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OXIDATION AND THERMAL DEGRADATION OF CAROTENOIDS

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BONNIE **TY P*** and **CHOO Y M***

Carotenoids are widely used in food applications. Their highly unsaturated nature makes them susceptible to degradation by oxidation and thermal processes, especially under severe processing and storage conditions. The mechanisms during auto-, photo-catalyzed and photosensitized-oxidations of trans β-carotene are discussed. The oxidation products formed are mixture of epoxides, apocarotenal and hydroxy compounds. Isomerization, oxidation and breakdown of the carotenoid molecule occur as a result of thermal degradation. Two types of thermal degradation products are formed: volatile and non-volatile. The volatile fraction consists of low molecular weight molecules which vapourizes. The non-volatile fraction is the residual fraction after vapourization of the volatile fraction. The mechanisms for formation of the two fractions are discussed.

INTRODUCTION

Carotenoids are linear C_{40} tetraterpenoid hydrocarbons comprising eight C_5 isoprene units with an extensive conjugated polyene chain as the light absorbing chromophore which gives them their brilliant colours. The structures of carotenoids confer on them many important physiological properties, such as antioxidant activity. They, therefore, play an essential role in protecting cells and organisms against lipid peroxidation. The highly conjugated polyene systems are extremely efficient quenchers of singlet molecular oxygen and free radical species in lipid phases (Sies *et al.*, 1992 ; Di Mascio *et* al., 1989) and have been associated with decreased risks of cancer, atherosclerosis and cataract (Poppel *et al.*, 1993; Rosseau *et al.*, 1992; Bunce, 1993)

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* Palm Oil Research Institute of Malaysia, P.O. Box 10620. 50720 Kuala Lumpur, Malaysia.

However, the very feature which confers the important properties on carotenoids also makes them unstable (Johnson, 1995). The structures break down with attack by free radicals, such as singlet molecular oxygen and other reactive species. The common degradation pathways are isomerization, oxidation and fragmentation of the carotenoid molecules. Heat, light and acids promote isomerization of the *trans*-form of carotenoids to the *cis*-form. Light, enzymes, prooxidant metals and co-oxidation with unsaturated lipids, on the other hand, induce oxidation. Pyrolysis occurs under intense heat with expulsion of low molecular weight molecules.

As the structures of carotenoids confer them their unique properties, any modification of the basic skeleton, such as cyclization, double bond migration, introduction of oxygen in various forms and chain shortening through thermal or chemical reaction, can result in loss of the properties. The oxidative breakdown products of carotenoids have, hitherto, received surprisingly little attention. In the literature, attention is mainly focused on the degradation of individual carotenes, such as *trans*-β-carotene. Studies have also been carried out in controlled model systems, such as solvents, but these do not really reflect the complex reactions occurring in dietary oils and fats. Even the simple degradation of a pure carotene gives rise to an overwhelmingly wide range of oxidation products. And thus far, only a few of the degradation products have been isolated and identified as the analysis of degradation products is rather tedious and time consuming. Many of the products occur only in small quantities with similar polarities and high reactivity, and hence are difficult to analyse. In the degradation of a mixture of carotenoids, the analysis for products will even be more difficult, if not impossible at all, to complete.

MECHANISMS OF CAROTENOIDS OXIDATIVE DEGRADATION

Oxidation is, by far, the major cause of carotenoid degradation. However, little information on the mechanism involved can be found in the literature.

Autoxidation of carotenoids is believed to follow the free radical route. El-Tinay and Chichester (1970) studied the rats of loss of β-carotene by reacting it with molecular oxygen in toluene at 60°C. The loss was linear with time, indicating an overall zero-order reaction kinetics, in which the reaction is independent of the concentrations of reactants. They suggested that the interaction of p-carotene and oxygen went through an activated dipole association complex formed in an equilibrium step. There was no induction period, unlike in the autoxidation of fats, suggesting that the reaction was not autocatalytic. Teixera et al. (1981) also observed no induction period in their study of oxygen uptake by B-carotene, decolouring it in a dehydrated food model.

However, other studies have shown the oxidation of carotenoids to be autocatalytic, with an induction period before rapid reaction begins. Goldman et al. (1983) studied the rate of decolourization of p-carotene at 35°C under reduced oxygen concentration and low water activity to simulate the conditions of dehydrated foods in impermeable packages. The result was a sigmoid-shaped p-carotene retention curve with three regions: an induction period of slow reaction, a fast reaction 'main' period and a retardation period-suggesting autocatalysis. Other studies (Budowski and Brondi, 1960; Chou and Breene, 1972; Kanner et al., 1978) also reported, for different systems with p-carotene, an induction period.

Based on the free radical theory, the general mechanism of p-carotene (BC•) oxidation is similar to that of lipid peroxidation (Emanuel et al., 1967; Karel, 1980). Burton and Ingold (19841, as shown below, proposed a specific mechanism of p-carotene oxidation by the addition of a peroxyl radical (ROO•) to β-carotene to form a resonance-stabilized, carbon-centred BC radical adduct (ROO-BC•).

$$\mathrm{BC\cdot} + \mathrm{ROO'} \rightarrow \mathrm{BROO\text{-}BC\cdot} \qquad (a)$$
$$\mathrm{ROO\text{-}BC\cdot} + \mathrm{ROO\cdot} \rightarrow \text{non-radical products} \qquad (b)$$
$$\mathrm{ROO\text{-}BC\cdot} + \mathrm{O_2} \rightarrow \mathrm{ROO\text{-}BC\text{-}OO\cdot} \qquad (c)$$

When the reaction follows equations (a) then (c), p-carotene is degraded without any free radical being trapped. This is *autoxidation*. In contrast, the *antioxidant* reaction follows equation (a), then (b), with consumption of radicals. Both reactions depend on the oxygen partial pressure (pO_2). At high pO_2 oxygen addition to the b-carotene-radical adduct is favoured, β-carotene-derived peroxyl radicals are formed, and most of the p-carotene are consumed by autoxidation. However, at low pO_2, addition of oxygen to the B-carotene-radical adduct is less favoured, and the adduct may trap a second peroxyl radical to produce an antioxidant effect.

