7; α-bergamotene, 17699-05-7; 2,6-dichloro-4-nitroaniline, 99-30-9; dibutyl phthalate, 84-74-2; palmitic acid, 57-10-3; methyl 3-methoxyoctadecanoate, 19013-36-6; bis(ethylhexyl) phthalate, 117-81-7.

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# Mechanism of Formation of Volatile Compounds by Thermal Degradation of Carotenoids in Aqueous Medium. 1. β-Carotene Degradation

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The study of the degradation of β-carotene during heat treatment at 97 °C in water shows that the kinetics of degradation is the same as that observed in organic solvents. Some volatile compounds produced during this treatment have been previously identified after thermal degradation of homogeneous solutions of β-carotene or after heating of plant products. However, decanal, 4-ethylbenzaldehyde, and cetoisophorone were identified and 2,6-dimethyldecahydronaphthalene and 2-hydroxy-2,6,6-trimethylcyclohexanone were tentatively identified for the first time as degradation products of β-carotene. The influence of temperature on the production of volatile compounds and the kinetics of formation of volatile and nonvolatile compounds shows that dihydroactinidiolide is the first compound produced during heat treatment of β-carotene, its precursor probably being mutatochrome. Kinetics studies indicate that dihydroactinidiolide may also be produced through 5,6-epoxy-β-ionone, which is an important reactional intermediate. This compound acts as precursor for different volatiles such as β-ionone, 2-hydroxy-2,6,6-trimethylcyclohexanone, and 2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde.

The formation of volatile compounds by thermal degradation of carotenoids during heat treatment of vegetable products has been mentioned by many authors. Compounds such as β-ionone, damascenone, and dihydroactinidiolide present in tea (Bricout et al., 1967), tobacco (Fujimori et al., 1976; Enzell, 1981), prune (Moutounet,

1978), grapes (Schreier et al., 1976), apricot (Crouzet et al., 1983), and mango (Sakho et al., 1985) are considered as degradative products of β-carotene (Demole and Berthet, 1972; Murray et al., 1972). On the other hand, 1,6,6-trimethyl-1,2-dihydronaphthalene was found in volatile compounds obtained from strawberry (Stoltz et al., 1970) peach or peach leaves (Kemp et al., 1971), or passion fruit (Murray et al., 1972). The presence of this compound is also cited in raw Australian rum (Allan, 1975) or in wine

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**238** *J. Agric. Food Chem.,* Vol. 38, No. 1, 1990

Kanasawud and Crouzet

(Schreier et al., 1976). According to Murray et al. (1972) this compound is probably produced by degradation of β-carotene. The different assumptions formulated concerning the presence of these compounds in vegetable products are founded on experimental results obtained from carotenoid degradation studies in model systems (Day and Erdmann, 1963; Mulik and Erdmann, 1963; Mader, 1964; Isoe et al., 1969; La Roe and Shipley, 1970; Olhoff, 1972; Schreier et al., 1979; Kawamaki, 1982). However, these reactions generally occurred under drastic conditions of temperature (100–220 °C), with considerable reaction times (to 72 h), in solvent media such as ethanol or benzene or in the solid state. All these conditions are very different from those encountered during heat treatment or long-time storage of food products.

On the other hand, the occurrence of biochemical pathways such as those found in tea fermentation (Sanderson et al., 1971) or photochemical degradation (Isoe et al., 1969) is always possible during the treatment of vegetable products and may be involved in the formation of the volatile compounds cited.

The purpose of the present work was to study the mechanism of formation of volatile compounds during heat treatment of β-carotene in water, in order to have a model more representative of the conditions found in vegetable products than the organic solutions generally used. However, it must be noticed that some compounds such as cations, anions, or antioxidants that could influence oxidation of β-carotene in foodstuffs are not present in the model studied.

## MATERIALS AND METHODS

**Heat Treatment.** A 50-mg portion of β-carotene suspended by sonication in 100 mL of distilled water in a sealed Kjeldahl flask wrapped in aluminum foil was heated at 97 ± 2 °C in an oil bath during different times. In some experiments, the suspensions were saturated with nitrogen or with oxygen before sealing the flask.

**Isolation of Volatile Compounds.** Two techniques were used for the isolation of volatile compounds produced during heat treatment of β-carotene.

(a) The more volatile compounds were obtained by gas stripping with nitrogen (45 mL/min) during 3 h and trapping on Tenax GC (80 mg). The trap was flushed by a stream of nitrogen (45 mL/min) at room temperature over 30 min in order to desorb water. Then, the desorption of volatiles was performed by heating the trap at 150 °C over 30 min under a stream of nitrogen (30 mL/min), and the compounds were trapped in a capillary U-shaped tubing cooled over the liquefaction temperature of nitrogen.

