Minor Constituents of Palm Oil

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ABSTRACT

Crude palm oil contains about 1% of minor components including carotenoids, tocopherols, sterols, triterpene alcohols, phospholipids, glycolipids and terpenic and paraffinic hydrocarbons. The nutritionally important components such as carotenes and tocopherols also improve stability of the oil. Although a highly valued product, carotene unfortunately is bleached or destroyed in refining because suitable recovery technology is not available. Thermal degradation of carotene, previously suspected of giving rise to undesirable chemicals, now is known to furnish mainly harmless hydrocarbons, most of which are removed by the deodorization step in refining. Tocopherols, being natural antioxidants, need to be carefully preserved during milling, refining, fractionation and modification of palm oils. The accumulation of tocopherols in the palm fatty acid distillate promises to provide a new source for the recovery of this valuable substance. The role played by phospholipids is frequently misunderstood because they can act in two ways, i.e. as an antioxidant synergist and a surface active agent to disperse impurities in oil. In crude palm oil the phospholipid content is small, because most of it is removed during milling; the phosphorus content is due mainly to inorganic phosphorus. Among the sterols, cholesterol constitutes too small a percentage to be of much concern. Sterols, triterpenoids and terpenoid hydrocarbons are also potentially useful side products should recovery technology become available. Other newly characterized minor and trace components also are discussed.

INTRODUCTION

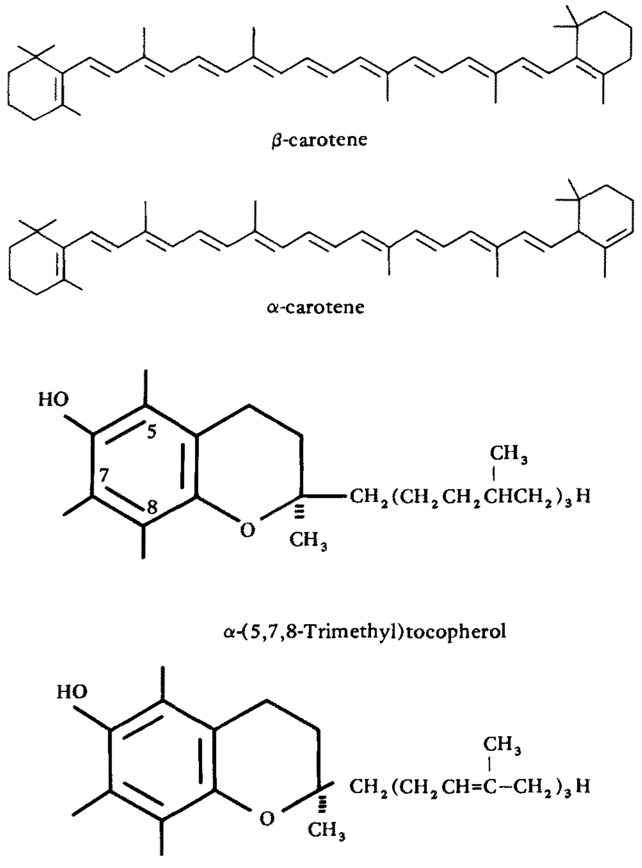
Crude palm oil contains approximately 1% of minor components including carotenoids, tocopherols, sterols, triterpenes, phospholipids, glycolipids, terpenic and aliphatic hydrocarbons and other trace impurities. Carotenes, which impart the distinctive orange-red color to palm oil, together with tocopherols contribute to the stability and nutritional value of the oil. To a great extent these and other minor constituents determine the quality characteristics of palm oil.

