Use of GC–MS Technique for Identification of Oxygenated Volatile Thermal Degradation Products of Canthaxanthin†

Tarik H. Roshdy* and Henryk Daun

Department of Food Science, Cook College, Rutgers University, New Brunswick, New Jersey 08903

Pure canthaxanthin was obtained from Hoffman La-Roche Inc., Nutley, NJ 07110. In our model system, canthaxanthin was heated at 210 °C for 30, 60, 120, and 240 min under a nitrogen blanket, resulting in a loss of 87, 96, 100, and 100%, respectively, of canthaxanthin. In this study, six oxygenated compounds from the volatile thermal degradation of canthaxanthin were tentatively identified by gas chromatography and mass spectrometry. They included (1) 4-methyl-3-penten-2-one, (2) 2,4,4-trimethyl-2-cyclohexen-1-one, (3) 1,1,5,6-tetramethyl-4-keto-5-cyclohexene, (4) 1,2,3,4-tetrahydro-4-keto-1,1,6-trimethylnaphthalene, (5) 2-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1-tolylethene, and (6) 2,6-dimethyl-8-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1,3,5,7-octatetraene. Proposed mechanisms of formation of these compounds as thermal degradation products of canthaxanthin are provided.

INTRODUCTION

Canthaxanthin (4,4′-diketo-β-carotene) has a symmetrical structure. It consists of eight isoprenoid units and eleven double bonds (conjugated polyene) with carbonyl group substitution at each end at positions C-4 and C-4′ on the ring of the molecule and a molecular weight of 536. Most carotenoids are characteristically nonpolar and water-insoluble (Davies, 1976). In 1964 canthaxanthin was introduced by Roche for the coloring of foods and feedstuffs.

Canthaxanthin is one of the two major food-coloring oxycarotenoids. It occurs in raw foods such as poultry, eggs, fish, and crustaceans. Canthaxanthin is also one of the three major carotenoids used as a colorant in food products as well as for pharmaceutical purposes. There is no information available on the effects of thermal food processing on canthaxanthin.

Canthaxanthin is insoluble in triglycerides. It is used in foods such as salad dressing, cheese, simulated meat products, sausage or frankfurters, spaghetti, pizza, or barbecue sauce, baked goods, gelatin mix (dessert or salads), confections, beverage, tomato soup, or cocktails as well as in pharmaceutical preparations (Bauernfeind, 1981).

Heat treatment of carotenoids degrades carotenes into new colorless compounds. Several authors investigated the thermal degradation products of carotenoids (Day and Erdman, 1963; Mulik and Erdman, 1963; Mader, 1964; Baldas et al., 1966, 1969; Enzell and Francis, 1968; Francis, 1969, 1972; LaRoe and Shipley, 1970; Kjosen et al., 1971; Eznell and Liaaen-Jensen, 1971; Vetter et al., 1971; Schreir et al., 1979; Ishiwatari, 1980; Onyewu et al., 1980–1982; Roshdy et al., 1986). Most of these studies were carried out in nonfood systems and emphasized the volatile products. However, to date, nothing has been published on the thermal degradation of canthaxanthin. The thermal degradation products of carotenoids are important for flavor and nutritive value of foods.

In a large popcorn plant, the popper has no direct temperature controls but the stack reading during operation is about 650 °F (343.3 °C) (Havighorst, 1970). Rost (1976) reported the isolation of polycyclic aromatic hydrocarbons upon heat treatment of crude edible oils at both the neutralizing temperature of 260 °C and the bleaching plus deodorizing temperature at 270 °C. In 1980 Ouyang et al. reported the formation of β-carotene and β-carotenals from β-carotene during simulated deodorization of palm oil at 210 °C for 4 h. Onyewu et al. (1980–1982) analyzed the thermal degradation compounds formed from β-carotene during simulated deodorization of palm oil at 210 °C for 4 h. The objective of this study was to heat canthaxanthin in a model system to simulate a processing condition such as the deodorization process of oils. A temperature of 210 °C was chosen to simulate the highest known temperature to which canthaxanthin may be exposed under anhydrous conditions, such as deodorization in a triglyceride oil prior to use in food or pharmaceutical materials. Glycerol was used as an analogue to triglycerides, because it has similar properties but does not degrade at this temperature.

MATERIALS AND METHODS

Equipment and Materials: Crystalline canthaxanthin (Lot No. 248013) obtained from Hoffman La-Roche, Inc., Nutley, NJ 07110; glycerol G-33 (glycerin) from Fisher Scientific Co., Pittsburgh, PA 15219; high-temperature oil (hot oil bath) HTP-100 Ucon-Fluid from Blue M Electric Co., Blue Island, IL; 200-plate spinning band distillation apparatus (K-500 400) from Kontes Glass Co., Vineland, NJ); Varian 3400 capillary gas chromatograph equipped with FID detector, Varian 4270 integrator, and GC glass capillary column (DB-1) 60 m long.