(b) The less volatile compounds were isolated by direct extraction with dichloromethane of the liquid obtained by elimination of undissolved carotenoids of the reactive medium.

**Gas Chromatography.** A Varian 3700 gas chromatograph fitted with a FID detector and an on-column injector was used. A WCOT glass capillary column (40 × 0.4 mm (i.d.)) coated with Carbowax 20 M, operated at 50 °C during 10 min and then programmed to 170 °C at 4 °C/min, was used to the separation of volatiles. The pressure of carrier gas, nitrogen, was 10 psi.

For quantitative determinations, a Shimadzu CR-1B integrator was coupled to the gas chromatograph; linalool was used as internal standard. The response coefficients of all compounds available were determined; for the other compounds this coefficient was assumed to be equal to 1.

**Gas Chromatography–Mass Spectrometry.** Two Hewlett-Packard 5992 and 5996 apparatus were used; they were, respectively, fitted with a WCOT glass capillary column (40 m × 0.4 mm (i.d.)) coated with Carbowax 20 M and a fused silica capillary column DB 5 (J&W) (25 m × 0.256 mm). The source temperature was 150 °C and the ionization energy 70 eV. The volatile compounds were identified by automatic search in library,
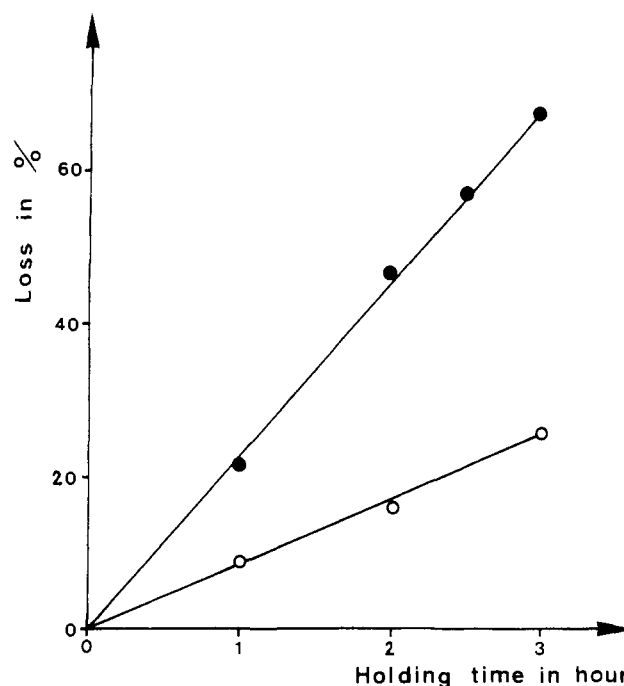


**Figure 1.** Kinetics of degradation of β-carotene during heat treatment at 97 °C in the presence of air (O) and in the presence of oxygen (●).

and the identifications were confirmed by Kovats index determination and when possible by comparison of retention times with those of authentic samples.

Reference compounds **9, 16, 18, 21, 35,** and **51** were donated samples; the other compounds were obtained from commercial suppliers.

**Separation of Nonvolatile Compounds.** Nonvolatile compounds recovered by direct extraction of the reactive medium with dichloromethane were separated by TLC on aluminum oxide F$_{254}$ type T (Merck) 20 × 20 cm, 1.5 mm thick. The development was operated in a dark room with use of acetone–petroleum ether (fraction 40 °C) (4:95, v/v).

The bands corresponding to the different compounds separated were scrapped, and the powder was extracted with acetone. After filtration under a Büchner, the solvent was evaporated under a stream of nitrogen. All these operations were conducted in darkness.

In some cases (identification of epoxy groups), the plate was vaporized after development with concentrated chlorhydric acid.

**Identification of Nonvolatile Compounds.** *Adsorption Spectrophotometry.* Adsorption spectra of β-carotene and of degradation products were recorded on a Perkin-Elmer 550 spectrophotometer in hexane. For the study of the kinetics of degradation of β-carotene the decrease in absorbance at 462 nm was followed as a function of reaction time (El Tinay and Chichester, 1970).

*Proton Magnetic Resonance.* A Brucker V M (369 MHz) was used with deuteriobenzene as solvent. The chemical shifts are given in ppm relative to TMS as internal standard.

## RESULTS

**Kinetics of Degradation of β-Carotene.** The degradation of β-carotene in the presence of air and oxygen was followed over 3 h at 97 °C (Figure 1). These results, characteristic of a zero-order reaction, agree with those previously reported by El Tinay and Chichester (1970) in a homogeneous solution of β-carotene in toluene heated between 60 and 90 °C.