In photosensitized oxidation, carotenoids, especially lycopene and b-carotene, are effective quenchers of singlet oxygen ($^1O_2$). The quenching of $^1O_2$ by b-carotene can be the physical quenching of (1) excited sensitizer molecules, or (2) singlet oxygen. Physical quenching proceeds by energy transfer from ‘0, to the carotenoid molecule [Equation (d)], leading to the formation of triplet-state oxygen ($^3O_2$). A similar *process* can occur between a carotenoid and an excited sensitizer. If truly catalytic, the carotenoid should remain intact [Equation (e)]; however, usually a chemical reaction sets in, destroying the carotenoid molecules (Di Mascio et al., 1989; Krinsky, 1989; Conn *et* al., 1991).

‘0, +CAROTENOID->$^3O_2$ +^{3}CAROTENOID (d)

^{3}CAROTENOID-> CAROTENOID+HEAT (e)

Carotenoids and neutral lipids are often closely associated because of their co-existence in nature, *e.g.* in crude palm oil. This means that their coupled-oxidation is often inevitable, and the process warrants study.

Budowski and Brondi (1960) reported that the addition of an unsaturated fat, or a mixture of methyl esters of fatty acids, to a solution of p-carotene in liquid paraffin accelerated the destruction of both the carotene and fatty acid methyl esters. There was a rapid increase in the oxidation rate suggesting that fats are pro-oxidants. They found the pro-oxidant effect to be more pronounced at low levels of fats, e.g. raising the level of fats from 0% to 5% (low concentration) showed a greater ‘pro-oxidant’ effect than raising the level from 5% to almost 100%. As there is competition between the fat and carotene for the fatty peroxide radicals, the carotene is rapidly attacked when there are less fats molecules around, and vice *versa* (Holman, 1949). They also observed that the higher the degree of unsaturation of the fat, the higher was the rate of autoxidation as unsaturated fats oxidize more rapidly than saturated ones and produce more radicals likely to attack carotene,

The coupled-oxidation of carotene with lipids under light, or photoxidation, proceeds in a different manner from autoxidation. Carnevale et al. (1979) studied the photo-catalyzed oxidation of p-carotene in fatty acid esters of different degrees of unsaturation under fluorescent light. Their findings, unlike those of Budowski and Brondi (19601, showed that, under fluorescent light, the higher the unsaturation, the slower is the rate of autoxidation. This means that a higher degree of unsaturation offers a greater protection to b-carotene against autoxidation. In this instance, sensitizers were absent and, therefore, the involvement of singlet oxygen was ruled out. The deterioration of the β-carotene was probably due to absorption of light in the visible region. They suggested that in the event that the degradation of p-carotene occurs as a free radical process, the unsaturated fatty acid esters provide substrates to divert the sequence in the chain process, and that the tendency to divert is enhanced by an increase in unsaturation. Jorgenson and Skibsted (1990) found that the sensitivity of carotenoids to non-sensitized direct light is dependent on the wavelength of irradiation. Also, the photo-catalyzed oxidation of b-carotene is more severe in ultraviolet than in visible light.

Warner and Frankel (1987) showed that adding very little p-carotene to soyabean oil (to a concentration of 5 - 20ppm) treated with citric acid and then exposing it to light sufficed to significantly decrease its flavour deterioration. Thus, even at such low concentrations, β-carotene effectively protected the oil against light deterioration by quenching singlet oxygen. They further suggested that the light stability of the oil conferred by B-carotene at concentrations below 20ppm is due to the protective effect of S-tocopherol from soyabean oil, and that b-carotene behaved synergistically with δ-tocopherols in preventing oxidation. Apparently, δ-tocopherol inhibits the free radical autoxidation of β-carotene, and it, in turn, protects the oil against photoxidation. A study by Haila and Heinonen (1994) on the action of @carotene on purified rapeseed oil exposed to light also showed a synergistic effect between p-carotene and γ-tocopherol. They found that the inhibition of oxidation was significantly greater for a combination of γ-tocopherol and S-carotene than the sum of the individual inhibitions. Another study by Haila et al. (1996) on the effect of lutein, lycopene and γ-tocopherols on the photo-and autoxidation of triglycerides also showed the synergistic effects of these carotenoids with γ-tocopherol.

Kiritsakis and Dugan (1985) also showed the protective effect of S-carotene against photosensitized oxidation in bleached olive oil in which chlorophyll was added as sensitizer. They found a decreased rate of peroxide formation in olive oil with low levels (6-7ppm) of p-carotene exposed to fluorescent light. They suggested that p-carotene acted as a singlet oxygen quencher, or was perhaps oxidized selectively, sparing the olive oil until all the carotene was destroyed as the oxidation proceeded.

Other studies also showed the protective effect of b-carotene against photosensitized oxidation of edible oils, such as in soyabean oil (Lee and Min, 1988; Jung and Min, 1991), soyabean and rapeseed oils (Suzuki et al., 19891, and olive oil (Fakourelis et al., 1987).

OXIDATION PRODUCTS

There are few studies on the formation, isolation and structural identification of the primary, secondary and final oxidation products of carotenoids. Mordi et al. (1991) investigated the autoxidation products of p-carotene. Pure β-carotene in benzene and in tetrachloromethane was reacted with molecular oxygen at 30°C in the dark. Figure *1* shows the primary products formed within the first few hours of oxidation: 5,6-epoxy-β-carotene [Figure *1(a)*], retinal [Figure *1(b)*], β-apo-13-carotenone [*Figure 1(c)*], β-ionone [Figure *1(d)*], β-apo-14'-carotenal [Figure *1*(e)], β-ionylidene acetaldehyde [Figure *1(f)*], 5,6,5', 6'-diepoxy-β-carotene, 5,8-epoxy p-carotene [Figure *1(g)*] and 5,8,5', 8'-diepoxy-p-carotene.

The product mixtures became even more complex as oxidation progressed. β-Apo-12'-carotenal [*Figure 1*(h)] was identified, as well as a number of shorter-chain mono-and di-oxygenated compounds, including β-cyclocitral [*Figure 1*(i)], 2,2,6-trimethylcyclohexanone [Figure *1*(j)], dihydroactinidiolide [*Figure* I(k);, 5,6-epoxy - β-ionone [*Figure 1*(l)] and 5,8-epoxy-β-ionone [Figure *1*(m)]. In the later stages of the oxidation, the longer-chain products, the epoxides and carbonyls were not detected because of further degradation. The end mixtures were mostly as in [*Figure 1*(d)] and [*Figure 1*(l)].