Experimental Procedure. *1. Heating of Glycerol.* In order to measure come-up time, 75 mL of degassed glycerol was placed in a 250-mL three-neck angle-type flask. The first neck was sealed with a glass stopper and secured with Teflon tape. The second was sealed with a glass stopper designed for a thermometer to pass through and immersed in the glycerol to measure its temperature. The third (middle) neck was connected to an adaptor containing a long tube ending with a glass filter to disperse the nitrogen gas as small bubbles. The flask containing the glycerol was immersed in a hot oil bath containing a second thermometer in order to read the oil bath temperature.

2. Heating Canthaxanthin in Glycerol. A 2-g portion of canthaxanthin was placed in a 250-mL three-necked flask with 75 mL of glycerol. One neck was plugged with a glass stopper; the

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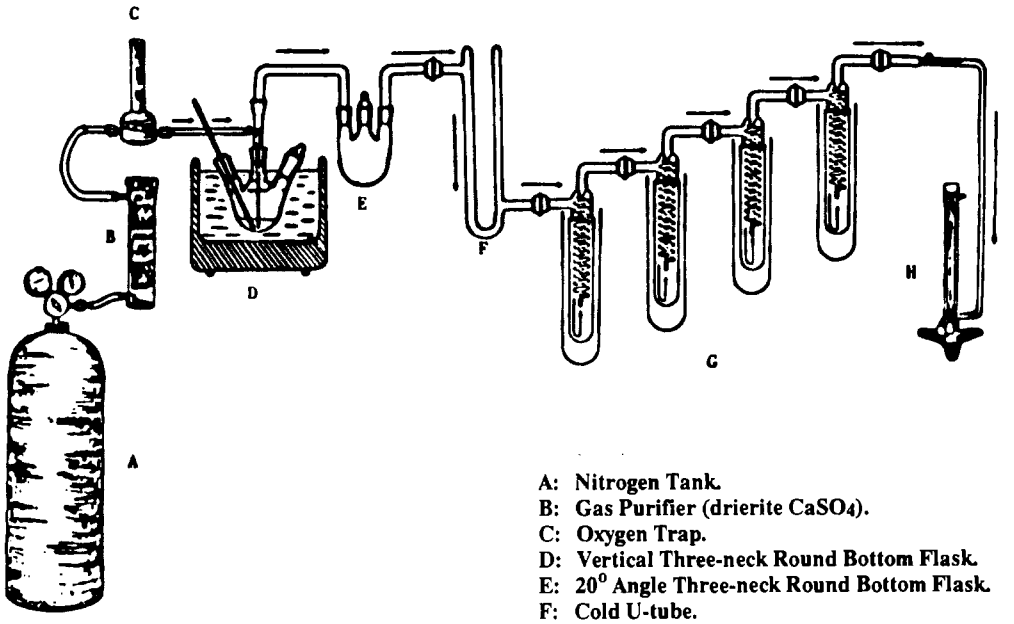


A: Nitrogen Tank.
B: Gas Purifier (drierite $CaSO_4$).
C: Oxygen Trap.
D: Vertical Three-neck Round Bottom Flask.
E: 20° Angle Three-neck Round Bottom Flask.
F: Cold U-tube.
G: Cold Traps with Inner Coiled Condensers.
H: Flowmeter

Figure 1. Experimental setup.

second neck was connected to the nitrogen gas. A stirrer rod was placed in the third neck (the middle neck), which was connected to an electric stirrer. After 30 min canthaxanthin was dispersed uniformly in the glycerol in the present of nitrogen. The flask containing the mixture was connected to the apparatus and then was immersed in the hot oil bath. The temperature of the canthaxanthin/glycerol inside the flask was monitored with a thermometer. The volatile thermal degradation products were collected into a series of cold coiled dry ice/acetone traps. Figure 1 shows a layout of the entire experimental apparatus. The condensed degradation product volatiles were collected by a solvent extraction technique. A schematic diagram of the entire experimental procedure is shown in Figure 2. Canthaxanthin was heated at 210 °C for 4, 2, and 1 h and 30 min.

3. Sample Preparation. The condensate from the five dry ice cold traps was extracted with diethyl ether. A 1.5-μL portion of heptane and 1.5 μL of dodecane were added to the condensate as internal standards. The volatile fraction were concentrated in two steps. Initial concentration used a 30 theoretical plate (3.18-cm diameter) Oldershaw column to concentrate the extracts at 40 °C to approximately 100 mL with a reflux ratio of 10:1. Final concentration was achieved where the thermal degradation isolate (100 mL) was concentrated at 40 °C with a reflux ratio of 20:1 to approximately 1–2 mL on a 200-plate spinning band distillation apparatus. The concentrated volatile thermal degradation products were subjected for analysis by gas chromatography and GC–mass spectroscopy.

4. Gas Chromatography Analysis. A 0.4-μL portion of each sample was injected into a Varian 3300 capillary GC. Initial column temperature was 50 °C with a rate of 2 °C/min up to 250 °C. The injector port temperature was 260 °C with a split ratio of 100:1, and the detector temperature was 275 °C. For further analysis, 0.4 μL of concentrated sample was injected into the injection port of the GC (Varian 3400) that was directly interfaced with a high-resolution analytical 8230 mass spectrometer.