**Identification of Volatile Compounds.** According to the results obtained in the kinetic study (70% of β-carotene degradation after 3 h of reaction in presence of oxygen at 97 °C), the β-carotene was treated under these
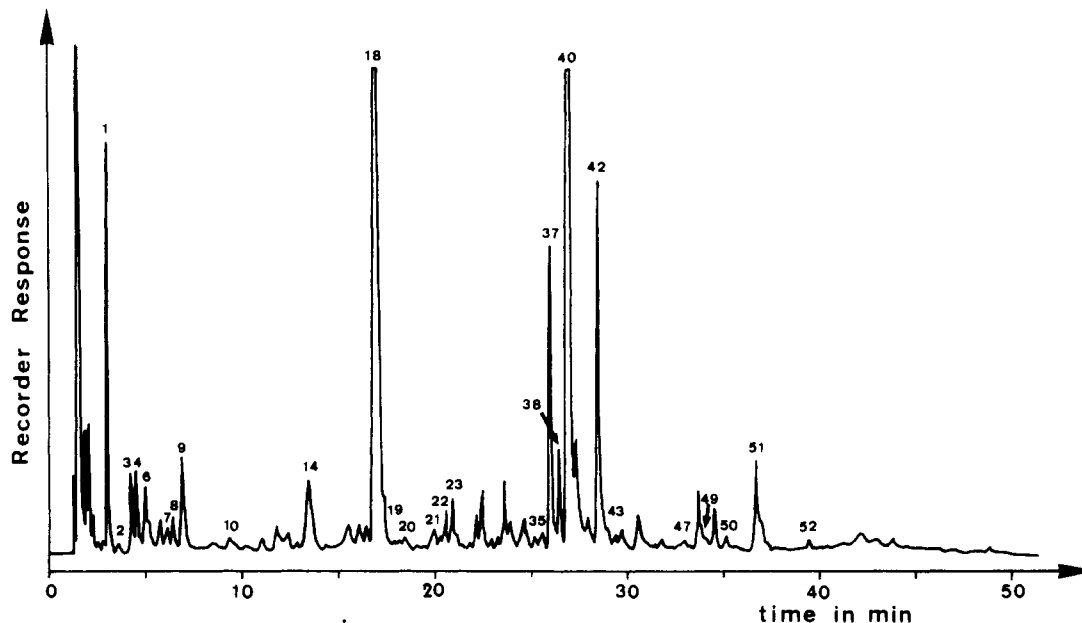
Carotenoid Volatile Formation

*J. Agric. Food Chem.*, Vol. 38, No. 1, 1990  **239**



**Figure 2.** Chromatogram of volatile compounds isolated by adsorption on Tenax GC and thermal desorption after treatment of β-carotene at 97 °C over 3 h in the presence of oxygen (glass capillary column, 40 m × 0.4 mm (i.d.), Carbowax 20 M operated at 50 °C over 10 min and then programmed to 170 °C at 4 °C/min).
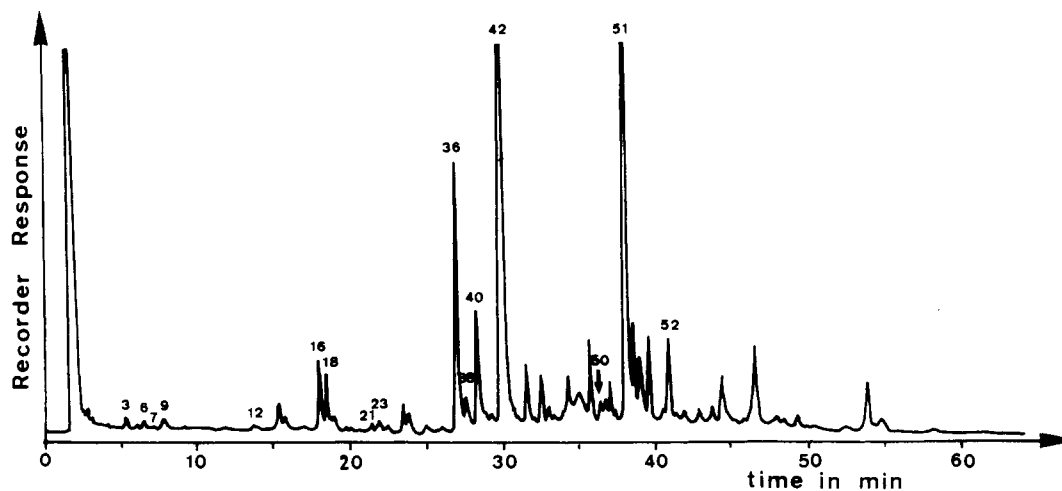


**Figure 3.** Chromatogram of volatile compounds isolated by solvent extraction using dichloromethane after treatment of β-carotene at 97 °C over 3 h in the presence of oxygen (glass capillary column, 40 m × 0.4 mm (i.d.), Carbowax 20 M operated at 50 °C over 10 min and then programmed to 170 °C at 4 °C/min).

conditions in order to increase the quantities of volatile compounds for identification purposes (Figures 2 and 3).

