE at pH 3.7. However, a completely different composition of products as found in heat-treated quince fruit juice was observed. Thus, diol 3 had to be excluded as precursor of compounds 14–16.

The results obtained after SDE at pH 3.7 of diol 4 are outlined in Figure 7. In these model reactions, compounds 14–16 as well as unidentified isomers of 14 and 15 were found in amounts very similar to the natural flavor composition of heat-treated quince fruit. Additionally, however, further degradation products of 4 were identified, i.e.

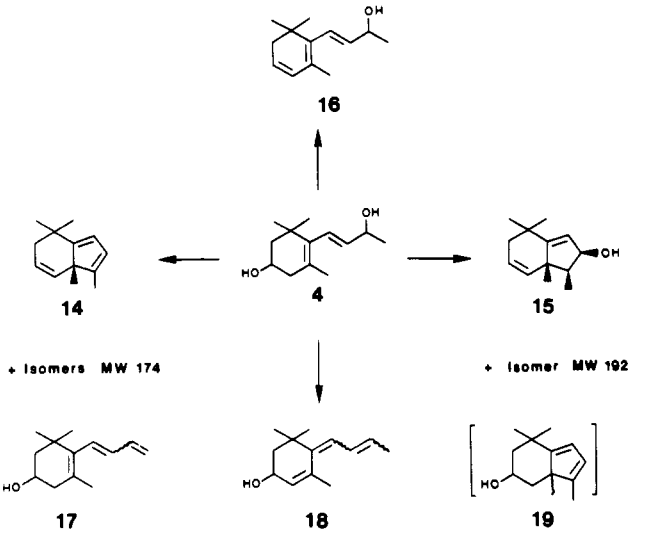

Figure 7. Products formed from 3-hydroxy-β-ionol (4) under SDE conditions at pH 3.7.

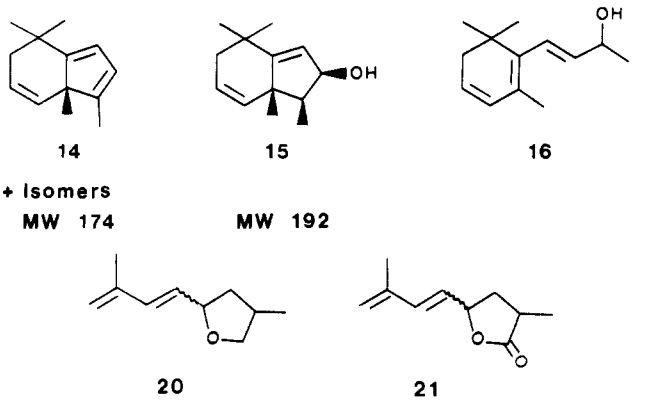

Figure 8. Products chemically formed from a glycosidic extract from quince fruit under SDE conditions at pH 3.7.

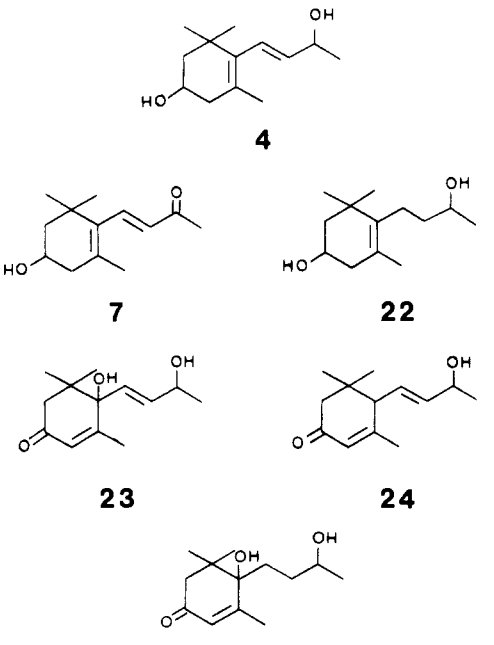

Figure 9. Structures of C_{13} aglycons identified after emulsin hydrolysis of quince fruit glycosides.

the norisoprenoids 17 and 18 and the tentatively assigned bicyclic alcohol 19 (Figure 7). These substances were not identified in quince fruit juice. As for the precursor

