Isolation of Additional Carotenoid Metabolites from Quince Fruit (*Cydonia oblonga* Mill.)

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(*S*)-Abscisic alcohol and the β-D-glucopyranoside of (4*R*,1′*E*,3′*E*)-4-(5′-hydroxy-3′-methyl-1′,3′-pentadienyl)-3,5,5-trimethyl-2-cyclohexen-1-one have been isolated and characterized in quince (*Cydonia oblonga* Mill.) fruit through spectral (NMR, MS) data. On the basis of the finding of these C_{15} terpenoids, oxidative degradation of plant carotenoids is discussed.

INTRODUCTION

Oxidative cleavage of carotenoids has been suggested as a pathway giving rise to the formation of a number of volatile degradation products (Enzell, 1985). Carotenoid metabolites so obtained include 13-carbon (C_{13}) norisoprenoids, common plant constituents with significant importance for the flavor of fruits (Winterhalter, 1992). Also, for quince fruit a considerable number of C_{13} norterpenes have been reported (Ishihara et al., 1986; Winterhalter and Schreier, 1988; Näf et al., 1990), with β-ionone derivatives **1–3** (cf. Figure 1) being the most predominant representatives (Güldner and Winterhalter, 1991; Winterhalter et al., 1991a). Most recently, the β-D-glucopyranosides of the irregular monoterpenoids **4** and **5** have been detected as additional carotenoid-derived products in quince fruit (Lutz et al., 1991; Winterhalter et al., 1991b). Conjugates **4** and **5** have been elucidated as progenitors of isomeric marmelo lactones as well as isomeric marmelo oxides, respectively, which are characteristic flavor constituents of quince essential oil (Tsuneya et al., 1980, 1983). Moreover, Näf and Velluz (1991) recently identified the glycosidically bound C_{12} norterpenoid structure **6** in an aglycon fraction of quince fruit as precursor of quince oxepine. These novel C_{10} and C_{12} structures **4–6** are obviously derived from the central part of the carotenoid chain, which is left after the cleavage of the endgroups. The finding of carotenoid-derived structures **1–6** suggests a hypothetical degradation of quince carotenoids as outlined in Figure 1. As a consequence of the assumed oxidative cleavage of quince carotenoids, this fruit should also contain 15-carbon (C_{15}) fragments. However, contrary to the finding of numerous C_{13} endgroups (Winterhalter and Schreier, 1988), information about the presence of C_{15} compounds in quince is still lacking. The search for C_{15} carotenoid metabolites in quince fruit was therefore the focus of this study.

EXPERIMENTAL PROCEDURES

General. NMR spectra were taken on Fourier transform Bruker AC 200 and WM 400 spectrometers. For the DEPT experiments the Bruker standard impulse sequence was used. Vapor-phase FTIR spectra were recorded on a Hewlett-Packard IRD system (5965B with a wide band MCT detector); UV spectra were obtained with a Hewlett-Packard diode array detector 1040A. CD spectra were recorded on an ISA Jobin Yvon CD 6 dichrometer. For flash chromatography (Still et al., 1978) Merck silica gel 60 (0.032–0.063 mm) was used. Thin-layer chromatography (TLC) was performed on silica gel 60 plates (Merck) with the RLCC stationary phase as developing solvent. The preparation of glycosidic XAD isolates (Günata et al., 1985) from quince fruit together with conditions of rotation locular countercurrent chromatography (RLCC) has been described previously (Güldner and Winterhalter, 1991). The only modification concerned the desorption of the glycosides from the XAD column; in the present case EtAc (1 L) was applied prior to MeOH elution.