The volatile compounds isolated under these conditions are given in Table I. Most of the components have been previously identified in the volatile fraction produced by thermal degradation of β-carotene in the solid state or in solution (La Roe and Shipley, 1970; Schreier et al., 1979; Drawert et al., 1981; Kawakami, 1982). On the other hand, decanal, 4-ethylbenzaldehyde, and cetoisophorone (2,6,6-trimethyl-2-cyclohexene-1,4-dione) were identified for the first time among the compounds produced during heat treatment of β-carotene and 2,6-dimethyldecahydronapthalene, and 2-hydroxy-2,6,6-trimethylcyclohexanone was tentatively identified on a mass spectral basis (Stenhagen et al., 1974; Viani et al., 1969).

**Influence of Oxygen Content on Volatile Compound Formation.** The results relative to the influence of oxygen content on the formation of volatile compounds during thermal treatment of β-carotene at 97 °C for 3 h are given in Table II. The quantities of the main

compounds identified in the previous section increase when the molecular oxygen content of the reaction medium increases (saturation of the medium by oxygen bubbling) whereas in the presence of a saturated medium in nitrogen only very low concentrations of volatiles were found. These results are indicative of the oxidative nature of the degradation process involved.

**Influence of Temperature on Volatile Compound Formation.** The influence of temperature on the production of volatile compounds by degradation of β-carotene was studied for a heat treatment of 3 h at temperatures from 30 to 90 °C (Figures 4 and 5). At 30 °C only dihydroactinidiolide was produced; most of the other compounds appear when temperatures reach 50 °C, and over this temperature the production of volatiles is greatly accelerated.

**Kinetics of Formation of Volatile Compounds.** The curves representative of the kinetics of formation of the main compounds identified in the volatile fraction produced during heat treatment of β-carotene at 97 °C for 1–4 h in the presence of molecular oxygen are given in

**240** *J. Agric. Food Chem.*, Vol. 38, No. 1, 1990

Kanasawud and Crouzet

**Table I. Volatile Degradation Products of β-Carotene by Thermal Degradation over 3 h at 97 °C under Oxygen**

| peak (Figures 2 and 3) | compound | $R_I{}^a$ | identification MS[b] | identification RT[c] |
|---|---|---|---|---|
| 2 | tridecane | 1291 | + | + |
| 3 | 2,6,6-trimethylcyclohexanone | 1317 | + | + |
| 6 | 2-methyl-2-hepten-6-one | 1327 | + | + |
| 7 | 2-methyl-2-hepten-4-one | 1356 | + | + |
| 9 | 2,6,6-trimethyl-2-cyclo-hexen-1-one | 1400 | + | + |
| 13 | decanal | 1491 | + | + |
| 16 | 2-hydroxy-2,6,6-trimethyl-cyclohexanone | 1588 | + | + |
| 18 | β-cyclocitral | 1616 | + | + |
| 19 | unknown (177, 95, 109, 184, 204) | 1651 | + | − |
| 20 | 2,2,6-trimethyl-2-cyclohexene-1,4-dione (cetoisophorone) | 1675 | + | − |
| 21 | ionene | 1685 | + | + |
| 22 | 4-ethylbenzaldehyde | 1712 | + | + |
| 23 | naphthalene | 1728 | + | + |
| 35 | β-damascone | 1815 | + | + |
| 36 | 2-hydroxy-2,6,6-trimethylcyclo-hexane-1-carboxaldehyde | 1860 | + | − |
| 38 | unknown (123, 43, 208, 135, 124) | 1879 | + | |
| 40 | β-ionone | 1929 | + | + |
| 42 | 5,6-epoxy-β-ionone | 1977 | + | − |
| 43 | β-methylionone | 1988 | + | − |
| 47 | (1,2,2-trimethyl-1-cyclopentyl)-2-pentene-1,4-dione | 2111 | + | − |
| 49 | (two isomers) | 2176 | + | − |
| 50 | 2,6-dimethyldecahydro-naphthalene | 2225 | + | − |
| 51 | dihydroactinidiolide | 2324 | + | + |
| 52 | 4-keto-β-ionone | 2421 | + | − |

*[a]* Retention index on Carbowax 20M. *[b]* Mass spectrometry. *[c]* Retention time.