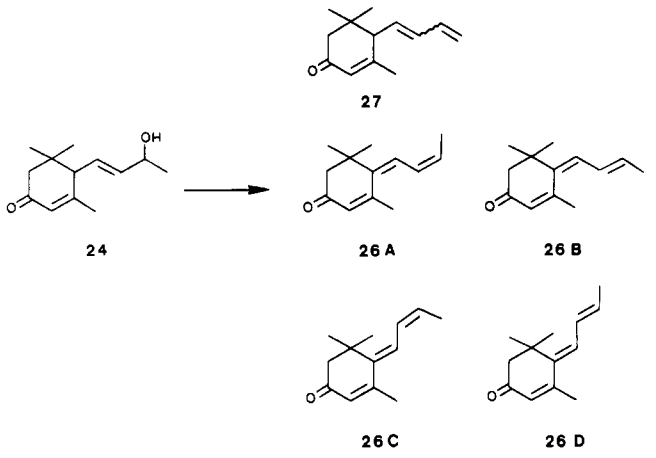

Figure 10. Degradation of 3-oxo-α-ionol (**24**) to the isomeric megastigmatrien-3-ones **26A–26D** and **27** (Aasen et al., 1972; Brunke, 1986; Strauss et al., 1987).

function of **4**, it therefore had to be concluded that this diol could not be the natural precursor of the mentioned quince fruit constituents. In analogy to the results of the model reactions shown in Figure 7, also in quince fruit, compounds **17–19** had to be found. Nevertheless, as for the C_{13} components from quince fruit, preferable dehydration in position 3 was observed, giving rise to a double bond in the 3,4-position.

The explanation of this finding could be that the diol **4** also occurs in a bound form in quince fruit. Thus, an isolation of quince fruit glycosides was performed. First of all, the glycosidic extract was subjected to SDE at pH 3.7, and the volatiles formed under these conditions were analyzed by HRGC and HRGC–MS. The results obtained are shown in Figure 8. As seen from Figure 8, the same C_{13} degradation products were obtained as in heat-treated quince fruit juice. In addition, marmelo oxide (**20**) (Tsuneya et al, 1983) and marmelo lactone (**21**) (Tsuneya et al., 1980) were detected.

In the following experiment, enzymatic hydrolysis of the glycosidic extract of quince fruit was carried out. As the major aglycon liberated by almond β-glucosidase, diol **4** was identified. At present, the exact structure of the sugar moiety is still unknown. Besides the main component **4**, enzymatic hydrolysis revealed the occurrence of some other glycosidically bound norisoprenoids in quince fruit, i.e. compound **7**, 3-hydroxy-7,8-dihydro-β-ionol (**22**), vomifoliol (**23**), 3-oxo-α-ionol (**24**), and 7,8-dihydrovomifoliol (**25**) (Figure 9).

Precursor of Megastigma-4,6,8-trien-3-ones. 3-Oxo-α-ionol (**24**) is well-known to be degraded in acidic medium to the megastigma-4,6,8-trien-3-ones **26A–26D** and the isomeric ketone **27** (Aasen et al., 1972; Brunke and Tumbrink, 1986; Strauss et al., 1987) (Figure 10). The four isomeric megastigma-4,6,8-trien-3-ones were all found among the quince fruit constituents.

Precursor of Theaspirones. In Figure 11, the different steps of chemical synthesis of theaspirones **28** described by Heckman and Roberts (1969) are outlined. In analogy to these reactions, in quince fruit dehydrovomifoliol (**9**) as free norisoprenoid and the glucosidic conjugate of vomifoliol (**23**), the so-called roseoside (Tschesche et al., 1976), were identified. 7,8-Dihydrovomifoliol (**25**), also identified in this study for the first time in quince fruit, can be considered the most probable theaspirone precursor. As hypothetically outlined in