Carotenoids

The carotenoid content of crude palm oils from Malaysia and Zaire varies between 500 and 700 ppm (1); larger amounts (800-1600 ppm) from Dura species have been reported from Nigerian sources (2). Malaysian palm kernel oil contains <12 ppm (3). A typical analysis of the composition of the carotenoids shows that α- and β-carotenes (Fig. 1) are the major components (ca 36 and 54%, respectively), and the rest are γ-carotene, lycopene and xanthopylls. Carotenes are the precursors of vitamin A, with β-carotene having the highest provitamin A activity. Considering that the estimated total world production is 6 million tons of crude palm oil, the accompanying amount of carotenes produced would be about 3000-4200 tons. Unfortunately, all this carotene is destroyed by present refining processes which traditionally produce only light colored to colorless oils for major consumers. The other factor is that suitable extraction technology is not yet available. The value of the available carotene to be used as Vitamin A would be close to that of the oil itself excluding processing costs. Even carotene concentrates would be of high commercial value.

Many attempts have been made to recover carotene from crude palm oil, and most of these depend either on chemically transforming the triglycerides, e.g. saponification or transesterification, so that they can be removed, or on using adsorbent materials, usually activated carbon, to selectively adsorb the carotene. Chemical transformation (4) is undesirable because the food use of the triglycerides becomes questionable. However, if fractional crystallizations were performed first to recover the glycerides, a carotene concentrate (5-7) could be obtained for further processing. The adsorption of carotenes on Fuller's earth and clays (8,9) generally is not as effective as activated carbon. Furthermore, the carotenes suffer oxidative or acid-catalyzed degradation. Several methods in the use of activated carbon have been described (7,10,11) and the protection of the adsorbed carotenes from oxidation usually is necessary. A recent patent (12) described reusable activated carbon, optimum pH conditions, use of antioxidants such as tocopherols to avoid oxidation and the choice of solvents for recovery of the adsorbed carotene from carbon.

The usual practice in palm oil refining is to "bleach" or remove the carotenes by heat and/or earth bleaching so as to produce light colored edible oil and other end products as required by consumers. Unfortunately, this means that the carotenes are chemically destroyed by such thermal or catalytic processes; this also gave rise to concern (4) as simple aromatic compounds such as toluene xylenes, ionene



β-carotene

α-carotene

α-(5,7,8-Trimethyl)tocopherol

γ-(7,8-Dimethyl)tocotrienol

FIG. 1. Major carotenes and tocopherols.

and 2,6-dimethylnaphthalene are produced. However, it was later shown that larger polycyclic aromatic hydrocarbons (13,14) are not produced from carotenes in refining; in fact, deodorization and fatty acid distillation by physical refining removes the simple degradation products of carotenes mentioned above. Carcinogenic aromatic hydrocarbons do not form, and other aromatic hydrocarbons detected at trace levels were lower in refined than in crude palm oils.

Carotene is known as an inhibitor of photooxidation and is expected to suffer ready oxidation in view of the extensive number of unsaturated bonds; it can, therefore, act as an antioxidant for the oil. Its peroxidized oxidation products, however, act as prooxidants to unsaturated glycerides (15). Poorer grade crude palm oil may suffer some autoxidation of the carotenes (16,17) to give volatile ionones as an off-flavor, but this does not present a problem to refining. The residual color of processed palm oil is not due to the degradation or oxidation of carotenoids although the cooxidation of carotene and fatty acid can cause significant color formation during thermal bleaching. The current practice in color removal is to avoid excessive thermal bleaching because degradation of carotenes at elevated temperatures also causes slight chemical changes in the triglycerides, but instead to use adsorptive earths operating at as low a temperature as possible.