**Table II. Volatile Compounds (μg) Formed by Thermal Degradation at 97 °C over 3 h of β-Carotene (50 mg) in the Presence of Air (1) or Oxygen (2) or after Nitrogen Flushing (3)**

| compound | quantity, μg 1 | quantity, μg 2 | quantity, μg 3 |
|---|---|---|---|
| 2,6,6-trimethylcyclohexanone | 0.0034 | 0.0102 | 0.0027 |
| 2-methyl-2-hepten-6-one | 0.0026 | 0.0051 | |
| 2-methyl-2-hepten-4-one | tr | 0.0069 | |
| 2,6,6-trimethyl-2-cyclo-hexen-1-one | 0.0048 | 0.0157 | |
| decanal | 0.0040 | 0.0045 | |
| 2-hydroxy-2,6,6-trimethyl-cyclohexanone | 0.0581 | 0.2250 | 0.0114 |
| β-cyclocitral | 0.0424 | 0.1003 | 0.0099 |
| ionene | 0.047 | 0.0098 | |
| naphthalene | 0.0142 | | 0.0028 |
| 2-hydroxy-2,6,6-trimethylcyclo-hexane-1-carboxaldehyde | 0.1761 | 0.4494 | 0.0226 |
| β-ionone | 0.1018 | 0.1959 | 0.0202 |
| 5,6-epoxy-β-ionone | 0.6978 | 0.3656 | 0.0826 |
| 2,6-dimethyldecahydro-naphthalene | 0.0238 | 0.0702 | 0.0030 |
| dihydroactinidiolide | 0.6249 | 1.380 | 0.1546 |
| 4-keto-β-ionone | 0.0659 | 0.2122 | 0.0098 |



**Figure 4.** Influence of temperature on the volatile compound formation during heat treatment of β-carotene at 97 °C in the presence of air: (O) 2-hydroxy-2,6,6-trimethylcyclohexanone; (□) β-cyclocitral; (●) β-ionone; (×) 2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde.



**Figure 5.** Influence of temperature on volatile compound formation during heat treatment of β-carotene at 97 °C in the presence of air: (▲) dihydroactinidiolide; (■) 5,6-epoxy-β-ionone.

Figures 6 and 7. For all the compounds studied, except 5,6-epoxy-β-ionone, the quantities increase during the first hours of the reaction, with a plateau between 2 and 4 h according to the nature of the product.