The products formed by autoxidation and coupled oxidation of carotenoids with lipids were of the same types. For β-cryptoxanthin in methyl linoleate kept at 37°C for three hours, similar epoxide derivatives were reported. The cryptoxanthin monoepoxides were shown to be 5,8-epoxy-5, 8-dihydro-β,β-caroten-3-ol and 5,6-dihydro-β,β-caroten-3-ol by mass spectrometry (Gross et al., 1983).

A mechanism for the formation of autoxidation products of p-carotene was suggested by Ong and Ooi (1982) (see Figure 2) involving action by the peroxyl radical. Recently, the peroxyl radical autoxidation products of β-carotene have been identified as a complex mixture of epoxy, hydroxy and carbonyl groups (Kennedy and Liebler, 1991; 1992; Handelman et al., 1991; Yamauchi et al., 1993).

Thermal Degradation of Carotenoids

The fact that carotenoid pigments are made up of a system ofconjugated double bonds makes them vulnerable to heat. When intense heat is applied, the tine structures are cleaved and molecular reactions occur, involving the double bonds. Two types of thermal degradation products are formed: a volatile fraction of low molecular weight molecules which is vapourized, and a non-volatile fraction from the larger fragments of the carotene molecules after cleaving off the volatile fraction. Much effort has gone into the identification of the volatile fractions, using headspace gas chromatography-mass spectrometry. The non-volatile fraction, however, has been very much neglected because of its complexity.