Tocopherols

Tocopherols and tocotrienols are present in crude Malaysian palm oils at 600-1000 ppm levels (18,19). These are important natural antioxidants which also function as vitamin E. It is now known (20) that tocopherols, especially α-tocopherol, are superior radical chain-breaking antioxidants compared to synthetic ones which sometimes are not acceptable in some countries. Hence, tocopherol content constitutes an essential quality parameter. Several methods have been developed for their analysis; direct analysis on the oil is possible by HPLC using a fluorescence detector (21), while complete compositional analysis previously has been performed by capillary GLC (22). The main constituents (Fig. 1) are ca. 44% γ-tocotrienol, 22% α-tocopherol and 12% δ-tocotrienol, the rest being α- and β-tocotrienols and β-, γ- and δ-tocopherols. Although palm oil is relatively resistant to oxidative deterioration due to the low levels of polyunsaturation, tocopherols still remain as useful natural antioxidants and their loss during processing must be minimized. Steam deodorization and distillation of free fatty acids invariably causes some loss (15-57%) of the tocopherols; therefore, over-vigorous conditions need to be avoided. The tocopherols can accumulate in the palm fatty acid distillate to about 0.8% or greater, and this has been looked to as a good source of tocopherol or vitamin E. Loss of this material is also of concern in fractionation or fractional crystallization, which invariably leaves most of the tocopherols in the liquid or olein fractions, thus rendering the solid stearin fractions deficient in antioxidants (Table I).

Sterols

Phytosterols, as may be expected, are present in palm oil, sitosterol, campesterol and stigmasterol being the major constituents while a minor amount of cholesterol also is present (23,24). The cholesterol level, as in other vegetable oils, is minimal and together with the other sterols is further reduced in refining. GLC analysis also shows the presence of minor sterols (Δ^5-avenasterol, Δ^7-stigmasterol and Δ^7-avenasterol) at 0-25 ppm (24-26).

Sterols and their esters, which also have been detected (27), do not seem to serve any useful function in the oil, neither do they have any detrimental effect on it. However, it has been suggested that certain sterols, e.g. Δ^5-avenasterol, can protect oils from oxidative polymerization during frying (28). Their presence and composition in the unsaponifiable fraction, as with other minor components, can serve as a unique fingerprint for the oil, e.g. for the detection of adulteration or blending. Sterols, if recovered, will have potential uses in the pharmaceutical industry for conversion into steroid derivatives (29) Future prospects may be in phytosterol insecticides (30) which should be a larger volume market.

Dimethylsterols or triterpene alcohols and methylsterols also have been determined for the unsaponifiable fraction of palm oil. Cycloartenol, 24-methylenecycloartenol, cycloartanol and α-amyrin have been determined by GLC (26,27). Gramisterol, obtusifoliol and citrostadienol are the major methylsterols. Triterpenoid methyl ethers also have been isolated from palm fruit pericarp and are presumed to occur at trace levels in the oil (31,32). Squalene is present at about 200-350 ppm in crude palm oil; sesquiterpene and diterpene hydrocarbons are present at much lower levels. These hydrocarbons together with paraffinic hydrocarbons and other volatile degradation or oxidized products are removed and concentrated in the palm fatty acid distillate during refining.

Polar Lipids

Phospholipids and glycolipids (34,35) are the polar lipids of palm oil, with the former receiving considerable attention because of the suspected deleterious effect of phosphorus on oil quality (36,37). Both types of lipids constitute an important part of cellular membranes, and they possess unique structures containing both lipophilic and hydrophilic functions. The main phospholipid in palm oil is represented by phosphatidylcholine and the major glycolipid is monogalactosyldiglyceride, as shown in Figure 2. Malaysian crude palm oil contains relatively low levels of phospholipids (5-130 ppm or 0.2-5 ppm as P) since the wet milling process ensures that only an estimated 4% of the phospholipids of the palm fruit remains in crude palm oil (Table IV). However, even such small quantities together with glycolipids can facilitate the dispersion of microparticulate impurities which include iron and other undesirable materials. Preliminary studies indicate that the content of glycolipids (1000-3000 ppm) (32) is actually higher than phospholipids. Both

TABLE I

Tocopherols in Palm Oils

	18, 19 ppm
Crude palm oil	600-1000
Crude palm olein	800-1000
Crude palm stearin	250-350
PFAD	150-8500
RBD palm oil	356-630
RBD palm olein	468-673
PKO (1)	80-100

