

## Palm Carotenoids, Tocopherols and Tocotrienols

*In the following article, Barrie Tan of the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, identifies important minor components of palm oil, discusses their chemistry and relationship to vitamin A and E activities, and examines their commercial potential.*

Oils from plant origin can be divided into seed oils and fruit oils. Although the number of oilseed sources is large, there are only two fruits for which oil production is of economic importance: oil palm (*Elaeis guineensis*) and olive (*Olea europaea*, *ssp. europaea*). Most of the olive harvest takes place in the Mediterranean region. Oil palms, meanwhile, are concentrated in southeast Asia.

The oil palm is a monoecious plant. The palm yields fruit for about 25 years, but has a life expectancy of at least 100 years. Each mature palm tree is capable of bearing about one bunch, containing 1,000-3,000 palm fruits, per month. The average weight of each bunch varies between 20-30 kg. The fig-like, ovoid-shaped fruit averages 2-5 cm in length and weighs 5-20 g.

Botanically, each fruit consists of a single seed, the kernel (containing the hard shell endocarp and the creamy endosperm within) and the succulent fibrous mesocarp. Palm oil is obtained from the mesocarp and palm kernel oil is from the endosperm. The predominant fatty acids in palm oil are palmitic, oleic, stearic and linoleic. Those of palm kernel oil are lauric, myristic, oleic and palmitic acids. The relative triglyceride composition, expressed in various permutations of saturated (S) and unsaturated (U) fatty acids, is SSS 6%, SSU 48%, SUU 43% and UUU 3%.

The fact that palm products possess relatively high levels of carotenoids and vitamin E is not new (1). However, the potential of extracting these natural substances has increased with the recent jump in palm oil production in southeast Asia.

### PALM PLANTINGS

Malaysia and Indonesia have approximately 1.5 and 0.4 million hectares of palm plantations, respectively. Palm oil is approximately 12 to 15 times higher in terms of productivity (expressed in kilograms per hectare per year) than many seed oils (palm oil, 3,900 kilograms; sunflower, 589 kilograms; rapeseed, 409 kilograms; soybean oil, 319 kilograms; corn oil, 254 kilograms). However, oil palm trees only grow in the tropics (10 degrees latitude above and below the Equator).

The major palm-producing nations are Malaysia, Indonesia, Thailand, Nigeria, Ivory Coast, Colombia, Venezuela and Papua New Guinea. On the other hand, soybean crops are grown in such temperate regions as the U.S., Argentina and China, as well as tropic and subtropic regions in Brazil, India and parts of Indonesia (2). Unlike oilseeds, to get a high yield, oil palm can

be commercially grown only on the global equatorial belt.

Malaysia produces 4.5 to 5.0 million metric tons (MT) of palm oil annually, mostly in west Malaysia. West and east Malaysia produced 4.12 million MT (90.7%) and 0.42 million MT (9.3%), respectively, in 1986/1987 (3). Indonesia produced 1.3 million MT in 1986/1987, mostly in western Kalimantan and northern Sumatra (3,4).

### PRODUCTION CONCENTRATION

Oil palm trees were introduced to southeast Asia in the late 1800s, but serious commercial planting did not begin until the late 1950s. Today Malaysia processes more than 98% of its crude palm oil domestically and exports 90% of its processed oil. In the processing step, the carotenoids are completely bleached by acid-activated clay filters and vitamin E is concentrated in the palm fatty acid distillate (PFAD) fractions.

Because palm oil is derived from a perennial crop, a reliable supply is available throughout the year as opposed to most vegetable oils, which are from annual seasonal crops. As a result, the minor components may be recovered from palm oil raw materials continuously and in a relatively small geographical area.

Malaysia and Indonesia are continuing to enlarge palm oil production. Malaysia is the largest exporter and second largest producer of edible oils; Indonesia is the seventh largest exporter and sixth largest producer of edible oils. It is estimated that by the year 2000, global palm oil production will reach 18 million MT annually (5), with Malaysia accounting for ten million MT (6). There are indications that palm oil production will continue to be concentrated in southeast Asia.

### PRODUCTION AND LABOR COSTS

It has been reported that the production of palm oil in southeast Asia has a clear cost advantage over that of seed oil in the U.S. and Europe (7). For example, the cost of production per MT is \$750 for rapeseed oil in West Germany and \$390 for soybean oil in the U.S.; the costs per MT for palm oil are \$215 in Malaysia and \$180 in Indonesia.