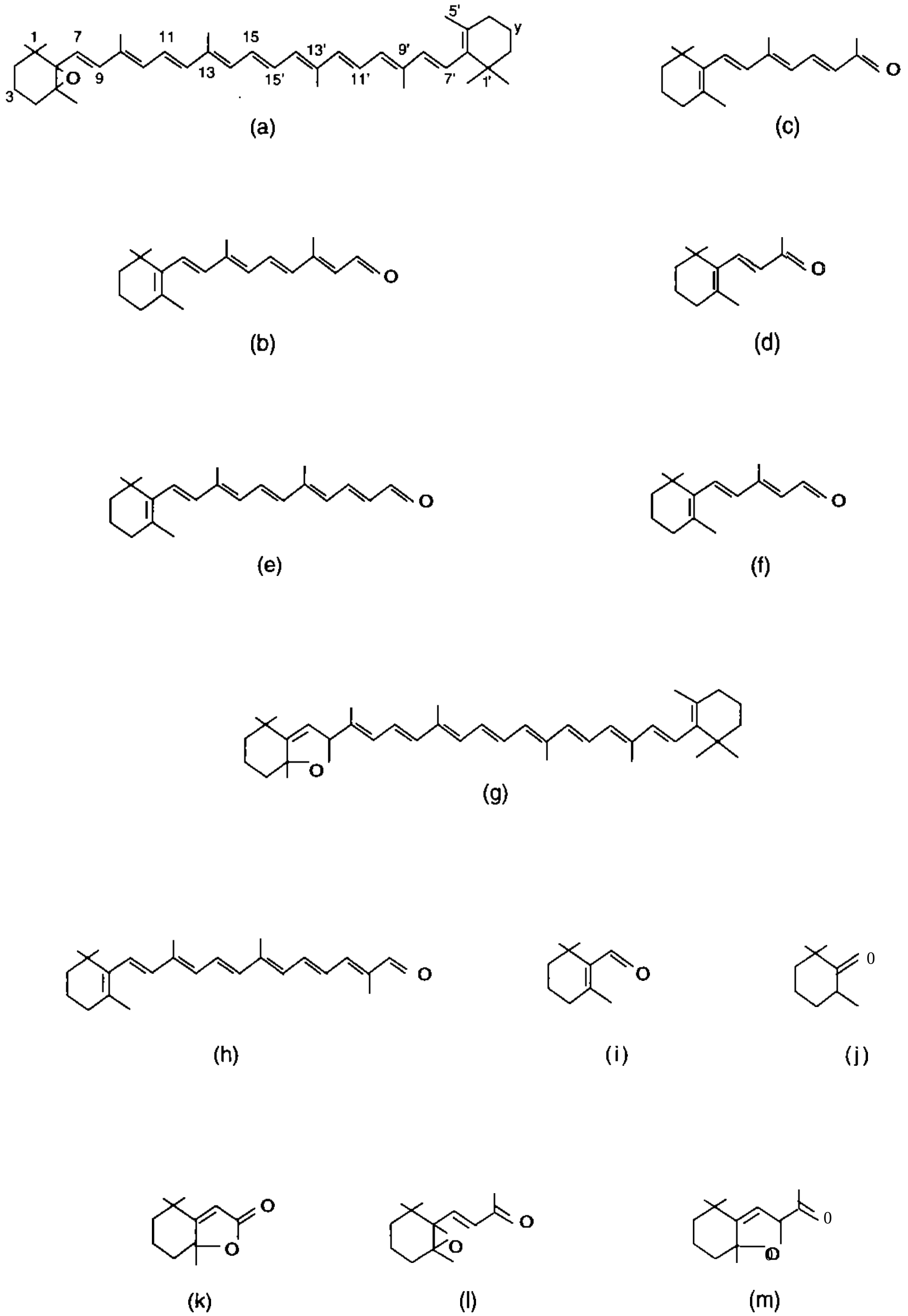


Figure 1. ***Autoxidation*** *products of* ***β-carotene.***

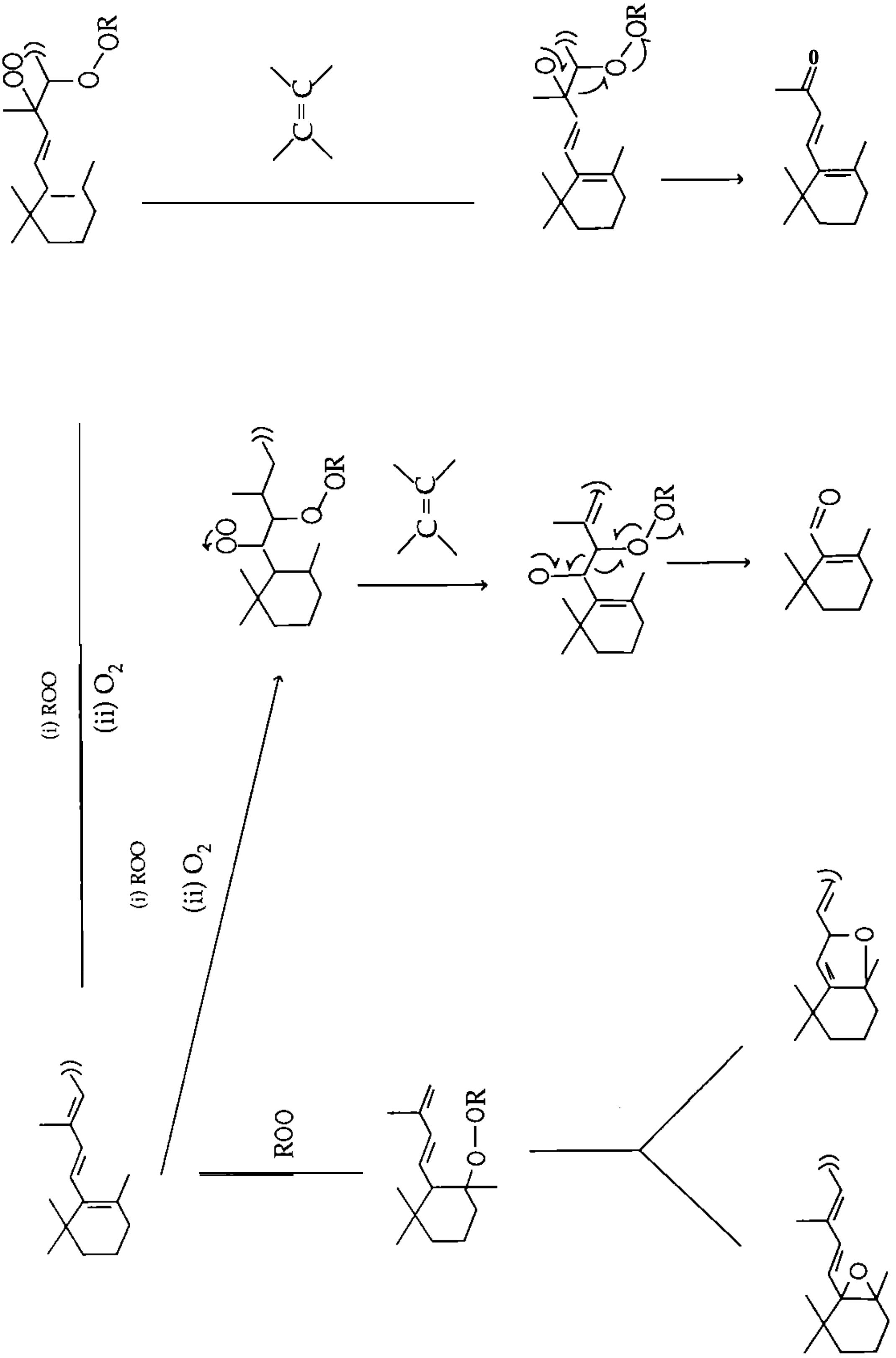


Figure 2. Mechanism of peroxyl radicals addition to β-carotene proposed by Ong and Ooi, 1982.

Mechanism and Products of Thermal Degradation

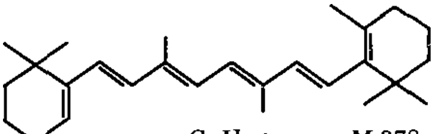
Carotenoids are widely used in the food industry and are often subjected to high temperatures, especially in the making of confectionery products. Extrusion cooking is one of the processes widely used for shaping starting materials. Over a short time, the product experiences the actions of high temperature (150°C to 220°C), high pressure and intense shearing, degrading the carotenoids by isomerization and thermal oxidation. Marty and Berset (1986) identified epoxy compounds resulting from extrusion cooking. Because the electron density of the double bonds decreases from the extremities of the polyene structure towards the centre, epoxidation occurs preferentially at the 5,6- and/or 5', 6'-carbon double bond. The internal stress from epoxy ring formation causes a subsequent rearrangement to a 5,8- (or 5',8'-) dihydrofuran ring. The possible sequential reactions are shown in Figure 3.

Marty and Berset (1988) showed that isomerization occurs simultaneously with the oxidation of carotenoids. They identified the cis isomers of p-carotene: 13,13'-di-*cis*-β-carotenes, 9,13'-di-*cis*-β-carotene, 15-*cis*-β-carotene, 13-*cis*-β-carotene, and 9,9'-di-*cis*-β-carotene.

They also found aldehyde and ketone derivatives from the oxidative breakdown of double bonds in the main chain of p-carotene (Marty and Berset, 1990). Pullman (1960) showed that the 7, S-carbon double bond in the polyene chain of p-carotene has the highest mobile index, 0.731, calculated with the molecular orbitals method and claimed that the electron structure favours the preferential oxidative breakdown of this double bond. The hypothesis was supported by the quantities of the five apocarotenals and one ketone detected. The chronological order of appearance was (1) β-apo-8'-carotenal (2) β-apo-10'-carotenal (3) β-apo-12'-carotenal (4) β-apo-14'-carotenal (5) β-apo-15-carotenal (6) β-caroten-4-one. *Figure* 4 (Marty and Berset, 1990) shows that extrusion cooking shortens the molecule sequentially, two carbon atoms at a time. β-Apo-15-carotenal can also be formed by direct cleaving of the central double bond.

Deodorization in the refining of edible oil requires very high temperatures, typically 170°C - 250°C (Gunstone, 1996), sufficient to degrade carotenoids. Ouyang et al. (1980) studied the non-volatile degradation products of p-carotene under conditions simulating palm oil deodorization. They reported the presence of 13-apo-β-carotenal, 15'-apo-β-carotenal and 14'-apo-β-carotenal.