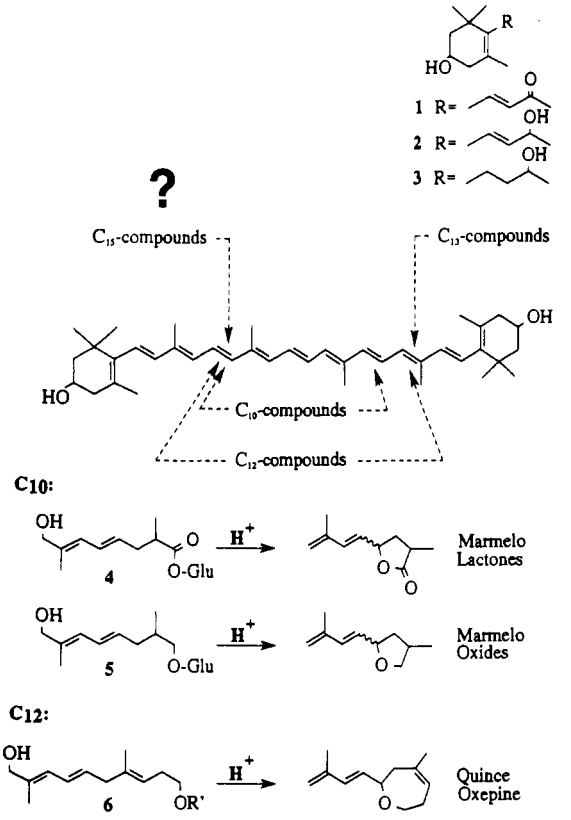

Figure 1. Carotenoid-derived products identified in quince fruit.

Plant Material. Fresh ripe quince (*Cydonia oblonga* Mill.) fruit (10 kg), grown near Würzburg, Germany, was available from the local market.

Derivatization and Purification of Peracetylated Glycoside 7. Combined RLCC fractions 15–22 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). Combined flash fractions 13–21 were finally purified by semipreparative HPLC [LiChrospher Si 100, 5 μm column, 250 × 16 mm (Knauer, Berlin), eluent pentane–Et_2O (2:8), flow rate 15 mL/min; Eurosil Bioselect C18, 10 μm column, 250 × 16 mm (Knauer, Berlin), eluent MeOH–H_2O gradient; UV detection in both cases 230 nm], thus yielding pure compound **7** as white crystals (50 mg; mp 89 °C): UV 230 nm; ^1H NMR, cf. Table I; ^{13}C NMR, cf. Table III; CD spectra, see Figure 2; thermospray MS 582 $[M + NH_4]^+$.

Deacetylation and Enzymatic Hydrolysis. To 10 mg of **7** in 5 mL of MeOH was added 5 mL of 0.02 M NaOMe solution.

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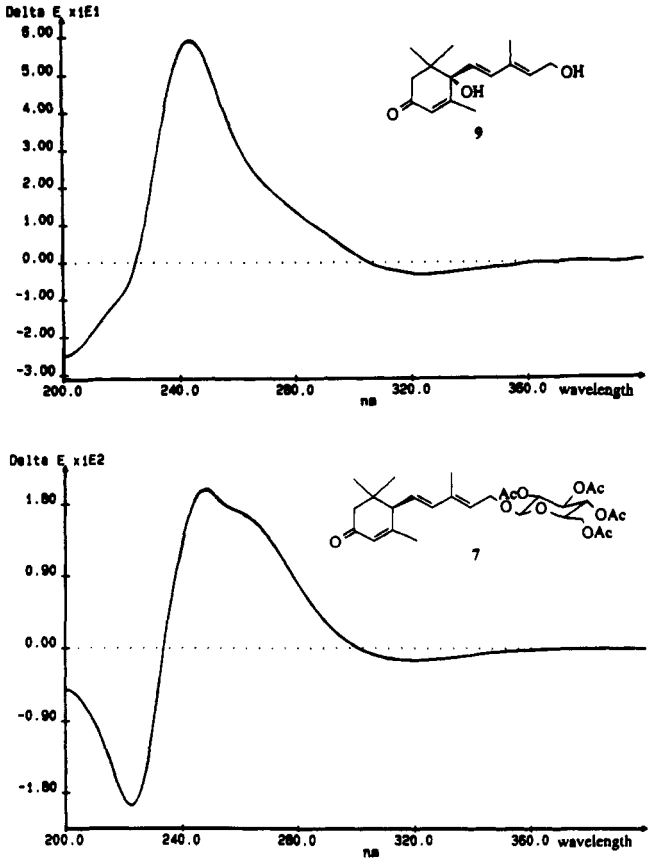

Figure 2. CD spectra (EtOH) of abscisic alcohol 9 as well as the C_{15} glucoside 7.