Dihydroactinidiolide and 2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde were found in larger quantities than the other compounds studied; for 5,6-epoxy-β-ionone, which is also quantitatively considerable, a maximum in production after 2 h of reaction was followed by a decrease of its concentration.
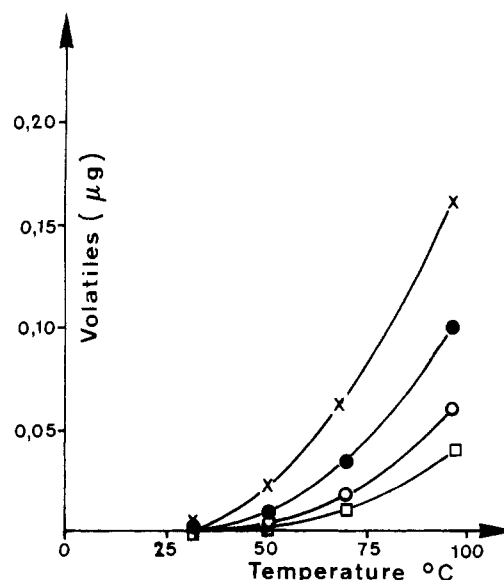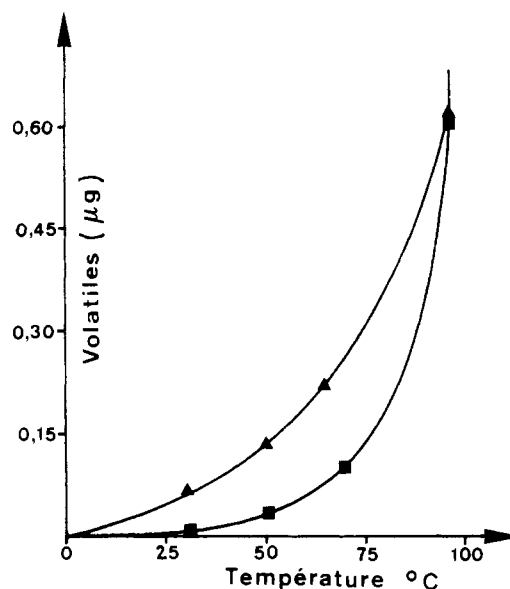
**Identification of Nonvolatile Compounds Produced during the Thermal Degradation of β-Carotene.** The nonvolatile compounds produced during the thermal treatment of β-carotene at 97 °C during 3 h were separated by TLC and isolated. From the study of their adsorption spectra and of stainings obtained after concentrated chlorhydric acid treatment (Table III), four degradation products were identified as 5,6-epoxy-β-carotene, neo-T-5,6,5′,6′-diepoxy-β-carotene, mutatochrome, and aurochrome (Karrer and Jucker, 1950; Tsukida and Zeichmeister, 1958; El Tinay and Chichester, 1970). The singlets at 1.10, 1.14, and 1.48 ppm in the ¹H NMR spectrum of the compound isolated from band 3 may be attributed to the methyl groups in positions 1 and 5 of mutatochrome (Barber et al., 1960; Vetter et al., 1971). For bands 5 and 6 peaks observed at 0.93 or 0.98 ppm and 1.14 or 1.15 ppm agree with the presence of methyl groups in positions 1 (0.95 and 1.14)
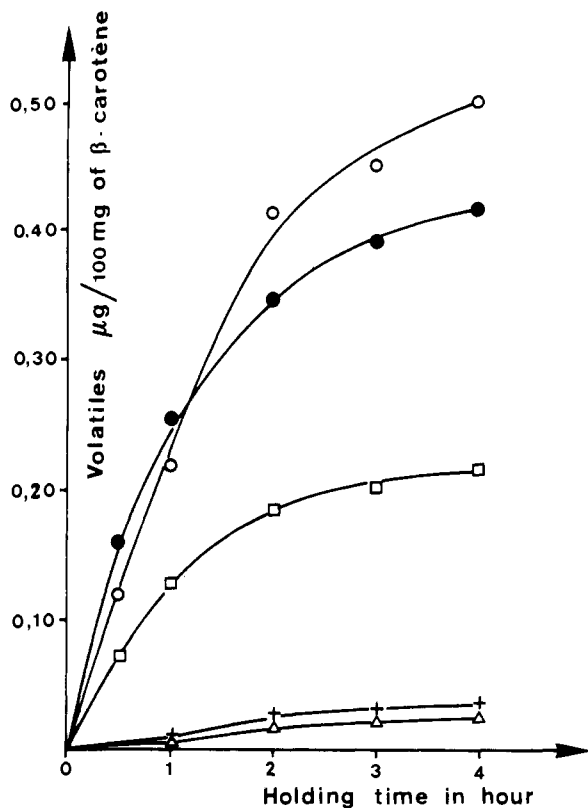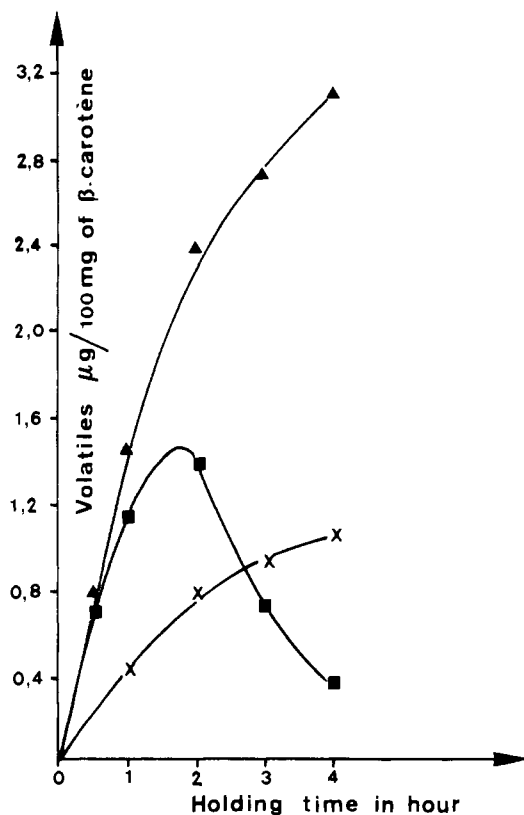
**Figure 6.** Kinetics of formation of volatile compounds during heat treatment of $\beta$-carotene at 97 °C in the presence of oxygen: (O) 2-hydroxy-2,6,6-trimethylcyclohexanone; (□) $\beta$-cyclocitral; (●) $\beta$-ionone; (△) 2,6,6-trimethylcyclohexanone; (+) 2,6,6-trimethyl-2-cyclohexen-1-one.