Labor cost per day for palm oil is higher for Malaysia (\$4.40) and lowest for Indonesia (\$1.50) (8). Thailand and the Ivory Coast maintain intermediate rates of \$2.20 and \$2.50, respectively. Such production and labor cost differentials, compared with the U.S. and the European Economic Community (EEC) countries, provide a clear impetus to consider the extraction of minor components of palm.

### HEALTH-RELATED APPLICATIONS

It has been established that tocopherol components have antioxidant properties (9) for food applications.

and carotenoids can inhibit light-initiated flavor deterioration in soybean oil without affecting color quality (10). More recently, medically related findings have been made concerning palm oil's minor components. For instance, it has been reported that palm oil has antithrombotic effects in rats (11). Whether these properties are derived from the "major" oleic acid (40% of the oil) and linoleic acid (10% of the oil) content and/or from the "minor" tocopherols and tocotrienols has not been proven.

The normal blood plasma level of vitamin E (>80% as  $\alpha$ -tocopherol, 10% as  $\gamma$ -tocopherol and 2% as  $\beta$ -tocopherol) is 0.7-1.6 mg/dl; less than 0.4 mg/dl is considered a deficiency. The daily requirement of  $\alpha$ -tocopherol is 10-15 mg. In mammalian tissues,  $\beta$ -carotene is converted to retinal by the enzyme  $\beta$ -carotene 15,15'-dioxygenase (EC 1.13.11.21). Vitamin A activity comes from preformed retinol (75%) and carotene-derived (25%) sources. The normal blood plasma level of vitamin A is 40-80  $\mu$ g/dl; less than 15  $\mu$ g/dl is considered a deficiency. The normal plasma value of carotene is usually more than 50  $\mu$ g/dl. The daily adult requirement of vitamin A is 1.5-1.8 mg, approximately tenfold lower than the recommended allowance for vitamin E.

When carotenoid-rich foods are estimated from those containing preformed vitamin A, it is the former that are associated with protective and anticancer effects (12,13). Epidemiologically, investigators strongly associate  $\beta$ -carotene with the prevention of lung cancer (14).

Nigerian children receiving red palm oil were reported to be in better health than those who did not (15,16). But the mechanism that connects palm oil and "better health" is unknown. Plasma from a healthy English subject showed a very different carotenoid profile to that of a healthy Nigerian subject (17). The large xanthophyll content from the English plasma in contrast to the larger carotene content from the Nigerian plasma is probably a reflection of a red palm oil diet in the latter. Detailed research on palm oil's minor components is needed but these possible health-related implications may stimulate interest in these non-saponifiable components.

## CAROTENOIDS

The name "carotene" is derived from carrot root (*Daucus carota*), which was isolated as a colored pigment in 1831. Interestingly, this pigment is related to the discovery of the technique of "chromatography" in 1906 by Russian botanist Michael Tswett. He separated carotenoid pigments from leaves on a chalk column into separate bands, and hence the words "chroma" for "color" and "graphy" meaning "writing."

Most of the approximately 500 known carotenoids are naturally occurring, typically pigmented (e.g., yellow-orange-red hues), and some 50 of these pigments possess vitamin A activity to varying degrees. Chemically, carotenoids are conjugated hydrocarbons that may be further classified as carotenes (without an oxygen molecule) and xanthophylls (with one or more oxy-

gen molecules). The polyene backbone of the pigment is characteristically connected to any two of the seven 9-carbon recognized end-groups. A semi-systematic nomenclature includes two Greek letters indicating the structures of the two end-groups. Therefore the semi-systematic nomenclature of common names  $\beta$ -carotene and  $\alpha$ -carotene are  $\beta,\beta$ -carotene and  $\beta,\epsilon$ -carotene, respectively. In palm oil, only  $\beta$ ,  $\epsilon$  and  $\psi$  end-groups have been identified. An illustrative list of 40-carbon carotenoid structures (up to 8 isoprene units) is shown in Figure 1.