After 12 h, the mixture was neutralized by adding 50 mg of Dowex 50 WX8 (H^+ form). After removal of the ion-exchange resin by filtration, the solvent was evaporated in vacuo and the deacetylated glucoside was taken up in 3 mL of H_2O. To this solution was added 10 mL of 0.2 M citric acid–phosphate buffer (pH 5.2) as well as 20 mg of a commerically available β-glucosidase (almond emulsin, Serva). Incubation under N_2 was carried out over 24 h at 37 °C. The liberated aglycon 8 was extracted with Et_2O and subjected to HRGC and HRGC–MS analyses: R_i (DB-5) 2005; EIMS (70 eV) m/z (%) 234 (M^+, 17), 219 (2), 191 (3), 178 (15), 160 (13), 159 (48), 147 (100), 145 (91), 138 (19), 137 (15), 135 (21), 133 (21), 123 (10), 121 (11), 119 (36), 117 (22), 115 (12), 105 (20), 91 (48), 79 (24), 77 (34), 55 (15), 41 (32).

Isolation of Abscisic Alcohol 9. Freshly prepared quince juice was obtained from 10 kg of cut fruits after crushing and pressing (Hafico press). The juice was neutralized (6 N NaOH) and subsequently extracted using Et_2O (24 h). The extract was dried over anhydrous Na_2SO_4 and carefully concentrated to 1 mL (Vigreux column) prior to flash chromatography (pentane–Et_2O gradient). Flash fractions 61–90 were further purified by semipreparative HPLC [LiChrospher Si 100, 5 μm column, 250 × 16 mm (Knauer, Berlin), eluent Et_2O; flow rate 20 mL/min; UV detection 230 nm]. Purified compound 9 (15 mg) showed the following chromatographic and spectral data: R_i (DB-5) 2154; UV 232 nm; ^1H NMR, cf. Table II; ^{13}C NMR, cf. Table III; CD spectra, see Figure 2; EIMS (70 eV) m/z (%) 232 ($M^+ - H_2O$, 2), 194 (8), 176 (36), 161 (43), 148 (20), 147 (17), 133 (26), 119 (17), 107 (26), 105 (37), 96 (100), 91 (40), 79 (40), 77 (46), 68 (60), 55 (36), 41 (51); FTIR (vapor phase, ν, cm^{-1}) 3642, 3038, 2975, 1696, 1625, 1449, 1384, 1251, 1012, 974, 833.

Capillary Gas Chromatography (HRGC). For HRGC a Hewlett-Packard 5890 gas chromatograph equipped with a J&W fused silica DB-5 capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm) was used. Split injection was employed. The temperature program was from 60 to 300 °C at 5 °C/min. The flow rate for the carrier gas was 2.0 mL/min of He and for the makeup gas 30 mL/min of N_2. For the detector gases the flow rates were 30 mL of H_2 and 300 mL/min of air. The injector temperature was kept at 220 °C and the detector temperature at 300 °C. Linear retention index (R_i) is based on a series of n-hydrocarbons (Kováts, 1958).

Table I. ^1H NMR Spectral Data (400 MHz, $CDCl_3$) of Acetylated Glucoside 7 (δ Relative to TMS; J in Hertz)