**Table III. Separation and Identification of Nonvolatile Compounds Produced during Thermal Degradation of $\beta$-Carotene at 97 °C over 3 h**

| band | $R_f$ | reactn with conc HCl | $\lambda_{max}$ (hexane), mm | | | identification |
|------|-------|------|-------|------|------|------|
| 1 | 0 | brown | 474.5 | 449 | 426 | nonidentified |
| 2 | 0.25 | brown | 425 | 398 | 381 | aurochrome |
| 3 | 0.26 | brown | 446 | 428 | 403 | mutatochrome |
| 4 | 0.32 | brown | 401 | 389 | | nonidentified |
| 5 | 0.50 | blue | 453 | 426 | | neo-T-5,6,5',6'-diepoxy-$\beta$-carotene |
| 6 | 0.55 | blue | 473.5 | 444.5 | 422 | 5,6-epoxy-$\beta$-carotene |
| 7 | 0.73 | brown | 478 | 451 | 422 | $\beta$-carotene |



**Figure 8.** Nonvolatile compounds produced after heat treatment of $\beta$-carotene at 97 °C for different times [I, 0 h; II, 1 h; III, 2 h; IV, 3 h] and separated by TLC on aluminum oxide $F_{254}$ type T: 1, starting; 2, aurochrome; 3, mutatochrome; 4, nonidentified; 5, neo-T-5,6,5',6'-diepoxy-$\beta$-carotene; 6, 5,6-epoxy-$\beta$-carotene; 7, $\beta$-carotene.

5,6-epoxy-$\beta$-carotene and of 5,6,5',6'-diepoxy-$\beta$-carotene. Independent of the fact that luteochrome has not been identified, these results are in good agreement with those reported by Marty and Berset (1986).

**Kinetics of Formation of Nonvolatile Compounds.** The quantities of the different oxygenated compounds identified among the degradation products of $\beta$-carotene were estimated from the intensities of the spots obtained after TLC for different times of heat treatment (from 1 to 3 h) of $\beta$-carotene at 97 °C (Figure 8). After 1 h only mono- and diepoxy derivatives and small amounts of mutatochrome were found; aurochrome only appears after 2 h of treatment. The quantities of monoepoxide are constant with time whereas the spot intensities of the other compounds increase with time.



**Figure 7.** Kinetics of formation of volatile compounds during heat treatment of $\beta$-carotene at 97 °C in the presence of oxygen: (×) 2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde; (■) 5,6-epoxy-$\beta$-ionone; (▲) dihydroactinidiolide.

and 5 (1.14) of an epoxide (Barber et al., 1960; Vetter et al., 1971) and provide confirmation of the presence of

## DISCUSSION

The results obtained in the present work show that the degradation of a water suspension of $\beta$-carotene at temperature of around 100 °C follows the same kinetics as the degradation of homogeneous organic solution of this pigment. The zero order observed in presence of air or oxygen is indicative of the presence of an excess of oxygen in the two cases (El Tinay and Chichester, 1970).
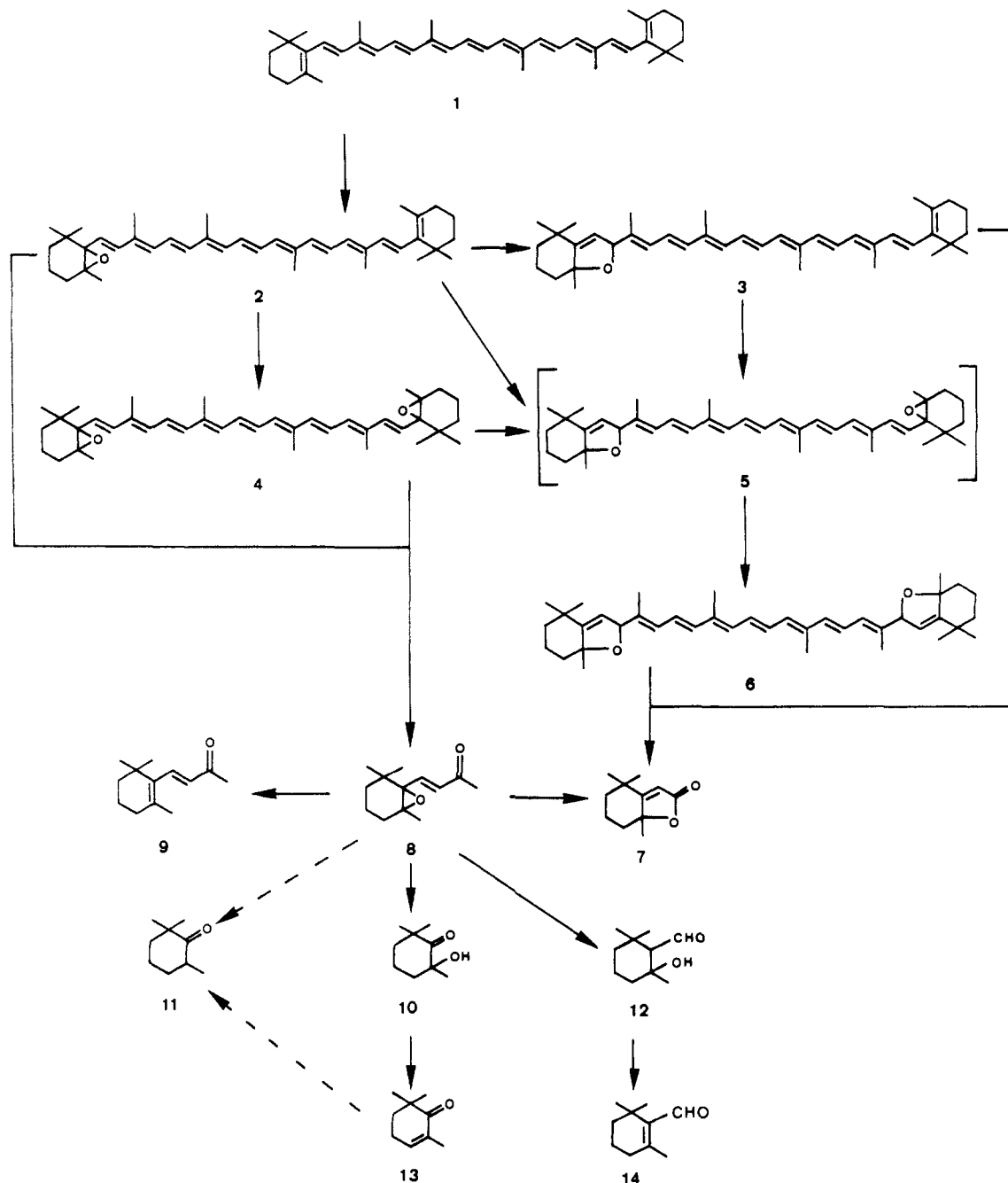
**Figure 9.** Reaction sequence for the formation of nonvolatile and volatile compounds during heating of $\beta$-carotene: 1, $\beta$-carotene; 2, 5,6-epoxy-$\beta$-carotene; 3, mutatochrome; 4, 5,6,5′,6′-diepoxy-$\beta$-carotene; 5, luteochrome; 6, aurochrome; 7, dihydroactinidiolide; 8, 5,6-epoxy-$\beta$-ionone; 9, $\beta$-ionone; 10, 2-hydroxy-2,6,6-trimethylcyclohexanone; 11, 2,6,6-trimethylcyclohexanone; 12, 2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde; 13, 2,6,6-trimethyl-2-cyclohexen-1-one; 14, $\beta$-cyclocitral.