Palm oil carotenoids were analyzed by nonaqueous reverse-phase HPLC and UV-VIS diode array detection. Isocratic elution using a ternary solvent mixture (60% acetonitrile, 35% methanol and 5% methylene chloride) at 2 ml/min on a 25 cm C-18 column resulted in an analysis time of 22 minutes (18). Carotenes predominate in palm oil with minor amounts of xanthophylls, the latter mostly mono- and di-epoxy  $\alpha$ - and  $\beta$ -carotene.  $\beta$ - and  $\alpha$ -carotene are the dominant components found in a two-to-one ratio. Depending on the age and origin of the oil, an average of 550 ppm of  $\alpha$ - and  $\beta$ -carotene alone in crude palm oil may be expected. Higher amounts of carotenoids in palm oil have been reported in the literature. Caution must be exercised to translate "total carotenes" obtained spectrophotometrically at a wavelength of about 450 nm into ' $\beta$ -carotene.' False high values for  $\beta$ -carotene have been rigorously established from single wavelength spectrophotometric measurements compared with measurements that followed HPLC separation (19). Figure 1 shows some exemplary palm oil carotenoids, but a more complete list may be obtained elsewhere (18,20).

Isograms (i.e., wavelength vs. absorbance) or spectrochromatograms (i.e., wavelength vs. retention time vs. absorbance) can be generated using the HPLC diode array detector. An isogram of palm oil carotenoids is shown in Figure 2, which identifies the major  $\beta$ - and  $\alpha$ -carotene as well as traces of  $\epsilon$ -carotene and *cis*- $\beta$ -carotene. Carrots and tomatoes are known to have high sources of carotenoids. Similar isogram plots of carrot oil carotenoids showed intermediate amounts of phytoene, phytofluene and  $\zeta$ -carotene in addition to the major  $\beta$ - and  $\alpha$ -carotene (21). In the case of tomato paste, the major carotenoid components were lycopene and phytoene with intermediate amounts of  $\beta$ -carotene and phytofluene (22). The following characteristics of palm oil carotenoids can be made from these comparisons:

- Palm oil contains the highest known concentration of agro-derived carotenoids.
- The preponderant palm oil pigments are  $\beta$ - and  $\alpha$ -carotene. The major carotenoids in palm oil are the same as in carrot oil, but the latter contains at least three intermediate amounts of other carotenoids.
- Fewer *cis* isomers of carotenoids are identified in palm oil. Generally, *cis* carotenoids have decreased or no vitamin A activity.
- Palm oil has the highest carotene-derived vitamin A activity. This is primarily due to  $\beta$ -carotene and, secondarily, to  $\alpha$ -carotene. For example, red palm oil

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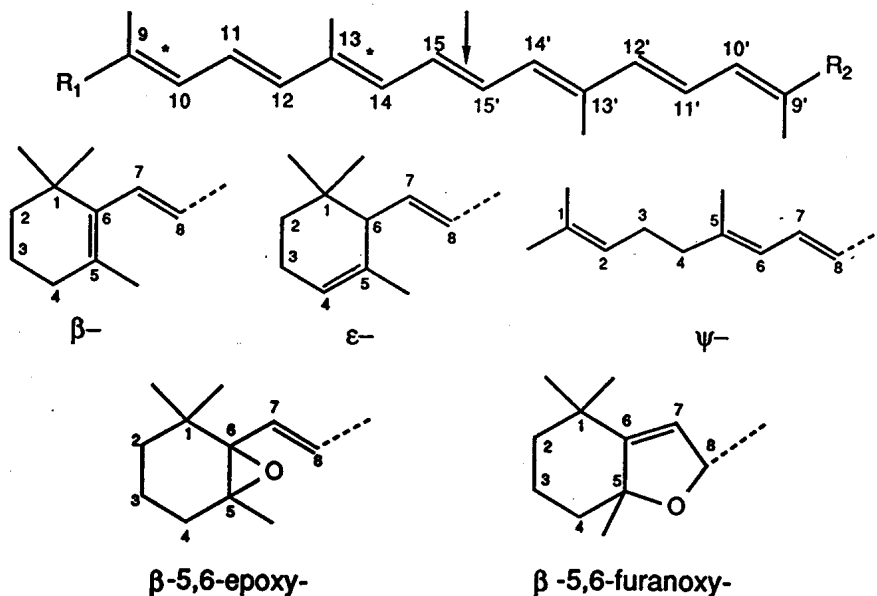


FIG. 1. Representative list of palm oil carotenoid structures [e.g.,  $\alpha$ -( $\beta$ , $\epsilon$ ),  $\beta$ -( $\beta$ , $\beta$ ),  $\epsilon$ -( $\epsilon$ , $\epsilon$ ) carotene, phytoene ( $\psi$ , $\psi$ ; 3 conjugated double bonds), lycopene( $\psi$ , $\psi$ ) and  $\beta$ -zeacarotene ( $\beta$ , $\psi$ )].  $R_1$  and  $R_2$  contain one of the three ( $\beta$ ,  $\epsilon$  and  $\psi$ ) side groups. In  $\beta$ -carotene, cleavage to vitamin A occurs at 15,15' (arrow) and *cis*-isomer usually occurs at position 9 or 13 (asterisks). Epoxy and furanoxy functions on the dominant  $\beta$ -ionone moiety are also found (18).