δ	signal	assignment
0.96, 1.05	2 × 3 H, 2s	$(CH_3)_2C5$
1.77	3 H, br s	CH_3-C3′
1.91	3 H, d, J = 1.3	CH_3-C3
2.01–2.09	4 × 3 H, 4s	4 × CO-CH_3
2.10	1 H, d, J = 16.8	H_aC6
2.36	1 H, d, J = 16.8	H_bC6
2.59	1 H, d, J = 9.3	HC4
3.69	1 H, dxdxd, J = 9.9, 4.8, 2.5	HC5″
4.16	1 H, dxd, J = 12.3, 2.5	H_aC6″
4.26	1 H, dxd, J = 12.3, 4.8	H_bC6″
4.31	1 H, dxd, J = 12.5, 7.5	H_aC5′
4.42	1 H, dxd, J = 12.5, 6.3	H_bC5′
4.55	1 H, d, J = 8.0	HC1″
5.01	1 H, dxd, J = 9.6, 8.0	HC2″
5.09	1 H, dxd, J = 9.9, 9.5	HC4″
5.22	1 H, dxd, J = 9.6, 9.5	HC3″
5.53	1 H, dxd, J = 7.5, 6.3	HC4′
5.55	1 H, dxd, J = 15.5, 9.3	HC1′
5.92	1 H, br s	HC2
6.17	1 H, d, J = 15.5	HC2′

Capillary Gas Chromatography–Mass Spectrometry (HRGC–MS). A Varian 3300 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 column and the same temperature program as mentioned above for HRGC analysis were used. The temperature of the ion source and all connection parts was 220 °C. The electron energy was 70 eV and the cathodic current 0.7 mA.

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

RESULTS AND DISCUSSION

Isolation and Characterization of Glucoside 7. A glycosidic isolate of quince fruit was obtained by passing neutralized quince juice through a column of Amberlite XAD-2 resin (Günata et al., 1985). For the desorption of retained glycosides elution was carried out, using first ethyl acetate and subsequently methanol as solvents. In this way, a crude prefractionation of quince glycosides could be achieved; i.e., treatment with ethyl acetate mainly eluted C_{10} conjugates together with the newly identified C_{15} glycosides, whereas the methanol fraction predominantly contained C_{13} glycoconjugates, including the most recently identified bound forms of ionone derivatives 1 and 2 (Güldner and Winterhalter, 1991; Winterhalter et al., 1991a).

For further separating the ethyl acetate fraction the solvent-free extract was subjected to rotation locular countercurrent chromatography (RLCC; Snyder et al., 1984). Monitoring of separated RLCC fraction by TLC revealed a major product in RLCC fractions 15–22, which after acetylation, flash chromatography, and a final purification by semipreparative HPLC could be obtained in a pure state. Thermospray MS analysis yielded a strong pseudomolecular ion at m/z 582, thus indicating a molecular mass of 564 ($C_{29}H_{40}O_{11}$). The unknown compound showed a UV absorption maximum at 230 nm, indicating an enone structure (Hesse et al., 1987). ^1H NMR and ^{13}C NMR data are given in Tables I and III, respectively. The ^1H NMR spectrum of 7 showed signals for four acetoxy groups, indicating a hexose as sugar moiety. The signals for the other protons of the sugar part were in good agreement with data previously obtained for tetra-O-acetylglucopyranosides (Güldner and Winterhalter, 1991; Lutz et al., 1991), and the coupling constant (J = 8.0 Hz) of the ano-

Table II. ^{1}H NMR Spectral Data (200 MHz, $CDCl_3$) of Abscisic Alcohol 9 (δ Relative to TMS; J in Hertz)

δ	signal	assignment
1.00, 1.09	2 × 3 H, 2s	$(CH_3)_2$C5
1.7	1 H, br s	O*H*
1.79	3 H, br s	CH_3-C3′
1.89	3 H, d, J = 1.7	CH_3-C3
1.92	1 H, br s	O*H*
2.23	1 H, dxd, J = 17.0, 1.1	H_aC6
2.46	1 H, dxd, J = 17.0, 0.8	H_bC6
4.30	2 H, d, J = 6.7	H_2C5′
5.70	1 H, d, J = 15.6	HC1′
5.71	1 H, br t, J = 6.7	HC4′
5.91	1 H, br s	HC2
6.33	1 H, d, J = 15.6	HC2′

Table III. ^{13}C NMR Spectral Data (100 MHz, $CDCl_3$) of Acetylated Glucosides 7 and Abscisic Alcohol 9