Onyewu et al. (1982) investigated the non-polar non-volatile thermal degradation products formed by heating p-carotene at 210°C for four hours and tentatively identified 3,7,10-trimethyl-11,12-*bis* (2,6,6-trimethylcyclohex-1-enyl)dodeca-1,3,5,7,9,11-hexane ($C_{33}H_{48}$) and 3,6-dimethyl-1,8-bis (2,6,6-trimethylcyclohex-1-enyl) octa-1,3,5,7-tetraene ($C_{28}H_{42}$). Edmunds and Johnstone (1965) proposed a mechanism for the formation of these compounds involving cyclization of an eight electron system, followed by a rearrangement to form a four-member ring intermediate. The four-ring system then looses toluene to form $C_{33}H_{48}$. Similarly, from a twelve electron system, $C_{28}H_{42}$ (structure shown below) is formed with the expulsion of dimethylcyclodecapentaene.



$C_{28}H_{42}$; M_r378

Onyewu et al. (1986) studied the non-volatile products of p-carotene in glycerol under conditions simulating palm oil deodorization and deep frying. The experiments were conducted in four different times and at four different temperatures. The highest loss of p-carotene (91%-97%) was observed at 210°C after four hours heating. Over 70 non-volatile compounds were observed. The non-polar fraction was of interest because of the possible presence of PAH, whereas the more polar fraction possessed flavour attributes or nutritive value. The compounds isolated are shown in Figure 6. Compound 1 ($C_{33}H_{48}$) had been reported earlier. Cleaving of the ionene moiety from p-carotene gave a radical which, on undergoing p-fission, formed compound 2 ($C_{26}H_{34}$), a octatetraene compound. Compounds 3-7 were thermal

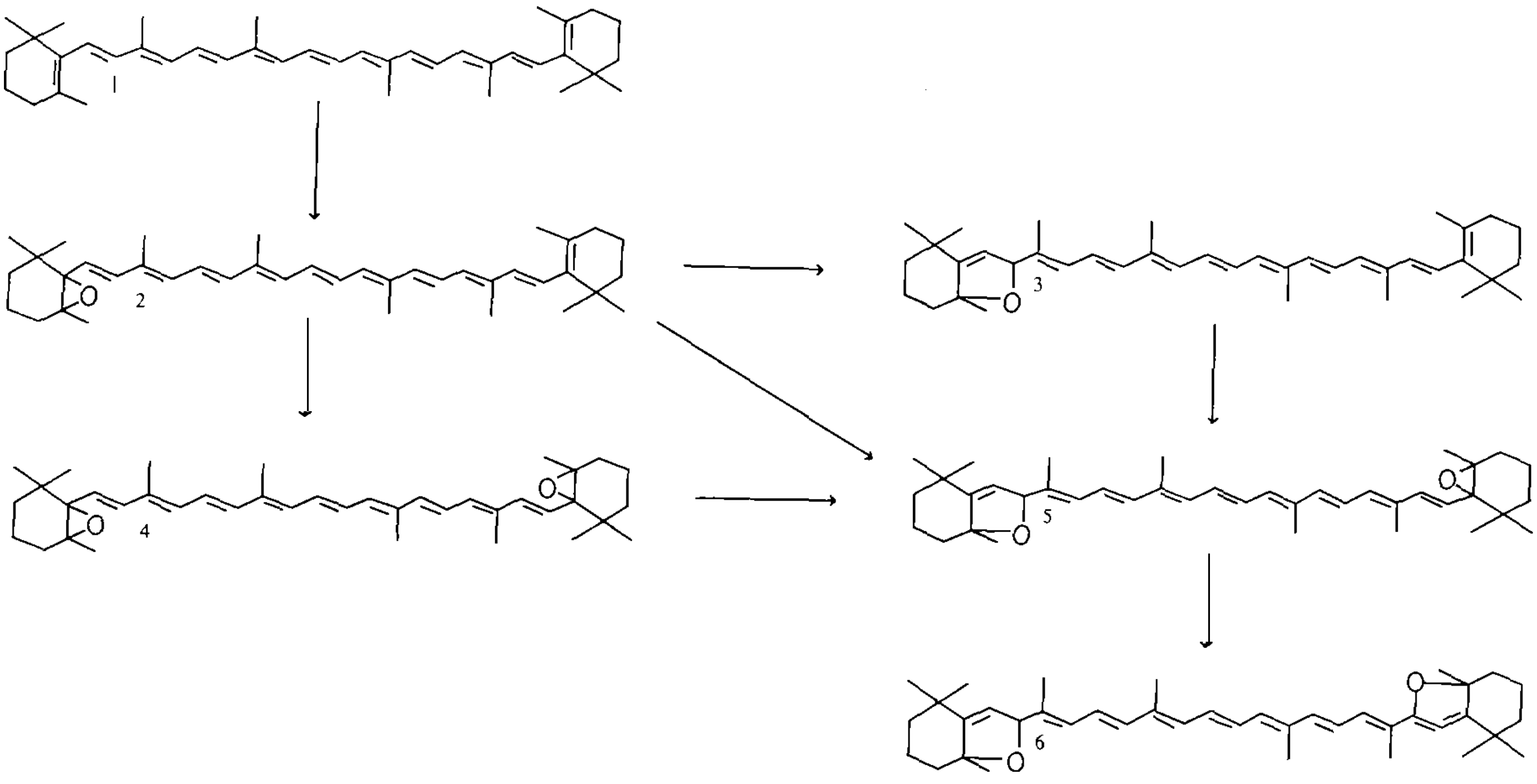


Figure 3. Reaction sequence for the formation of β-carotene epoxides during extrusion cooking or heating. 1. β-Carotene; 2. β-Carotene 5, 6-epoxide; 3, β-Carotene 5, 8-epoxide; 4, β-Carotene 5,6,5'6'-diepoxide; 5. β-Carotene 5,6,5'8-diepoxide; 6. β-Carotene 5,8,5',8'-diepoxide.