RESULTS AND DISCUSSION

Gas Chromatographic-Mass Spectrometric Analysis of the Volatile Fraction. Figures 3 and 4 show the GC separation profile of the volatile thermal degradation products of canthaxanthin after being heated at 210 °C for 240 min. Figure 5 shows the GC–MS separation profile of the volatile thermal degradation products of heated canthaxanthin. All figures containing two mass

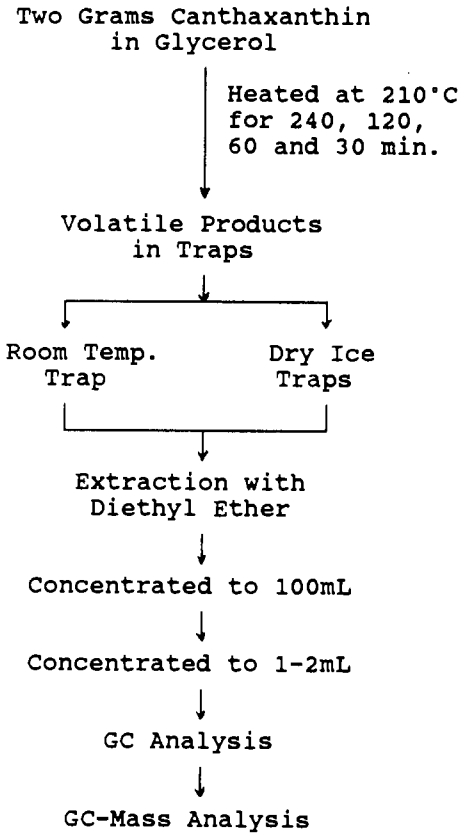


Figure 2. Flow chart of experimental procedure.

spectra are arranged such that the upper is the identified peak and the lower the matching spectrum from the National Bureau of Standard (NBS) library.

The mass spectrum of peak 1 shows a molecular ion peak at *m/e* 98. Some of the major fragment ion peaks appear at *m/e* 98, 84, 83, 74, 59, and 55. The base peak is at *m/e* 83. The fragmentation pattern of this compound is the same as the published mass spectrum of 4-methyl-3-penten-2-one. The structure of this compound is shown in Table I with molecular formula $C_6H_{10}O$.

Table II shows all identified oxygenated volatile ther-

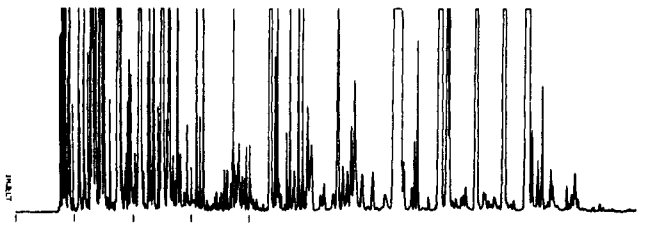


Figure 3. Gas chromatography profile of the volatile thermal degradation products of canthaxanthin heated at 210 °C for 4 h.

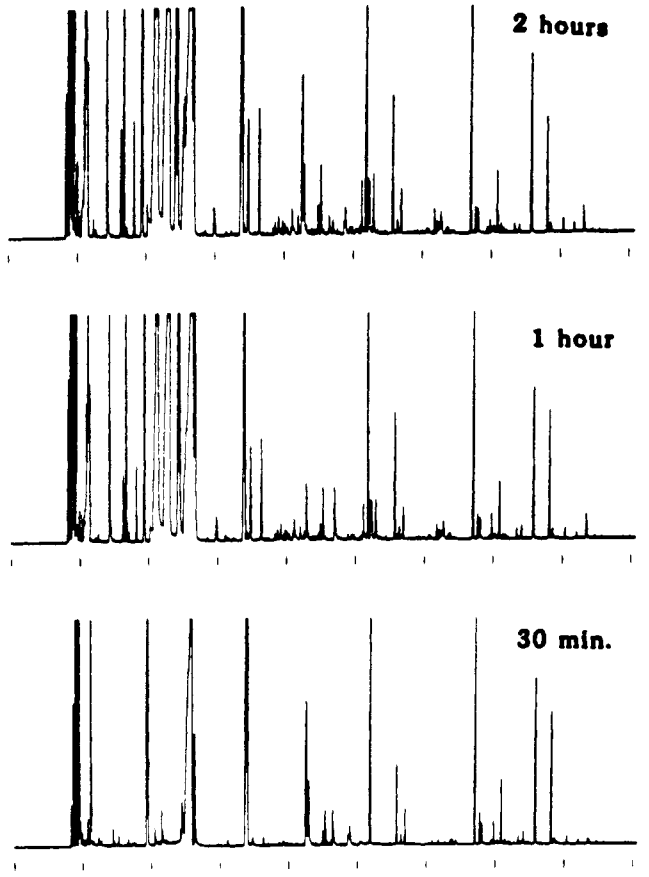


Figure 4. Gas chromatography profile of the volatile thermal degradation products of canthaxanthin heated at 210 °C for 2, 1, and 0.5 h.