7			9		
δ^a	DEPT	assignment	δ^b	signal	assignment
12.8	CH_3	CH_3-C3′	12.8	q	CH_3-C3′
23.7	CH_3	CH_3-C3	19.0	q	CH_3-C3
27.3	CH_3	CH_3-C5	23.0	q	CH_3-C5
27.9	CH_3	CH_3-C5	24.2	q	CH_3-C5
36.5	C	C5	41.5	s	C5
47.6	CH_2	C6	49.8	t	C6
56.2	CH	C4	59.3	t	C5′
65.3	CH_2	C5′	79.5	s	C4
125.8	CH	C2	126.8[d]	d	C1′
126.1[c]	CH	C1′	128.3[d]	d	C2
126.7[c]	CH	C4′	131.6[e]	d	C4′
132.6	C	C3′	134.8[e]	d	C2′
137.4	CH	C2′	134.9	s	C3′
161.9	C	C3	162.8	s	C3
199.1	C	C1	198.0	s	C1
sugar part					
20.6–20.9	CH_3	CO-CH_3			
62.0	CH_2	C6″			
68.5	CH	C4″			
71.3	CH	C2″			
71.9	CH	C5″			
72.9	CH	C3″			
99.4	CH	C1″			
169.3	C	*C*O-CH_3			
169.4	C	*C*O-CH_3			
170.3	C	*C*O-CH_3			
170.6	C	*C*O-CH_3			

[a] Chemical shifts were assigned on the basis of a DEPT experiment. [b] By comparison with data published for the corresponding carotenoid endgroup (Englert, 1985). [c–e] Interchangeable values in each column.

meric proton (δ 4.55) indicated a β-glycosidic linkage. The NMR spectra were similar to data previously reported for the β-D-glucopyranoside of the C_{13} compound 3-oxo-α-ionol (Anderson et al., 1977), and the signals of the aglycon part were in good agreement with data published for the corresponding 3-oxo carotenoid endgroup (Englert, 1985). However, the ^{13}C NMR spectrum showed in addition to 6 sugar carbons 15 further signals, including 1 carbonyl function as well as 3 double bonds. These data indicated the presence of a C_{15} terpenoid compound, structurally related to 3-oxo-α-ionol, with all spectral data being in accordance with structure 7 (cf. Figure 3). The arrangement of the substituents at the C3′/C4′ double bond was evaluated by a nuclear Overhauser effect (NOE) experiment: irradiation at 1.77 ppm [CH_3-C(3′)] increased the signals for H_2C(5′) as well as HC(1′) but had no influence on HC(4′), thus suggesting *E* configuration at the C3′/C4′ double bond. To determine the absolute stereochemistry at C4, the CD spectrum of 7 (cf. Figure 2) was compared with data previously reported for structurally related compounds (Ohloff et al., 1973). The similarity

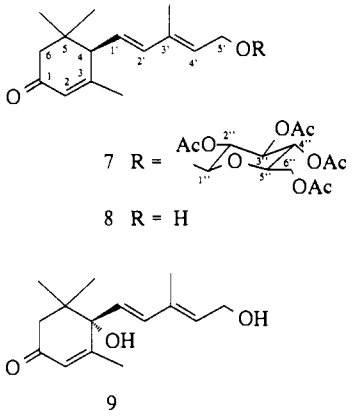

Figure 3. Structures of the newly identified quince constituents.

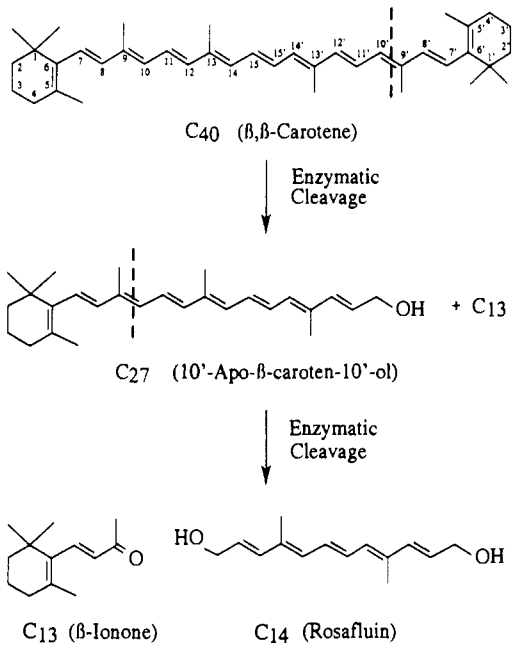

Figure 4. Proposed pathway of carotenoid degradation in rose flowers (cf. text).