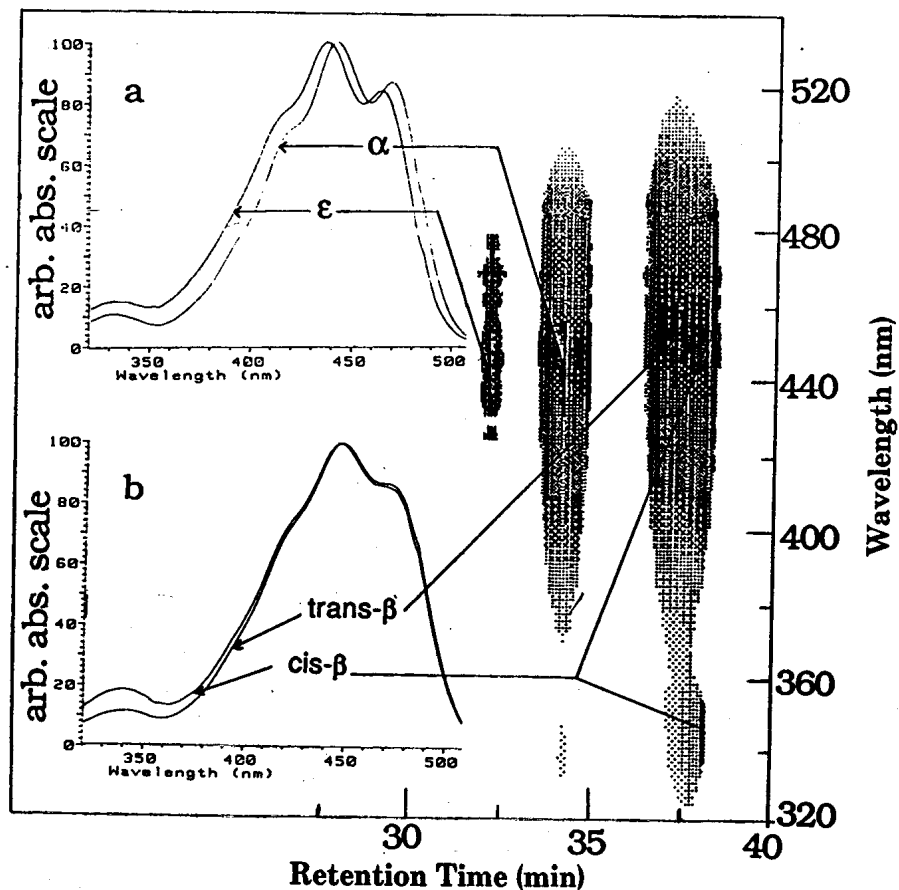


FIG. 2. HPLC isogram (wavelength vs absorbance) of major palm oil carotenoids was obtained using a UV-VIS diode-array detector. Spectral inserts include a)  $\alpha$ -carotene (422, 444, 470 nm) and  $\epsilon$ -carotene (418, 438, 466 nm), and b) all-*trans*- $\beta$ -carotene (426, 449, 472 nm) and *cis*- $\beta$ -carotene (possibly 9-monocis isomer; 424, 446, 469 nm).

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has 15-fold more vitamin A activity than carrots and 300-fold more than tomatoes (21).

### TOCOPHEROLS AND TOCOTRIENOLS

Vitamin E was first reported in the early 1920s; at that time, it was associated with sterility and reproduction. The Greek meaning for "tocopherol" is "to bear offspring." The other vitamin E homolog—tocotrienol—was discovered in 1955. These compounds are fat-soluble and light yellow in color.

Chemically, tocopherols and tocotrienols are methyl-substituted chromanols with a three-isoprene moiety side chain (Fig. 3). The structures of these two homologs are readily distinguishable. Tocopherols have a saturated side chain with chiral carbons at positions 2, 4' and 8', and tocotrienols have an unsaturated (but unconjugated) side chain at positions 3', 7' and 11'. Because of their structures, there exist diastereoisomers of tocopherols and *cis-trans* isomers of tocotrienols (9). The chemical and IUPAC names of  $\alpha$ -tocopherol are 2,5,7,8-tetramethyl-2-(4',8',12'-trimethyl tridecyl)-6-chromanol and 2R,4'R,8'R- $\alpha$ -tocopherol, respectively.