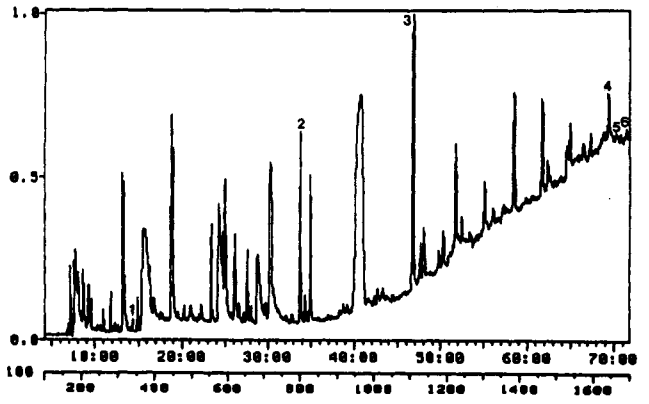


Figure 5. GC-MS profile of the volatile thermal degradation products of canthaxanthin heated at 210 °C for 4 h.

mal degradation product names, molecular formulas, and their molecular weights (MW) formed during heating of canthaxanthin.

The mass spectrum of peak 2 shows a molecular ion peak at m/e 138. Some of the major fragment ion peaks appear at m/e 138, 123, 110, 109, 96, 95, 82, 81, 79, 77,

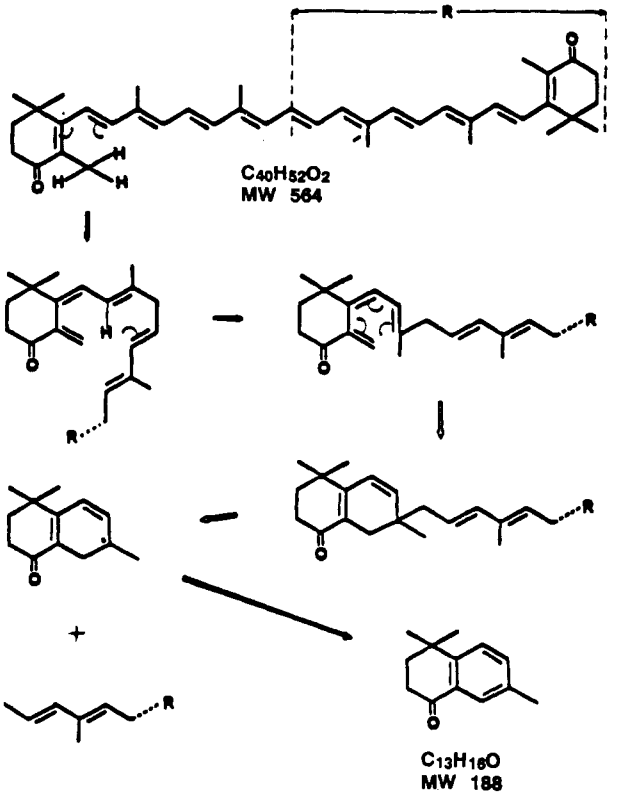


Figure 6. Postulated mechanism of formation of peak 4 identified as 1,2,3,4-tetrahydro-1,1,6-trimethyl-4-ketonaphthalene (MW 188) from canthaxanthin (MW 564).

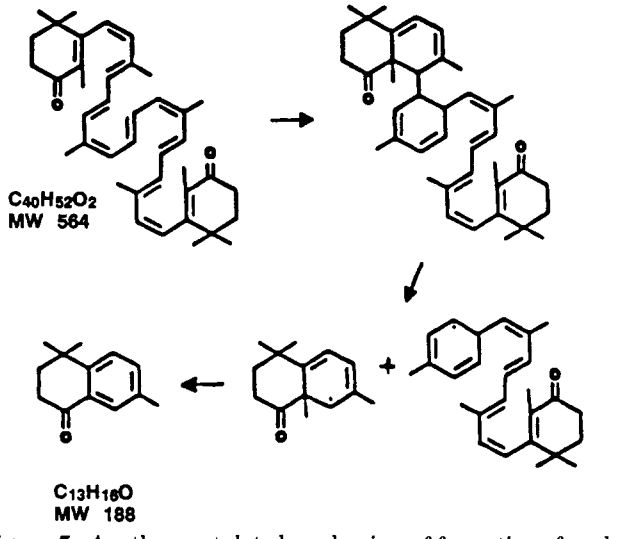


Figure 7. Another postulated mechanism of formation of peak 4 identified as 1,2,3,4-tetrahydro-1,1,6-trimethyl-4-ketonaphthalene (MW 188) from canthaxanthin (MW 564).

67, 55, 53, and 51. The base peak is at m/e 95. The fragmentation pattern of this compound is the same as the published mass spectrum of the 2,4,4-trimethyl-2-cyclohexen-1-one. The structure of this compound is shown in both Figure 10 and Table I with molecular formula $C_9H_{14}O$.