On the other hand, the volatile compounds produced under the conditions studied are the same as those identified after heat treatment of homogeneous solutions of $\beta$-carotene or detected in biological products submitted to drying processes (Bricout et al., 1967; Fujimori et al., 1976; Moutounnet, 1978; Flament and Ohloff, 1985) or in heated juices (Schreier et al., 1976; Crouzet et al., 1983; Sakho et al., 1985).

Dihydroactinidiolide (DHA) is the only compound formed during heat treatment of $\beta$-carotene at 30 °C for 3 h under these conditions. It can be assumed that this compound, the most frequently cited among heat-induced volatiles of fruit products, is the first volatile compound produced during heat treatment of $\beta$-carotene. Its precursor is probably the mutatochrome according to the structural analogy and the results obtained

concerning the kinetic of formation of nonvolatile compounds from $\beta$-carotene.

The considerable increase of the quantity of DHA with reaction time at 97 °C (Figure 7) requires the participation of precursors other than mutatochrome. Among the nonvolatile compounds, aurochrome and perhaps luteochrome identified by Marty and Berset (1986) during heat degradation of $\beta$-carotene certainly act as precursors of dihydroactinidiolide. However, according to the small variation of the quantity of aurochrome detected by TLC, this contribution is assumed to be very weak. On the contrary the kinetics of formation of volatile compounds (Figures 6 and 7) shows clearly that 5,6-epoxy-$\beta$-ionone is a reactional intermediate that can give dihydroactinidiolide. The epoxy ketone is also the precursor of $\beta$-ionone, 2-hydroxy-2,6,6-trimethylcyclohexanone, and

Carotenoid Volatile Formation

*J. Agric. Food Chem.*, Vol. 38, No. 1, 1990 **243**

2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde whereas from the results published at present (Sanderson et al., 1971) it was generally assumed that this role was played by $\beta$-ionone.

If the formation of 2,6,6-trimethyl-2-cyclohexen-1-one from 2-hydroxy-2,6,6-trimethylcyclohexanone and of $\beta$-cyclocitral from 2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde through a dehydration process is clear, the 2,6,6-trimethylcyclohexanone may originate from different compounds such as $\beta$-ionone (Sanderson et al., 1971), epoxy-5,6-$\beta$-ionone, or 2,6,6-trimethyl-2-cyclohexen-1-one (Figure 9).

## ACKNOWLEDGMENT

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