Paper and gas chromatography were used for vitamin E analyses in 1950s and 1960s, but HPLC techniques were utilized in the mid-1970s. Today, C-18 reverse-phase columns are used for separating  $\alpha$ -tocopherol from its esters and other fat-soluble vitamins whereas silica and other modified normal-phase columns are used for the separation of tocopherol isomers and their tocotrienol counterparts (unpublished results). Further analytical and preparative work on vitamin E separation is under investigation. Despite isomeric identification compromise, there is some merit to using pulsed voltammetric techniques for vitamin E analyses (23).

Vegetable oils contain tocopherols, particularly the  $\gamma$ -isomer (highest in corn and soybean) and  $\alpha$ -isomer (highest in sunflower and cottonseed) (23–25). With the exception of  $\delta$ -tocopherol in soybean,  $\beta$ - and  $\delta$ -

isomers are not found in oil in significant amounts (Table 1). Most commercial oils are devoid of tocotrienols. Palm oil characteristically has the highest levels of  $\gamma$ - and  $\alpha$ -tocotrienol, and the total tocotrienols represent about 83% of the palm oil vitamin E content. Coconut and sunflower oils have minor quantities of tocotrienols. Wheat germ oil is not considered a significant commercial oil but it has an unusually high concentration of tocopherols relative to other oils (24). The descending order of total tocopherols and tocotrienols in commercial oils is as follows: corn, soybean, palm (800–1100 ppm) > cottonseed, sunflower, rapeseed (550–800 ppm) > peanut, olive (150–350 ppm) > coconut, palm kernel ( $\leq$  50 ppm).

More than 85% of palm oil vitamin E content consists of  $\gamma$ -tocotrienol,  $\alpha$ -tocotrienol and  $\alpha$ -tocopherol and, to a lesser extent,  $\delta$ -tocotrienol (Table 2). Total vitamin E content is concentrated sixfold in the palm fatty acid distillate (PFAD) compared with the crude palm oil (CPO), while a 20-fold concentration is realized for the total sterols. This selective distribution allows the potential extraction of vitamin E isomers in the PFAD byproducts while significantly decreasing the sterols in the eventual refined oil. Findings show the following characteristics of palm oil tocopherols and tocotrienols:

- Palm oil has a high concentration of vitamin E and this content is comparable to that found in corn and soybean oil.

- The preponderant palm oil vitamin E components are  $\gamma$ - and  $\alpha$ -tocotrienol and  $\alpha$ -tocopherol; tocotrienols constitute 83% of total vitamin E content.

- PFAD byproducts have 4,000–6,000 ppm of vitamin E; relative distribution of the isomers is similar to that found in CPO.

### VITAMIN A AND E ACTIVITIES

To understand and assign vitamin A and E activities, it is necessary to distinguish (a) isomers of natural and synthetic origins, (b) structural requirements for activities, and (c) definitions of activities. Practically all nature-derived tocopherols have three chiral carbons and they are believed to be the d form (i.e., R confirmation). In contrast, the only synthetic form of vitamin

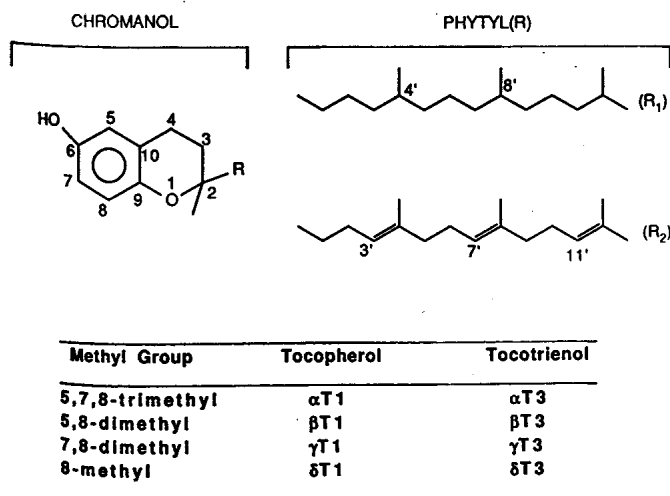


FIG. 3. Vitamin E structures of tocopherols (T1; with R<sub>1</sub> phytyl chain) and (T3; with R<sub>2</sub> phytyl chain). Chiral positions of tocopherol are 2, 4' and 8', and the non-conjugated triene positions of tocotrienol are 3', 7' and 11'.