The mass spectrum of peak 3 shows a molecular ion peak at m/e 152. Some of the major fragment ion peaks appear at m/e 152, 81, 137, 95, 67, and 55. The base peak is at m/e 110. The fragmentation pattern of this compound is the same as the published mass spectrum of 5-methyl-2-(1-methylethyl)-2-cyclohexen-1-one. The structure of this compound is shown in Table I with molecular formula $C_{10}H_{16}O$.

The mass spectrum of peak 4 shows a molecular ion

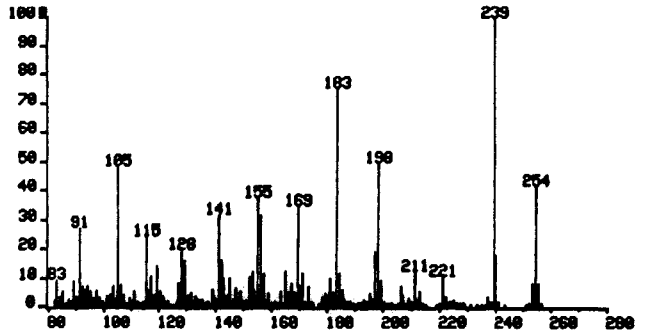


Figure 8. Mass spectrum of 2-(1,1,5-trimethyl-4-ketocyclohex-1-enyl)-1-tolylethene (peak 5) with m/e 254.

Table I. Summary of Identified Oxygenated Volatile Thermal Degradation Products during Heating of Canthaxanthin at 210 °C for 4 h

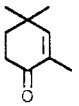
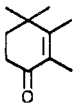
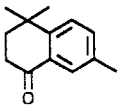
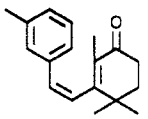
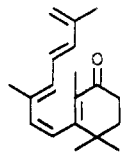
compound	molec formula	MW
	$C_6H_{10}O$	98
	$C_9H_{14}O$	138
	$C_{10}H_{16}O$	152
	$C_{13}H_{16}O$	188
	$C_{18}H_{22}O$	254
	$C_{19}H_{26}O$	270

Table II. Oxygenated Volatile Thermal Degradation Products Formed during Heating of Canthaxanthin

peak no.	identified compound	molec formula	MW
1	4-methyl-3-penten-2-one	$C_6H_{10}O$	98
2	2,4,4-trimethyl-2-cyclohexen-1-one	$C_9H_{14}O$	138
3	1,1,5,6-tetramethyl-4-keto-5-cyclohexene	$C_{10}H_{16}O$	152
4	1,2,3,4-tetrahydro-4-keto-1,1,6-trimethylnaphthalene	$C_{13}H_{16}O$	188
5	2-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1-tolylethene	$C_{18}H_{22}O$	254
6	2,6-dimethyl-8-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1,3,5,7-octatetraene	$C_{19}H_{26}O$	270

peak at m/e 188. Some of the major fragment ion peaks appear at m/e 145, 115, 91, 128, 105, 77, 65, and 51. The base peak is at m/e 173. The fragmentation pattern of this compound is the same as the published mass spectrum of 1,2,3,4-tetrahydro-4-keto-1,1,6-trimethylnaphthalene. Figures 6 and 7 show two different proposed mechanisms for the formation of 1,2,3,4-tetrahydro-4-keto-1,1,6-trimethylnaphthalene (MW 188) from canthaxanthin. The structure of this compound is shown in Figures 6 and 7 and Table I with molecular formula $C_{13}H_{16}O$.

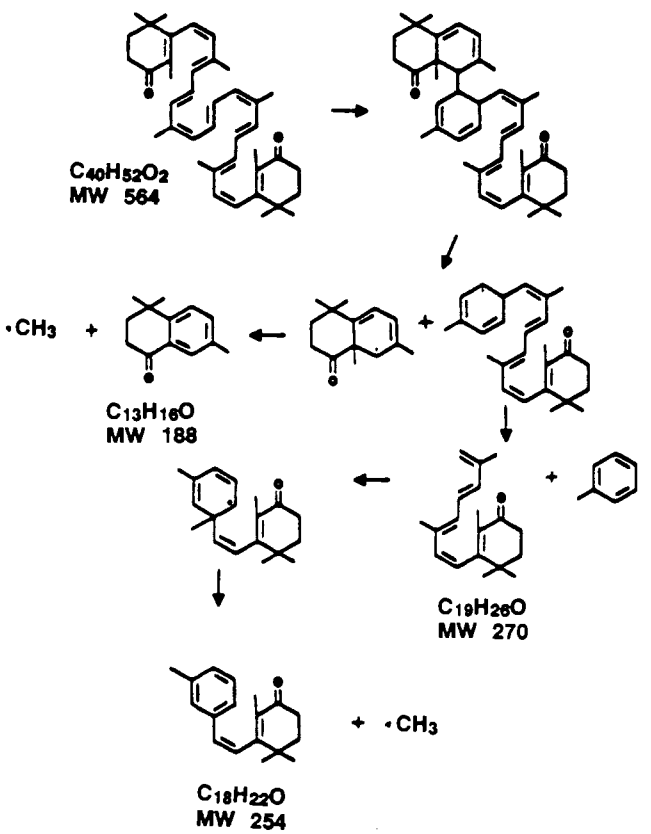


Figure 9. Postulated mechanism of formation of peak 5 (2-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1-tolylethene) and peak 6 (2,6-dimethyl-9-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1,3,5,7-octatetraene) (MW 270) from canthaxanthin (MW 564).