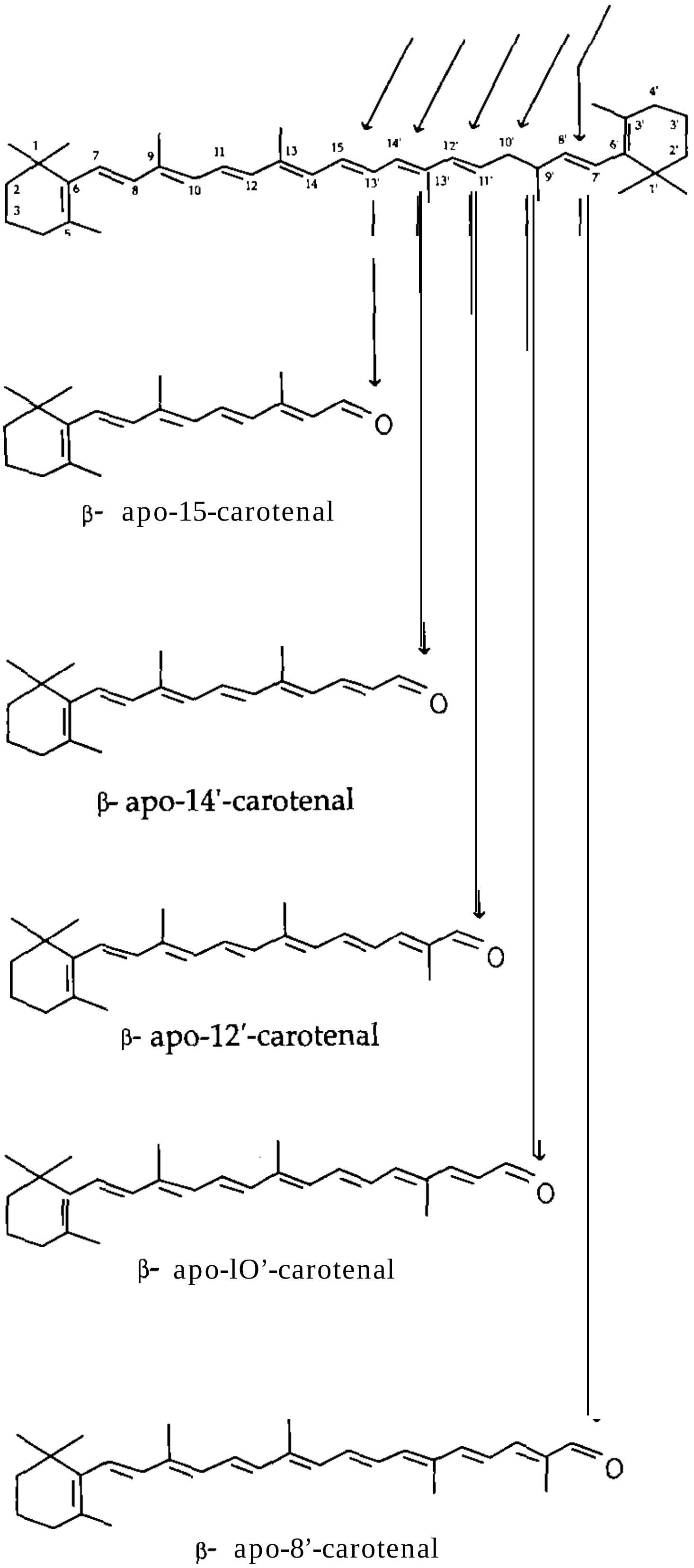


Figure 4. Positions of oxygen attack on the polyene chin of β-carotene corresponding to the formation of five apocarotenals isolated after extrusion cooking.

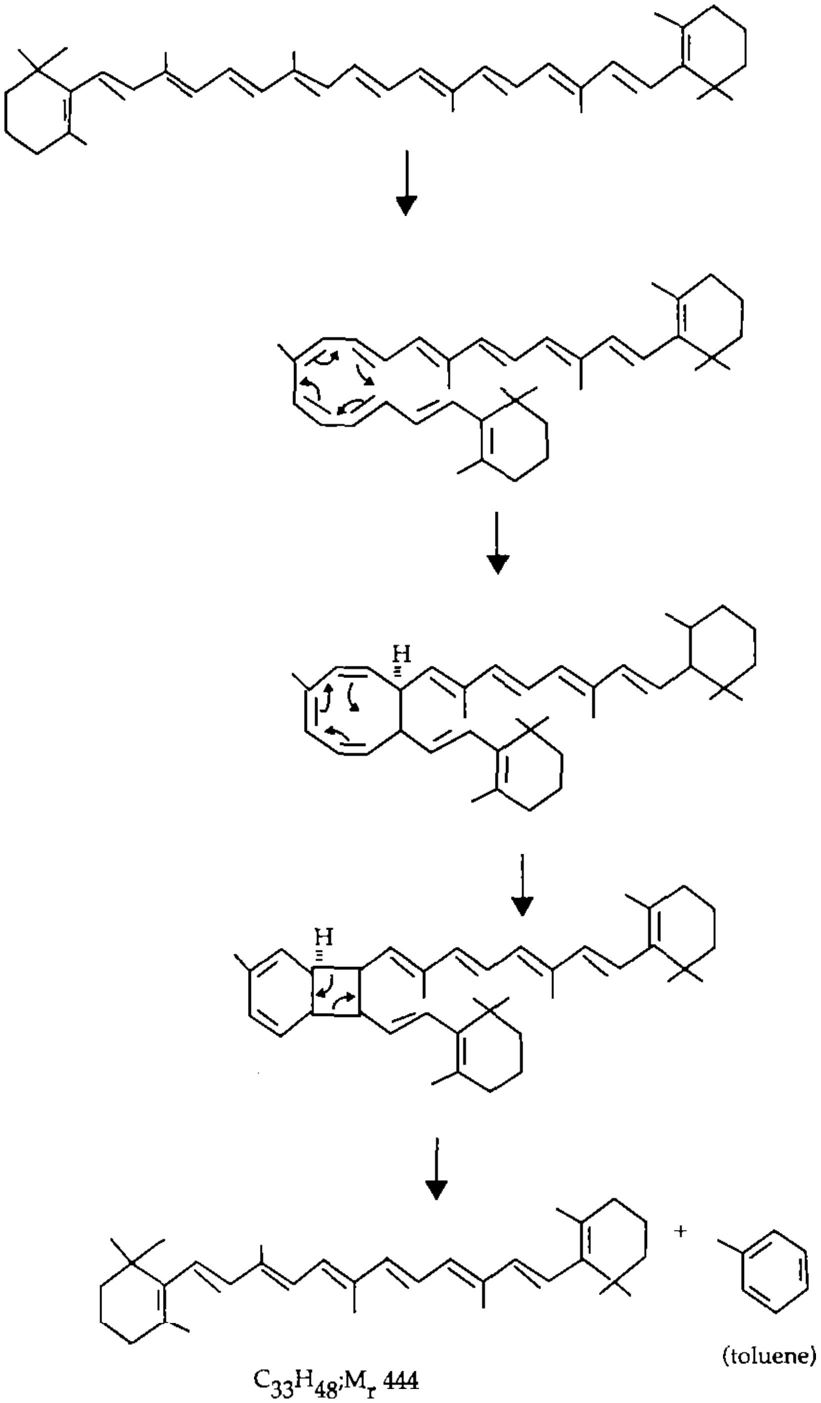
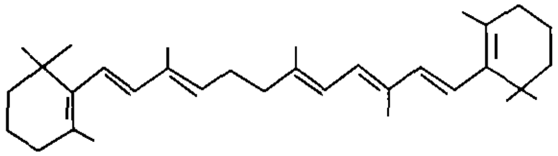