TABLE 1

Tocopherol and Tocotrienol Contents in Oils<sup>a</sup>

Oils	Tocopherol (ppm)				Tocotrienol (% of total)
	$\alpha$	$\beta$	$\gamma$	$\delta$	
Corn	223	32	790	26	0
Soybean	100	8	625	261	0
Palm	152	ND <sup>b</sup>	ND	ND	83 <sup>c</sup>
Cottonseed	389	ND	387	ND	0
Sunflower	599	15	38	7	3.7 <sup>c</sup>
Rapeseed	184	ND	380	12	0
Peanut	139	3	189	18	0
Olive	162	9	10	ND	0
Coconut	5	ND	ND	6	69 <sup>c</sup>

<sup>a</sup>Data were obtained from ref. 23–25.

<sup>b</sup>ND indicated trace or absence of vitamin E isomer.

<sup>c</sup>Tocotrienols are found in palm ( $\alpha$ , 205;  $\gamma$ , 439;  $\delta$ , 94 ppm) sunflower ( $\alpha$ , 25 ppm), and coconut ( $\alpha$ , 5;  $\beta$ , 1;  $\gamma$ , 19 ppm).

TABLE 2

Vitamin E and Sterol Isomers in Palm Oil Fractions

Oil fraction	Vitamin E <sup>a</sup> (%)					Sterols <sup>b</sup> (%)			
	$\alpha$ T1	$\alpha$ T3	$\gamma$ T3	$\delta$ T3	$\gamma$ T1	CH	CM	ST	$\beta$ S
CPO <sup>c</sup>	22	20	36	7	12	4	22	12	61
PFAD <sup>d</sup>	23	24	38	15	—	11	23	14	52

<sup>a</sup>T1 and T3 represent tocopherol and tocotrienol (Fig. 3).

<sup>b</sup>These sterols are: CH, cholesterol; CM, campesterol; ST, stigmasterol;  $\beta$ S,  $\beta$ -sitosterol.

<sup>c</sup>Total vitamin Es and sterols in crude palm oil (CPO) are 600-1000 ppm and 270-300 ppm, respectively.

<sup>d</sup>Total vitamin Es and sterols in palm fatty acid distillate (PFAD) are 4000-5000 ppm and ca. 6500 ppm, respectively.

E is the  $\alpha$ -isomer of tocopheryl acetate but it is racemic (labeled with a prefix 'all-rac') at each of the three asymmetrical carbons (9). Therefore, there are four geometric/positional isomers from natural sources ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -forms from the chromanol ring) and eight diastereoisomers of synthetic all-rac- $\alpha$ -tocopheryl acetate (from confirmations found in the isoprenoid side chain) (Fig. 3).

The situation with carotenoids is less complex. The type of nature-derived carotenoids is clearly a function of the sources (e.g.,  $\beta$ -,  $\alpha$ - and  $\gamma$ -carotene,  $\beta$ -cryptoxanthin, lutein). Natural carotenoids typically have a significant amount of xanthophylls (18,22). Synthetic carotenoids are limited to  $\beta$ -carotene, canthaxanthin,  $\beta$ -apo-8'-carotenal and its acid ester. Synthetic all-trans- $\beta$ -carotene formulations frequently have impurities of  $\alpha$ -carotene and detectable levels of *cis*- $\beta$ -carotene (unpublished results).

In order to have vitamin E activity, the molecule must have a basic tocol structure—that is, a chromanol attached to three isoprene units at position 2. Other structural features that affect the vitamin E activity include the number of methyl groups on the chromanol (3,  $\alpha$ -; 2,  $\beta$ - and  $\gamma$ -; 1,  $\delta$ -designations) confirmation at C-2 (R or S), presence of double bonds on the side chain (tocopherol or tocotrienol), and the methyl confirmations at position 4' and 8' (R or S) of the isoprenoid side chain.

The presence of provitamin A activity requires the carotenoid molecule to have at least one  $\beta$ -ionone end-group and a highly unsaturated and conjugated isoprenoid backbone (Fig. 1). Other structural features that affect carotenoid-derived vitamin A activity include the degree of isomerization (*cis-trans* isomers of the polyene backbone) and formation of oxy-, hydroxy-, epoxy- and furanoxo-derivatives (xanthophylls).