with the CD spectra reported for (*R*)-α-ionone strongly supports *R* configuration at C4. On the basis of these results the unknown structure was assigned as being the β-D-glucopyranoside of (4*R*,1′*E*,3′*E*)-4-(5′-hydroxy-3′-methyl-1′,3′-pentadienyl)-3,5,5-trimethyl-2-cyclohexen-1-one. Glucoside 7 is to our best knowledge reported as a natural product for the first time.

Enzymatic hydrolysis of deacetylated 7 with a specific β-glucosidase (almond emulsin) finally yielded aglycon 8, which gave a mass spectrum similar to that previously reported for racemic 8 (Widmer et al., 1982). Ketoalcohol 8 has earlier been used by these authors as key intermediate in the synthesis of the carotenoids rhodoxanthin and zeaxanthin.

Isolation of Abscisic Alcohol 9 from Quince Juice. A polar extract of quince was obtained by continuous extraction of the neutralized juice with diethyl ether. After flash chromatographic preseparation and subsequent HPLC purification, a major compound of the extract was obtained in a pure state. The EIMS spectrum indicated a molecular mass of 250. Vapor-phase FTIR data showed an α,β-unsaturated carbonyl group (1696 and 1625 cm^{-1}) and a broad O–H stretching band at 3642 cm^{-1} together with absorption bands at 974 and 833 cm^{-1}, characteristic of an *E*-configurated as well as a trisubstituted double bond, respectively. The UV spectrum with a maximum

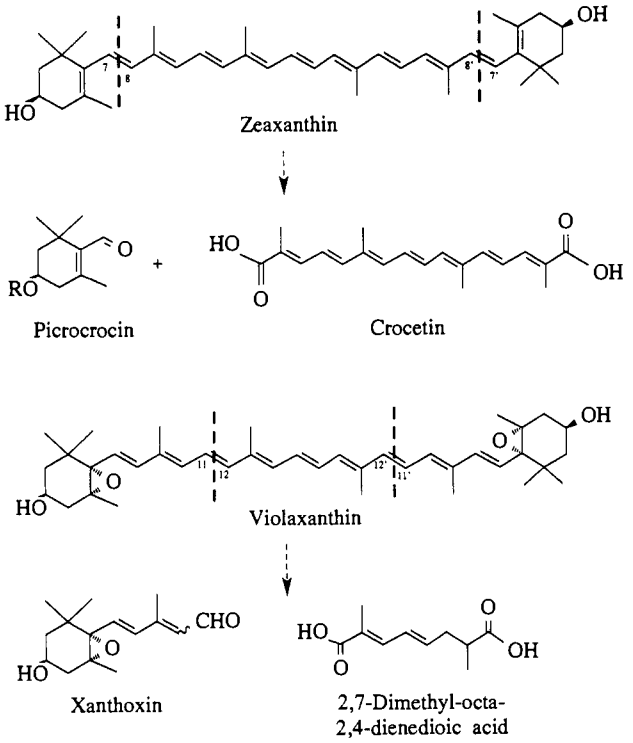

Figure 5. Proposed pathways of carotenoid degradation in saffron (top) and tomato (bottom).

at 232 nm confirmed the enone structure. The ^1H NMR spectral data (cf. Table II) were in good agreement with those published for abscisic alcohol **9** (Linforth et al., 1987a), which was previously used as an intermediate in the synthesis of the plant hormone abscisic acid (Mayer et al., 1976). Also, the ^{13}C NMR data (cf. Table III) are in accordance with those of structure **9**. Comparison of the CD spectrum (cf. Figure 2) with that reported for (*S*)-abscisic acid (Ohloff et al., 1973) indicated *S* configuration at C4. A NOE experiment for elucidation of the configuration at the 3′/4′ double bond failed due to partial decomposition of the NMR sample of **9**. The suggested *E* configuration is therefore tentative. In addition to free abscisic alcohol **9**, a glycoconjugated form could also be detected in RLCC fractions 23–40. This was apparent after treatment of the separated glycosides using a non-selective glycosidase. This treatment liberated abscisic alcohol **9** as a major aglycon. The elucidation of the entire structure of the glucoconjugated form of C_{15} alcohol **9** is the subject of active research.