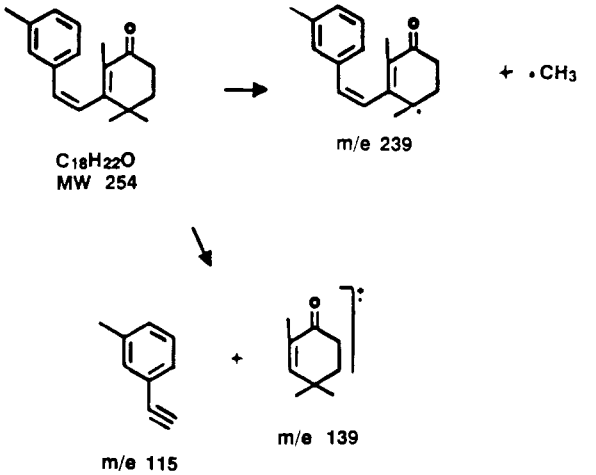


Figure 10. Postulated formation of fragment ions of peak 5 from 2-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1-tolylethene with m/e 254.

Figure 8 shows spectrum of peak 5 with a molecular ion peak at m/e 254. Some of the major fragment ion peaks appear at m/e 239, 198, 183, 169, 155, 141, 128, 115, 105, 91, and 83. The base peak is at m/e 239. This compound was identified as 2-(1,1,5-dimethyl-4-keto-5-cyclohexen-6-yl)-1-tolylethene. Figure 9 shows the proposed mechanism for the formation of mass unit 254 from canthaxanthin. Figure 10 shows the formation of fragment ions such as m/e 239, 139, 115, and 91 from mass unit 254. The proposed structure of this compound is shown in Figures 9 and 10 and Table I with molecular formula $C_{18}H_{22}O$.

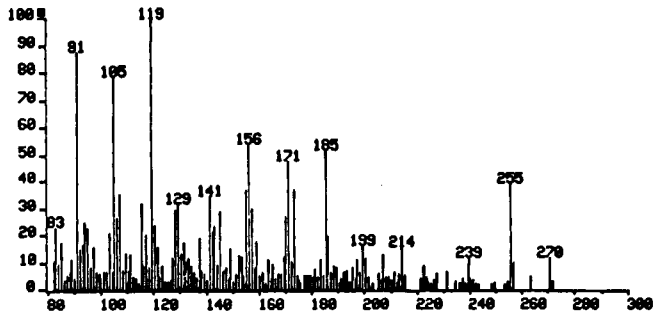


Figure 11. Mass spectrum of 2,6-dimethyl-8-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1,3,5,7-octatetraene (peak 6) with m/e 270.

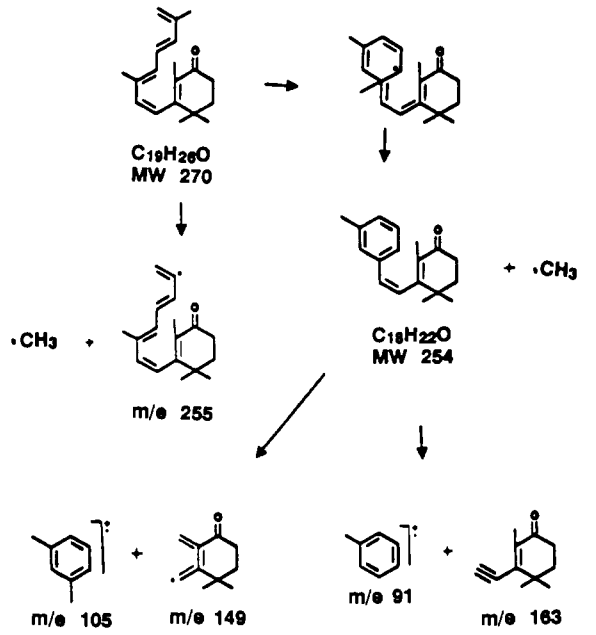


Figure 12. Postulated mechanism of formation of 2,6-dimethyl-8-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1,3,5,7-octatetraene (peak 6) from canthaxanthin (MW 564).

Figure 11 shows spectrum of peak 6 with a molecular ion peak at m/e 270. Some of the major fragment peaks appear at m/e 255, 239, 185, 171, 163, 156, 155, 149, 141, 129, 128, 119, 105, 91, and 83. The base peak is at m/e 119. This compound was identified as 2,6-dimethyl-8-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1,3,5,7-octatetraene. The proposed structure of this compound is shown in Table I with molecular formula $C_{19}H_{26}O$. Figure 9 shows the proposed mechanism for the formation of mass unit 270 from canthaxanthin. Figure 12 shows the formation of fragment ions such as m/e 255, 163, 149, 105, and 91 from mass unit 270.