The International Unit (IU) has been defined as the activity of 1 mg of dl- $\alpha$ -tocopheryl acetate in preventing fetal resorption in vitamin E-deprived female rats (9). The d- $\alpha$ -isomers and free alcohols have higher activities than dl- $\alpha$ -tocophenyl acetate. Beta-carotene is the best known carotenoid conversion to vitamin A. Ten IU of vitamin A activity is equivalent to 1  $\mu$ g vitamin A retinol (or one retinol equivalent), 6  $\mu$ g  $\beta$ -carotene and approximately 12  $\mu$ g other  $\beta$ -ionone end-group carotenoids. Activity also may be defined as Retinol Equivalent (RE). In most domestic animals and man, 4 to 10  $\mu$ g  $\beta$ -carotene is equivalent in activity

to 1  $\mu$ g retinol (26). Experimental data indicate that digestion and absorption in the intestines and deposition in tissues are responsible for inefficient and different conversion. A ratio of 6-to-1 is an acceptable mean.

Table 3 shows vitamin activities from palm oil carotenoids, tocopherols and tocotrienols. Carotenoids with *cis* isomers and oxygenated functions have less vitamin A activities than their parent compounds. Carotenoids that have one  $\beta$ -ionone ring will have less than or equal to 50% activity of  $\beta$ -carotene (2  $\beta$ -ionone rings). The ringed  $\epsilon$ -ionone and  $\psi$  (acyclic) side chains have no vitamin A activity. For example,  $\alpha$ -carotene ( $\beta$ , $\epsilon$ -carotene) has half the activity of  $\beta$ -carotene, while lycopene ( $\psi$ , $\psi$ -carotene) and  $\alpha$ -zeacarotene (7', 8'-dihydro- $\epsilon$ , $\psi$ -carotene) are both vitamin A inactive (Fig. 1). Most vitamin A inactive palm oil carotenoids have  $\psi$ , $\psi$ -side chains and they contribute only to a small extent to the total palm oil carotenoids (20).

Table 3 also shows that d- $\alpha$ -tocotrienol has about one-third the activity of d- $\alpha$ -tocopherol, and the activities of other tocotrienols are even smaller than that of d- $\alpha$ -tocotrienol. It is also important to note that all other isomers and their corresponding synthetic racemic mixtures have lesser activities than d- $\alpha$ - and dl- $\alpha$ -tocopherols. Tocopherols (as free alcohols) have antioxidant activities but their esters do not. The  $\delta$ - and  $\gamma$ -tocopherols are better food antioxidants but  $\alpha$ - and  $\beta$ -tocopherols are better *in vivo* antioxidants (24,27-29). It has been reported that there was coprotection of  $\beta$ -carotene and  $\delta$ -tocopherol during singlet oxygen-initiated oxidation of methyl linoleate (30). Also, it has been suggested that a low concentration of  $\beta$ -carotene in membranes may retard the oxidative destruction of  $\alpha$ -tocopherol (31).

## ECONOMIC POTENTIAL

Vitamin E and carotenoids can be classified as food additives. Tocopherols, ascorbic acid esters, gallic acid esters, tert-butylhydroxyanisole (BHA) and di-tert-butylhydroxytoluene (BHT) are among the most important antioxidants. Tocopherols are used in retarding lipid oxidation in food products. Carotenoids are most important food colorants in yellow to red coloration (e.g., poultry and fish) and fertility (e.g., cattle and sows). Examples of natural and synthetic carotenoids that are used (EEC number in parentheses) as food

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TABLE 3

Vitamin A and E Activities from Palm Oil Carotenoid, Tocopherol and Tocotrienol Isomers

Carotenoid	Vitamin A activity (%) <sup>a</sup>	Tocopherol/tocotrienol	Vitamin E activity (%) <sup>c</sup>
$\beta$ -carotene <sup>b</sup>	100	d- $\alpha$ -tocopherol <sup>b</sup>	149
-9-cis <sup>b</sup>	38	-dl- $\alpha$	110
-13-cis <sup>b</sup>	53	-dl- $\alpha$ , acetate	100
-5,6-epoxide <sup>b</sup>	21	-dl- $\alpha$ , succinate	89
-5,8-epoxide <sup>b</sup>	50	d- $\alpha$ -tocotrienol <sup>b,d</sup>	45
-5,8,5',8'-diepoxide <sup>b</sup>	?	d- $\beta$ -tocopherol <sup>d</sup>	75
-9-hydroxy	50-60	-dl- $\beta$	30
$\alpha$ -carotene <sup>b</sup>	50-54	d- $\beta$ -tocotrienol	8
-9-cis	13	d- $\delta$ -tocopherol <sup>d</sup>	5
-5,6-epoxide <sup>b</sup>	25	-dl- $\delta$	1
$\gamma$ -carotene <sup>b</sup>	42-50	d- $\delta$ -tocotrienol <sup>b</sup>	?
$\beta$ -zeacarotene <sup>b</sup>	20-40	d- $\gamma$ -tocopherol <sup>d</sup>	15
lycopene <sup>b</sup>	inactive	-dl- $\gamma$	15
$\epsilon$ -carotene <sup>b</sup>	inactive	d- $\gamma$ -tocotrienol <sup>b</sup>	1.5