Biodegradation of Carotenoids. Recent studies on carotenoid-derived plant constituents strongly support earlier proposals that oxygenase systems are responsible for the cleavage of carotenoids in intact plants (Enzell, 1985). The finding of an increasing number of site-specific degradation products contradicts alternatively discussed photochemical degradation pathways, since in the latter case a more random pattern of fragments can be expected. Characteristic cleavage products of carotenoids have, e.g., been detected in rose flowers, for which Eugster and Märki-Fischer (1991) recently postulated the pathway outlined in Figure 4. The authors proposed a dioxygenase system generating first C_{13} norisoprenoids and C_{27} degraded carotenoids by cleavage of the polyene chain in the 9,10 or 9′,10′ position. The so-obtained C_{27} fragment can further serve as substrate for the assumed dioxygenase, thus explaining the finding of C_{14} fragments, such as rosafluin, in rose flowers (cf. Figure 4).

In other plants similar enzymes—however, with different site specificity—seem to be involved in carotenoid degradation. In saffron, e.g., carotenoid cleavage products mainly consist of C_{10} endgroups and C_{20} polyenes (cf. Figure 5), which are obviously derived from a specific cleavage of the carotenoid chain in the 7,8 position (Pfander and Schurtenberger, 1982). Another example is tomato (cf. Figure 5), containing a pattern of products that can be rationalized by an assumed cleavage of the polyene chain in the 11,12 position (Linforth et al., 1987b). For quince fruit, our results indicate that obviously a less site-specific oxidase seems to be present, since the finding of C_{13} as well as C_{15} endgroups—combined with the finding of C_{10} and C_{12} fragments from the central part of the polyene chain—requires cleavage of the carotenoid chain in the 9,10 or 11,12 position (cf. Figure 1). Information about such cleavage enzymes, however, is still lacking in the literature.

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LITERATURE CITED

Anderson, R. C.; Gunn, D. M.; Gibson, J. A. Smoke flavoring composition for tobacco. Ger. Offen. DE 2634306, 1977; *Chem. Abstr.* **1977**, *86*, 152851s.

Englert, G. NMR of carotenoids—new experimental techniques. *Pure Appl. Chem.* **1985**, *57*, 801–821.

Enzell, C. Biodegradation of carotenoids—an important route to aroma compounds. *Pure Appl. Chem.* **1985**, *57*, 693–700.

Eugster, C. H.; Märki-Fischer, E. *Angew. Chem.* **1991**, *103*, 671–689.

Güldner, A.; Winterhalter, P. Structures of two new ionone glycosides from quince fruit (*Cydonia oblonga* Mill.) *J. Agric. Food Chem.* **1991**, *39*, 2142–2146.

Günata, Y. Z.; Bayonove, C. L.; Baumes, R. L.; Cordonnier, R. E. The aroma of grapes. I. Extraction and determination of free and glycosidically bound fractions of some grape aroma components. *J. Chromatogr.* **1985**, *331*, 83–90.

Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*; Thieme: Stuttgart, 1987; pp 15–18.

Ishihara, M.; Tsuneya, T.; Shiota, H.; Shiga, M.; Nakatsu, K. Identification of new constituents of quince flavor (*Cydonia oblonga* Mill. = *C. vulgaris* Pers.). *J. Org. Chem.* **1986**, *51*, 491–495.

Kováts, E. sz. *Helv. Chim. Acta* **1958**, *41*, 1915–1932.

Linforth, R. S. T.; Bowman, W. R.; Griffin, D. A.; Marples, B. A.; Taylor, I. B. 2-*trans*-ABA alcohol accumulation in the wilty tomato mutants *flacca* and *sitiens*. *Plant, Cell Environ.* **1987a**, *10*, 599–606.