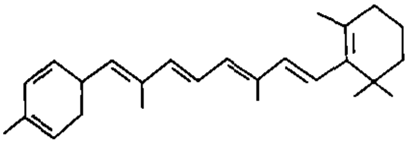
Figure 5. Proposed mechanism for formation of mass unit 444: 3,6,10-trimethyl-1,12-bis (2,6,6-trimethylcyclohex-1-enyl) dodeca-1,3,5,7,9,11-hexaene.

Compound #1



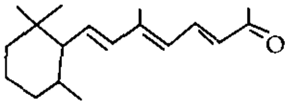
$C_{33}H_{48}$, Molecular weight 444
3,7,10-trimethyl-1,12-bis (2,6,6-trimethy-cyclohex-l-enyl) dodeca-1,3,5,7,9,11-hexaene

Compound #2



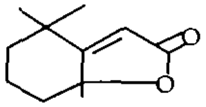
$C_{26}H_{34}$, Molecular weight 346
3,7,-dimethyl-8-tolyl(2,6,6-trimethy-cyclohex-l-enyl)octa 1,3,5,7-tetraene

Compound #3



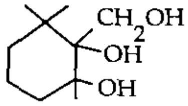
$C_{18}H_{26}O$, Molecular weight 258
β-apo-13-carotene

Compound #4



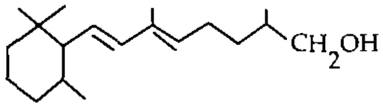
$C_{11}H_{16}O_2$, Molecular weight 180
dihydroactinidiolide

Compound #5



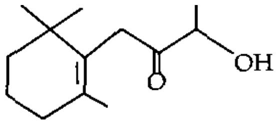
$C_{10}H_{20}O_3$, Molecular weight 188
2,-hydroxymethy-1,3,3-trimethy-1,2-cyclohexandiol

Compound #6



$C_{19}H_{29}O$, Molecular weight 274
β-apo-14-carotenol

Compound #7



$C_{13}H_{22}O$, Molecular weight 210
1-(2,6,6-trimethylcyclohex-1-enyl)-3-hydroxy-2-butanone

Figure 6. Non-volatile degradation products of β-carotene.