CONCLUSIONS

Thermal degradation products of canthaxanthin formed under time and temperature conditions in our model system resulted and led to the following conclusions:

1. Heating canthaxanthin at 210 °C for 240, 120, 60, or 30 min resulted in the loss of 100, 100, 96, and 87%, respectively, of canthaxanthin.

2. Six oxygenated volatile thermal degradation products of canthaxanthin were tentatively identified by gas chromatography and mass spectrometry. They included (1) 4-methyl-3-penten-2-one, (2) 2,4,4-trimethyl-2-cyclohexen-1-one, (3) 1,1,5,6-tetramethyl-4-keto-5-cyclohexene, (4) 1,2,3,4-tetrahydro-4-keto-1,1,6-trimethylnaphthalene, (5) 2-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1-tolylethene, and (6) 2,6-dimethyl-8-(1,1,5-trimethyl-4-keto-5-cyclohexen-6-yl)-1,3,5,7-octatetraene.

3. None of the above compounds either in processed foods or as canthaxanthin thermal degradation products have been reported previously in the literature. This study was the first on canthaxanthin thermal degradation.

LITERATURE CITED

Baldas, J.; Porter, Q. N.; Cholnoky, L.; Szabolcs, J.; Weedon, B. C. L. Mass Spectrometry of Carotenoid Epoxides and Furanoid Oxides. *Chem. Commun.* **1966**, *23*, 852.

Baldas, J.; Porter, Q. N.; Leftwick, A. P.; Holzel, R.; Weedon, B. C. L.; Szabolcs, J. Mass Spectrometry of Carotenoid Ketones. *Chem. Commun.* **1969**, *26*, 415.

Bauernfeind, J. C. Natural Food Colors. In *Carotenoids as Colorants and Vitamin A Precursors*; Academic Press: New York, 1981.

Davies, B. H. Crotenoids. In *Chemistry and Biochemistry of Plant Pigments*; Goodwin, T. W., Ed.; Academic Press: New York, 1976; Vol. 2.

Day, W. C.; Erdman, J. C. Ionene: A Thermal Degradation Product of β-carotene. *Science* **1963**, *141*, 808.

Enzell, C. R.; Francis, G. W. Mass Spectrometric Studies of Carotenoids. Part 1. Occurrence and Intensity Ratios of M-92 and M-106 peaks. *Acta Chem. Scand.* **1968**, *22* (3), 1054.

Enzell, C. R.; Liaaen-Jensen, S. Mass Spectrometric Studies of Carotenoids. Part 5. Steric Effects in In-Chain Elimination Reactions. *Acta Chem. Scand.* **1971**, *25* (1), 271.

Francis, G. W. Mass Spectrometric Studies of Carotenoids. Part 3. The Fragmentation of Some 6-keto-carotenoids. *Acta Chem. Scand.* **1969**, *23* (8), 2916.

Francis, G. W. Factors Affecting the Intensity Ratio of the M-92/M-106 Ions in the Mass Spectra of Carotenoids. *Acta Chem. Scand.* **1972**, *26* (4), 1443.

Havighorst, C. R. Automatic Popcorn Production. *Food Eng.* **1970**, *42* (No. 12), 76–78.

Ishiwatari, M. Thermal Reaction of β-carotene. Part I. *J. Anal. Appl. Pyrolysis* **1980**, *2*, 153–167.

Isler, O. Introduction. In *Carotenoids*; Isler, O., Ed.; Birkhauser Verlag: Basel, Stuttgart, 1971.

Isoe, S.; Hyeon, S. B.; Sakan, T. Photo-oxygenation of Carotenoids. I. The Formation of Dihydroactinidiolide and β-ionone from β-carotene. *Tetrahedron Lett.* **1969**, *4*, 279.

Kjosen, H.; Liaaen-Jensen, S.; Enzell, C. R. Mass Spectrometric Studies of Carotenoids. Part 4. In-chain Elimination Reactions. *Acta Chem. Scand.* **1971**, *25* (1), 85.

LaRoe, E. G.; Shipley, P. A. Whiskey Composition: Formation of α- and β-ionone by Thermal Decomposition of β-carotene. *J. Agric. Food Chem.* **1970**, *18*, 174.

Mader, I. β-carotene: Thermal Degradation. *Science* **1964**, *144*, 533.

Marusich, W. L.; Bauernfeind, J. C. Oxycarotenoids in Poultry Feed. In *Carotenoids as Colorants and Vitamin A Precursors*; Bauernfeind, J. C., Ed.; Academic Press: New York, 1981.

Matz, S. A. Specialized Equipment for Potato Chip Processing. In *Snack Food Technology*; AVI: Westport, CT, 1976.