<sup>a</sup>1 RE of vitamin A activity (or 1  $\mu$ g retinol) is defined as 6 $\mu$ g  $\beta$ -carotene or about 12  $\mu$ g of a carotenoid with one  $\beta$ -ionone end-group.

<sup>b</sup>Significant isomers found in palm oil.

<sup>c</sup>1 IU of vitamin E activity is defined as 1 mg synthetic dl- $\alpha$ -tocopheryl acetate.

<sup>d</sup>Unofficial value.

colorants include  $\beta$ -carotene (E160a), canthaxanthin (E161g),  $\beta$ -apo-8'-carotenol (E160e) and its ester (E160f), bixin (E160b), lycopene (E160d), astaxanthin and zeaxanthin.

If vitamin E (e.g., for atherosclerosis and thrombosis protection) and carotenoids (e.g., for cancer and radiation protection) were used in therapeutic drugs, their applications would greatly increase.

Recently, it was reported that oil palm leaves and leaflets contained large quantities of  $\alpha$ -tocopherol and no tocotrienols (32,33). It was estimated that palm leaves and leaflets from frond pruning and oil palm replanting yield about 5 million tons (dry weight) annually. On a dry basis,  $\alpha$ -tocopherol was found in unusually high concentrations in leaflets (0.32-0.56%) (33) and leaves (0.18-0.28%) (32). A trace amount of  $\beta$ -tocopherol (0.3% of  $\alpha$ -tocopherol) was also reported in the leaves.

Table 4 shows the comparative recoveries of major components in palm products. From the large volume

TABLE 4

Potential Annual Recoveries from Palm Minor Components		
Item	Annual amounts (tons)	Major isomers
Vitamin Es	800	$\gamma$ T3, $\alpha$ T3, $\alpha$ T1 <sup>a</sup>
PFAD <sup>a,b</sup>	26,000	$\alpha$ T1
Pruning	380	$\alpha$ T1
Replanting		
Carotenoids	4,450	$\beta$ - and $\alpha$ -carotene
CPO <sup>a,b</sup>	9,800	$\beta$ -carotene
Pruning <sup>c</sup>	150	$\beta$ -carotene
Replanting <sup>c</sup>		

<sup>a</sup>See Table 2 and Figure 3 for explanation of abbreviations.

<sup>b</sup>The  $\delta$ T3 is of intermediate amount. The  $\beta$ - and  $\alpha$ -carotene ratio is about 2:1.

<sup>c</sup>Rigorous analyses were not given (see ref. 35);  $\beta$ -carotene was the presumed major isomer.

of leaf byproducts, recoveries of  $\alpha$ -tocopherol and  $\beta$ -carotene can be exceedingly high provided economic extraction is achievable. Interestingly, these two palm components have the highest vitamin E and A activities, respectively (Table 3). The present annual carotenoid market is greater than \$100 million and it is expected that natural carotenoids will be higher priced than synthetic carotenoids.

The Palm Oil Research Institute of Malaysia (PORIM) and Japan's Ministry of International Trade and Industry (MITI) have completed a 5-year project on pilot plant extraction of vitamin E from PFAD. PORIM has claimed that a possible income of \$26.4 million could be derived from vitamin E from PFAD. The nutritional and medical implications of the dominant  $\delta$ - and  $\alpha$ -tocotrienol from PFAD are not clear. However, with the exception of vitamin E isomers in PFAD, other palm products have largely  $\alpha$ -tocopherol (d-form),  $\beta$ -carotene (mostly all-*trans*) and all-*trans*- $\alpha$ -carotene (Table 4). This is a distinct advantage in the light of purity requirements in drug formulation.

Malaysia and Indonesia account for 77% of the 8.52 million MT world palm oil production, and this 8.52 million MT represents 16% of total world oil production (34). In view of the dramatic oil production in southeast Asia and the large concentration of vitamin E and carotenoids in palm byproducts, the technical/commercial extraction of these chemicals is due.

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