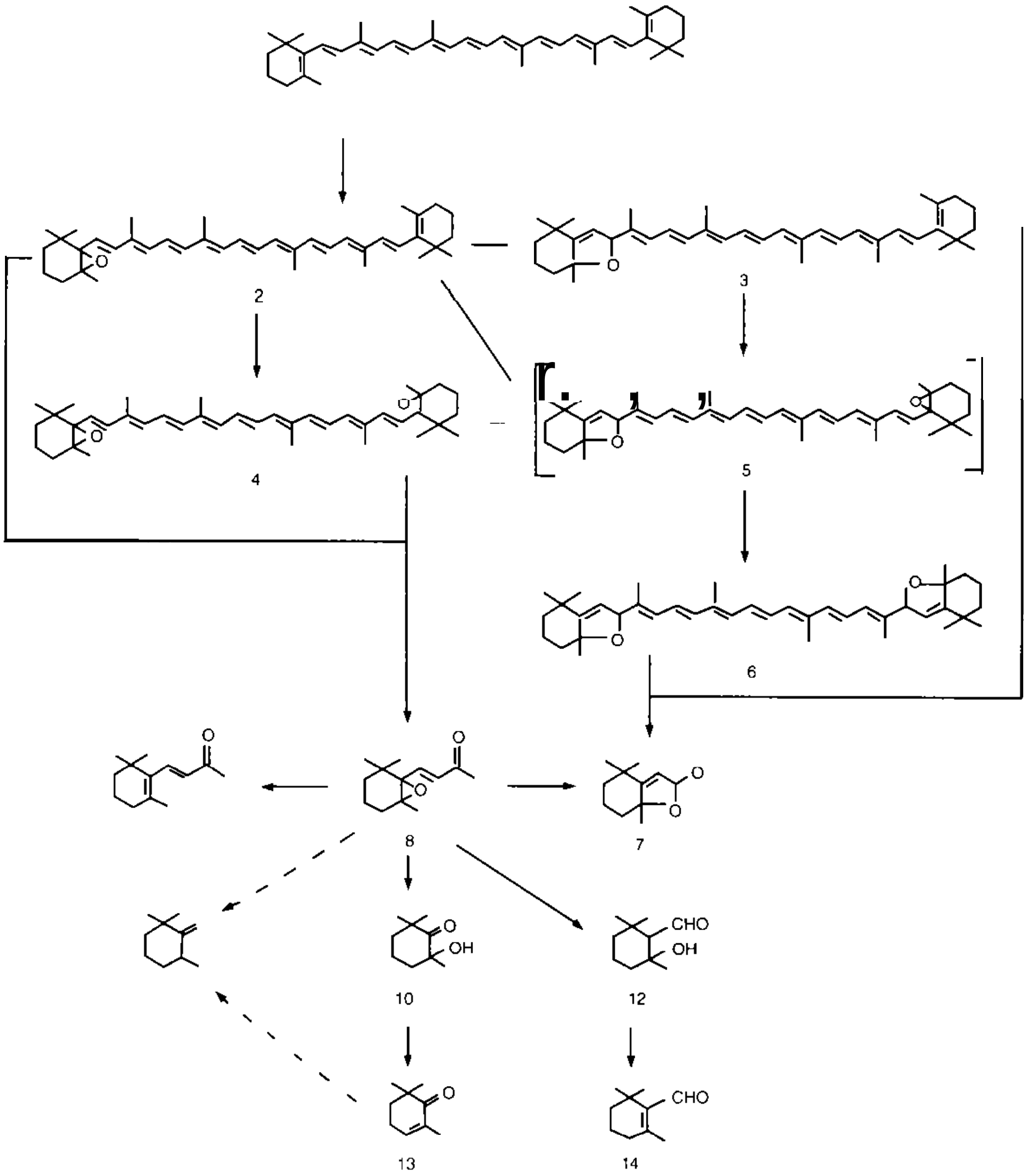


Figure 7. Reaction sequence for the formation of non-volatile and volatile compounds during heating of p-carotene: 1. β-Carotene; 2. 5,6-epoxy-β-carotene; 3. Mutatochrome; 4. 5,6,5',6'-Diepoxy-β-carotene; 5. Luteochrome; 6. Aurochrome; 7. Dihydroactinidiolide; 8. 5,6,-Epoxy-β-ionone; 9. β-Ionone; 10. 2-Hydroxy-2,6,6-trimethylcyclohexanone; 11. 2,6,6-Trimethylcyclohexanone; 12. 2-Hydroxy-irimethylclohexane-1-carboxaldehude; 13. 2,6,6-Trimethyl-2-cyclohexen-1-one; 14. β-Cyclocitral.

oxidation products. Dihydroactinidiolide (Compound 4), a lactone present in a large amount, is an important flavour in food. Compounds 6 ($C_{19}H_{29}O$) and 7 ($C_{13}H_{22}O$) were similar to vitamin A-type compounds. Based on their molecular structures, they may also have nutritive value, e.g. vitamin A activity such as for Compounds 1 ($C_{33}H_{48}$), 2 ($C_{26}H_{34}$) and 7 ($C_{13}H_{22}O$). No polycyclic aromatic hydrocarbons (PAH) were detected in the non-polar fraction. Rost (1976) found that the amount of PAH in thermally neutralized oil, or in bleached and deodorized oil, was in the order of 6 11 x 10^{-3} ppm, much lower than that in crude palm oil (see *Table* I). The concentration is too low to threaten human health.

Kanasawud and Crouzet (1990) studied the mechanism for formation of volatile and non-volatile compounds during heat treatment of β-carotene in water (*Figure* 7). They found that dihydroactinidiolide [*Figure 7(7)*] was the first compound formed, probably from mutatocbrome [*Figure 7(3)*]. 5,6-Epoxy-β-ionone [*Figure 7(8)*] was the intermediate product, and the precursor for volatiles such as β-ionone [*Figure 7(9)*], 2-hydroxy-2,6,6-trimethylcyclohexanone [*Figure 7(10)*], 2,6,6-trimethylcyclohexanone [*Figure 7(11)*], 2-hydroxy-2,6,6-trimethylcyclohexane-1-carboxaldehyde [*Figure 7(12)*], 2,6,6-trimethyl-2-cyclohexen-1-one [*Figure 7(13)*] and β-cyclocitral [*Figure 7(14)*].

Other studies on the thermal degradation of B-carotene are listed in ***Table 2. These*** studies were done in conditions not representative of the practical conditions in the food or dietary oil system and focused mostly on the volatile compounds.

CONCLUSIONS

As carotenoids are widely used in food, their stability in food systems is of major importance. There is always concern that when carotenoids are subject to drastic conditions, their important physiological properties are lost, and that the oxidation products formed pose a threat to human health. It is, therefore, very reassuring to find from the studies thus far, that despite changes to the original structures of carotenoids, many of the products formed still possess nutritive value and flavour attributes. Indeed, even under the drastic conditions of extrusion cooking and deep frying PAH, which are known carcinogens, were not detected above background levels. The findings, therefore, should allay the fears of using carotenoids in food even when drastic processing conditions, such as high temperature and pressure, are involved.

TABLE 1. POLYCYCLIC AROMATIC HYDROCARBONS CONTENT (µg/kg of oil) IN THERMALLY TREATED PALM OIL*

Polycyclic aromatic hydrocarbon	Crude palm oil	Thermal neutralization (260°C)	Bleaching and deodorization (260°C)
Anthracene	7	2	3
Phenanthrene	9	2	0
Fluoranthene	3	3	1
Pyrene	6	2	1
Benz (a) anthracene	1	1	0
Chrysene			
Total			

* Source: Rost (1976).

TABLE 2. OTHER THERMAL DEGRADATION STUDIES OF CAROTENOIDS

Thermal degradation conditions	Volatile products identified	References
A mixture of a- and β-carotenes heated at 260°C for 24 hours.	2,6-Dimethylnaphthalene	Jones and Sharpe (1948)
A 1% solution of β-carotene in benzene heated at 188°C for 72 hours.	Toluene, m-xylene, 2, 6-dimethylnaphthalene	Day and Erdman (1963)
A dispersed sample of β-carotene in water heated in a sealed glass ampule at 188°C for ‘72 hours.	Toluene, m-xylene, 2, 6-dimethylnaphthalene	Mulik and Erdman (1963)
Melted p-carotene heated under vacuum at 240°C for a prolonged period.	Toluene, m-xylene, 2, 6-dimethylnaphthalene	Mader (1964)
Pyrolytic degradation of lycopene and ~-carotene by heating to 250°C for 10 minutes in CO,.	Toluene, m-xylem, 2, 6-dimethylnaphthalene	Schwitzer et al. (1959)
β-Carotene pyrolyzed at 400°C and 700°C in nitrogen.	Polynuclear aromatic hydrocarbon	Halaby and Fagerson (1971)
β-Carotene heated at 190°C and 220°C for 10 minutes in nitrogen and air.	Toluene, m-xylene, ionene, 2,6-dimethylnaphthalene, β-cyclocitral, β-ionone, dihydroactinidiolide, 5,6-epoxy-β-ionone	Schreir et al. (1979)
β-Carotene heated under vacuum at 200°C to 350°C for 24 hours as a geothermal reaction of carotenoids.	Toluene, xylene, ionene, 2,6-dimethylnaphthalene with molecular weights of 136, 240, 346 and 444	Ishiwatari (1980)

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