TABLE II

Sterols in Palm Oil and Palm Oil Products

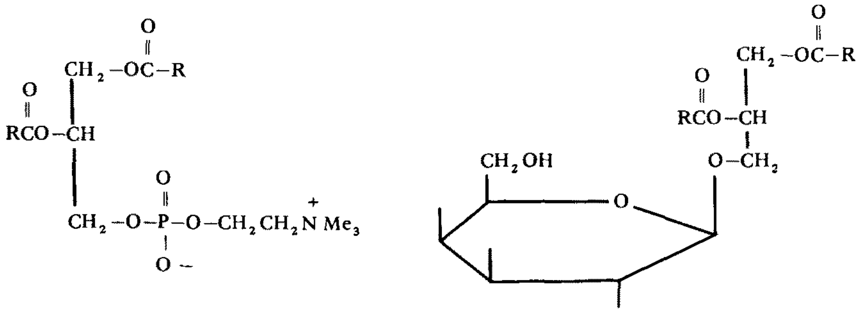
CPO (23)	360-620
CPO (24)	326-527
CP Olein (23)	270-440
RBD palm oil (23)	110-160
PKO (1)	1000

TABLE III

Terpenoids and Other Minor/Trace Components in ppm[a]

	CPO	PFAD
Triterpene alcohols (unsaponifiable) (25,26)	est 40-80	
Triterpene alcohols (unsaponifiable) (1)	640	
Methylsterols (unsaponifiable) (25,26)	est 40-80	
Squalene	200-500	12000-18000
Phytoene (33)	1500	2300
Sesqui- and di-terpene hydrocarbons	ca 30	ca 500
Aliphatic alcohols (unsaponifiable) (1)	ca 100-200 (160)	
Aliphatic hydrocarbons	ca 50	4000-8000
Methyl esters	ca 50	ca 4000
Methyl ketones		ca 100
Wax esters	Trace	

[a] Unless otherwise stated data from Ref. 31 and 32. CPO and PFAD are crude palm oil and palm fatty acid distillate, respectively.



Phosphatidylcholine

Monogalactosyl diglyceride

FIG. 2 Representative major polar lipids.

TABLE IV

Phospholipids and Inorganic Phosphates in Palm Oils[a]

Oil	Phospholipids (as P)[b] ppm	Inorganic phosphate as P/ppm
Crude palm oil	5-130 (0.2-5.4)[b]	7-20
Crude palm olein	7 (0.3)	4.9
Crude palm stearin	33 (1.4)	9.3
Bleached palm olein	3 (0.1)	0.9
RBD Palm olein[c]	6 (0.3)	0.8
NBD Palm stearin[c]	n.d.[d]	n.d.[d]
Total extracts[e]	1000-2000 (42-83)	

[a] From Ref. 35 and 38.

[b] Factor 24 was used for conversion of phospholipids to phosphorus, which is shown in parenthesis.

[c] RBD and NBD are refined, bleached and deodorized and neutralized, bleached and deodorized, respectively.

[d] Not detectable.

[e] Total lipids as extracted from the palm fruit mesocarp.

lipids are almost completely removed in refining processes which may include washing, phosphoric acid treatment and adsorption by clays or earths.