Mulik, J. D.; Erdman, J. G. Genesis of Hydrocarbons of Low Molecular Weight in Organic-rich Aquatic Systems. *Science* **1963**, *141*, 806.

Onyewu, P. N. Isolation and Characterization of Two Nonpolar Components from Thermal Degradation Products of β-carotene. M.S. Thesis, Rutgers University, New Brunswick, NJ, 1980.

Onyewu, P. N.; Daun, H.; Ho, C. T. Model System to Analyze Thermal Degradation Products of Carotenoids. Paper presented at the 41st Annual IFT Meeting, Atlanta, GA, 1981.

Onyewu, P. N.; Daun, H.; Ho, C. T. Formation of Two Nonpolar Thermal Degradation Products of β-carotene. *J. Agric. Food Chem.* **1982**, *30*, 1147.

Roshdy, T. H. Thermal Degradation of Canthaxanthin in a Model system Under Time and Temperature Conditions of Various Food Processing. Ph.D. Dissertation, Food Science Department, Rutgers University, New Brunswick, NJ, 1986.

Rost, H. E. Influence of Thermal Treatments of Palm Oil on the Content of Polycyclic Aromatic Hydrocarbons. *J. Chem. Ind.* **1976**, 162.
Schreir, P.; Drawert, F.; Bhiwaparkar, S. Volatile Decomposition Compounds Formed by Thermal Degradation of β-carotene. *Chem. Mikrobiol. Technol. Lebensm.* **1979**, *6* (3), 90.
Vetter, W.; Englert, G.; Rigassi, N.; Schwieter, U. Spectroscopic Methods. In *Carotenoids*; Isler, O., Ed.; Birkhauser Verlag: Basel, 1971.
Weedon, B. C. L. Occurrence. In *Carotenoids*; Isler, O., Ed.; Birkhauser Verlag: Basel, Stuttgart, 1971.

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Processing Effects during Commercial Debittering of California Navel Orange Juice

Dan A. Kimball*

California Citrus Producers, Inc., 525 East Lindmore Avenue, Lindsay, California 93247

Seth I. Norman

Dow Chemical, U.S.A., Larkin Laboratory, 1691 North Swede Road, Midland, Michigan 48674

The advent of commercial debittering of citrus juices in the United States has resulted in concern regarding the compositional and nutritional changes that occur with the use of adsorbents. Such a commercial system was recently built by Dow Chemical at California Citrus Producers, Inc., Lindsay, CA. Treated and untreated lots of California Washington navel orange concentrate were analyzed by four professional laboratories and the laboratories at CCPI for 27 general citrus juice components (including those required for nutritional labeling), 10 minerals, and 20 amino acids. Significant changes included a reduction of limonin, the bitter component of citrus juices and the object of the debittering, and a reduction in essential oils and pulp that can be replenished without violation of the standards of identity for frozen concentrated orange juice or concentrated orange juice for manufacturing. Mineral increases were found to result from the use of mineral-laden water in reconstituting navel concentrate prior to treatment and not from the use of the adsorbent itself.

Excessive bitterness in citrus juices processed from early and mid season Washington navel oranges [*Citrus sinensis* (L.) Osbeck] results from the development of limonin from its precursor, limonoate A-ring lactone, found primarily in the membrane tissues of the fruit. When these membranes are ruptured during processing, the limonoate A-ring lactone comes into contact with the acid environment of the juice, which precipitates the slow conversion to the bitter limonin (Maier and Beverly, 1968). This delayed bitter development has resulted in the sale of bitter juices at reduced prices. High limonin juices, such as early and mid season navel juice, generally cannot be blended into commercial orange juices due to the penetrating flavor of the limonin bitterness. The fresh-market value of Washington navel oranges places them second in popularity among citrus varieties in the world. Limonin does not have time to develop when the fruit is consumed fresh and thus does not affect the fresh-market quality. Limonin bitterness is primarily a problem for the processor of navel juice from fresh-market culls. Debittering of navel orange juice opens up the possibility of blending early and mid season navel concentrates into consumer products without affecting the juice quality or consumer acceptance.

Methods to commercially reduce the limonin bitterness in processed citrus juices have been investigated for decades (Dekker, 1988). Most methods constitute a lack of economic feasibility or violate federal standards of identity for frozen concentrated orange juice (FCOJ) or concentrated orange juice for manufacturing (COJFM). The use of polymeric adsorbents to selectively remove limonoids from citrus juices has proved to be the preferred method for commercial processors (Johnson and Chandler, 1986; Konno et al., 1982; Maeda et al., 1984; Nisperos and Robertson, 1982; Shaw and Buslig, 1986). Such systems have been used commercially in other parts of the world outside the United States.

With the advent of commercial debittering, questions have arisen concerning the nutritional and compositional changes that take place during debittering. Recently a study was reported that gave preliminary findings on the effects of debittering navel orange juice (Kimball and Norman, 1990). In this study a wider variety of effects were explored to determine if significant nutritional changes occurred that may be of concern to the consumer. Also, significant compositional changes that might

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