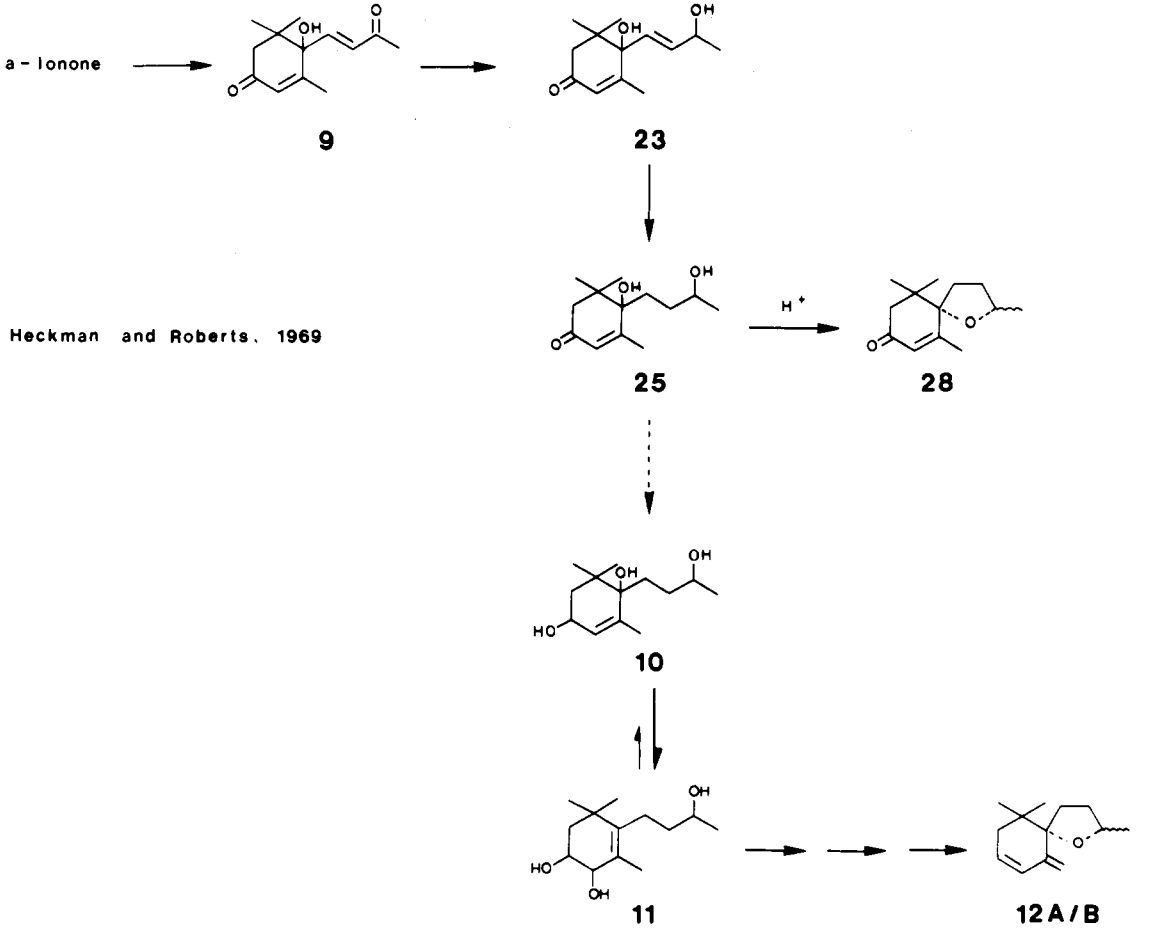

Figure 11. Biomimetic reactions rationalizing the theaspirone generation and potential role of 7,8-dihydrovomifoliol (**25**) as intermediate of vitispirane **12A/12B** formation.

Figure 11, this component may also play a role as intermediate in the formation of triols **10** and **11** discussed above in connection with the generation of vitispiranes **12A/12B** (Figure 3).

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Registry No. **1**, 113110-02-4; **2A1B**, 36431-72-8; **3**, 27185-80-4; **4**, 33759-63-6; **5**, 14398-34-6; **6**, 29790-30-5; **7**, 116296-75-4; **8**, 28494-34-0; **9**, 39763-33-2; **11**, 99810-27-2; **12** (isomer 1), 116296-27-6; **12** (isomer 2), 116296-76-5; **13**, 116296-78-7; **16**, 116296-79-8; **26A**, 5164-79-4; **26B**, 5492-79-5; **26C**, 5298-13-5; **26D**, 5164-78-3.

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