A detailed study (38) of phospholipids in crude palm oil showed unexpectedly that most of the phosphorus determined in the oil was in fact inorganic phosphate rather than from phospholipids. Typically, the inorganic phosphorus content is about eight times that of the phospholipid phosphorus. Detailed studies of these two forms of phosphorus compounds in crude palm oil indicate that they are unlikely to be the direct cause of some oil quality problems such as poor bleachability or increased susceptibility to oxidation. The two forms of phosphorus play differing roles; apart from stabilizing colloidal dispersions, phospholipids also can be described as antioxidant synergists while inorganic phosphorus may be undesirable. Inorganic phosphate is not desirable because it accompanies the prooxidant metal iron in correlating with the free fatty acid (but not residue red color) values of the oil. Thus, occasional problems in oil quality (e.g. poor heat bleachability and color stability) previously suspected to be caused by phosphorus are not easily defined; the role of phosphorus probably is indirect even though inorganic phosphate is observed to increase with the content of free fatty acid and prooxidant metals, especially in poor quality oils. Residual phosphorus in bleached and deodorized oil caused by poor processing or treatment also is known to correlate well with the free fatty acid escalation during transport (37). Therefore, it is generally prudent practice to avoid any increase in phosphorus content, e.g. avoidance of a phosphoric acid "slid" after degumming during refining. While phosphate or rather phosphoric acid can react chemically with phospholipids, its reaction with other glyceride components at high temperatures cannot be dismissed.

Studies of the role of phospholipids in crude palm oil will be obscured by the presence of predominantly larger quantities of inorganic phosphorus. Only when the two sources of phosphorus could be analyzed independently was it possible to reconcile the known antioxidant synergistic property of phospholipids; thus, increasing amounts of phospholipids were found with decreasing levels of the prooxidant metal iron to a minimum value before increasing amounts of free fatty acid raise the values of iron content again. Adding phospholipids to palm oil also is known to increase its oxidative stability, as is limiting quantities of residual water (36). Phospholipids (and glycolipids) can cause reverse micelle, vessicle or emulsion droplet formation; this means that prooxidant metal ions and their hydrophilic salts may be removed from the lipid phase so that they are rendered less effective in promoting autoxidation. The direct sequestering of metal ions by the polar lipids also cannot be ruled out in the antioxidant synergist action. Phospholipids are not by themselves antioxidants, but work only in conjunction with antioxidants such as tocopherols (39).

Glycolipids, although present in larger amounts than phospholipids, do not appear to contribute much to the quality of crude palm oil. They show weak but not too significant linear correlations to iron content and residue red color; at worst they could, with phospholipids, contribute to increasing the microparticulate and other impurities in the oil.

Impurities

Non-lipid components of palm oil, excluding moisture, may be referred to as impurities. The extraction of palm fruit mesocarp for oil also causes the accumulation of small amounts of inorganic and organic contaminants. Metallic contaminants such as iron or copper are well known prooxidants in catalytic amounts, with the latter metal about an order of magnitude more potent. Iron impurities are derived from the wear and tear of oil mill machinery and can be minimized by using stainless steel at strategic points in the milling process. Metallic iron and particulate iron may be reduced by magnetic traps and filters so that their levels become less than the normal ca 5 ppm in crude palm oil.

Most of the residual iron is likely particulate (38,40) and in admixture with other microparticulate inorganic material (e.g. containing compounds of Ca, Mg, phosphate etc.) as well as protein and cellulosic matter. These probably are held in colloidal suspension as evidenced by the fact that significant amounts can be precipitated by centrifugation (38). The presence of polar lipids (phospho- and glycolipids) may be partially responsible for this colloidal behavior. Washing or raffinating (41) can alleviate this problem and alkali treatment (e.g. alkali refining) is quite effective. A superdegumming technique which has been described (42) appears promising as a mild and effective method for treatment of palm and other oils.

Much less is known of other impurities such as phenolic compounds, tannins and trace flavonoids. Recently some UV absorbing and fluorescent compounds including p-hydroxybenzoic and vanillic acids among a larger number of phenolic compounds have been identified (43). Most of these originate from sepals, exocarp, fiber and shells of the palm fruit. The presence of these and other polar impurities should be of concern because they may form light absorbing materials on oxidation. Poor quality crude palm oils with high FFA content would be a special problem as these impurities are rendered more soluble. Apart from iron and carotenoid degradation products it is conceivable that these materials also may be involved in causing the formation of several colored compounds with molecular weights lower as well as exceeding those of triglycerides, as has been reported (44).

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