Linforth, R. S. T.; Bowman, W. R.; Griffin, D. A.; Hedden, P.; Marples, B. A.; Taylor, I. B. 2,7-Dimethyl-octa-2,4-dienedioic acid, a possible by-product of abscisic biosynthesis in the tomato. *Phytochemistry* **1987b**, *26*, 1631–1634.

Lutz, A.; Winterhalter, P.; Schreier, P. Isolation of a glucosidic precursor of isomeric marmelo oxides from quince fruit. *Tetrahedron Lett.* **1991**, *32*, 5943–5944.

Mayer, H. J.; Rigassi, N.; Schwieter, U.; Weedon, B. C. L. Synthesis of abscisic acid. *Helv. Chim. Acta* **1976**, *59*, 1424–1427.

Näf, F.; Näf, R.; Uhde, G. Synthesis of nature-identical flavour chemicals. In *Flavour Science and Technology*; Bessière, Y., Thomas, A. F., Eds.; Wiley: Chichester, U.K., 1990; pp 3–20.

Näf, F.; Velluz, A. Isolation of acyclic precursors of the marmelo oxides, the marmelo lactones and the quince oxepine from quince fruit (*Cydonia oblonga* Mill.). *Tetrahedron Lett.* **1991**, *32*, 4487–4490.

Ohloff, G.; Otto, E.; Rautenstrauch, V.; Snatzke, G. *Helv. Chim. Acta* **1973**, *56*, 1874–1882.

Pfander, H.; Schurtenberger, H. Biosynthesis of C_{20}-carotenoids in *Crocus sativus*. *Phytochemistry* **1982**, *21*, 1039–1042.

Snyder, J. K.; Nakanishi, K.; Hostettmann, K.; Hostettmann, M. Application of rotation locular countercurrent chromatography in natural products isolation. *J. Liq. Chromatogr.* **1984**, *7*, 243–256.

Still, W. C.; Kahn, M.; Mitra, A. Rapid chromatographic technique for preparative separations with moderate resolution. *J. Org. Chem.* **1978**, *43*, 2923–2925.

Tsuneya, T.; Ishihara, M.; Shiota, H.; Shiga, M. Isolation and identification of novel terpene lactones from quince fruit (*Cydonia oblonga* Mill., Marmelo). *Agric. Biol. Chem.* **1980**, *44*, 957–958.

Tsuneya, T.; Ishihara, M.; Shiota, H.; Shiga, M. Volatile components of quince fruit (*Cydonia oblonga* Mill.). *Agric. Biol. Chem.* **1983**, *47*, 2495–2502.

Widmer, E.; Zell, R.; Grass, H.; Marbet, R. Technical procedures for the synthesis of carotenoids and related compounds from 6-oxo-isophorone. VII. Synthesis of rhodoxanthin and (3*RS*,3′*RS*)-zeaxanthin from the C_{15}-ring component. *Helv. Chim. Acta* **1982**, *65*, 958–967.

Winterhalter, P. Oxygenated C_{13}-norisoprenoids: important flavor precursors. In *Flavor Precursors——Thermal and Enzymatic Conversions*; Güntert, M., Takeoka, G., Teranishi, R., Eds.; ACS Symposium Series 490; American Chemical Society: Washington, DC, 1992.

Winterhalter, P.; Schreier, P. Free and bound C_{13} norisoprenoids in quince (*Cydonia oblonga*, Mill.) fruit. *J. Agric. Food Chem.* **1988**, *36*, 1251–1256.

Winterhalter, P.; Harmsen, S.; Trani, F. A C_{13}-norisoprenoid gentiobioside from quince fruit (*Cydonia oblonga*, Mill.). *Phytochemistry* **1991a**, *30*, 3021–3025.

Winterhalter, P.; Lutz, A.; Schreier, P. Isolation of a glucosidic precursor of isomeric marmelo lactones from quince fruit. *Tetrahedron Lett.* **1991b**, *32*, 3669–3670.

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