Minor Components in Edible Oils and Fats: Their Nutritional Implications

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MINOR COMPONENTS IN EDIBLE OILS AND FATS

Minor components in edible oils and fats are largely the non-glyceride components. These are termed minor because of their very low concentrations relative to the triglycerides content which is in excess of 99%. Modern analytical methods have enhanced our ability to analyze these minor components. Newer technologies allow the concentration, extraction and recovery of these components. There is also a growing awareness that these non-glyceride components have unique and interesting properties that can enhance the nutritional qualities of the oil. These include the fat soluble vitamins or their precursors (Vitamins D, E and the carotenoids), sterols, methylsterols, triterpene alcohols, squalene and oryzenols. The most important minor component in edible oils is vitamin E. This consists of a mixture of lipid-soluble phenols containing an aromatic chromanol head and a side chain of 16-carbon atoms. The tocopherols which are the most common vitamin E isomers have a saturated hydrocarbon tail. On the other hand, tocotrienols occurring largely in palm oil and rice bran oil are the farnesylated analogues of the tocopherols having an unsaturated isoprenoid tail. Depending on the number and position of the methyl groups on the chromanol ring, the tocopherols and tocotrienols are termed α–, β-, γ–, and δ-tocopherol and tocotrienol isomers.

Carotenoids and their derivatives are generally responsible for the yellow-red coloration of many fruits, cereals, vegetables and crude palm oil. Over 75 different carotenoids have been recorded but the most common isomers are the α–, β–, and γ-carotene, lycopene and xanthophylls. Carotenoids are the precursors of vitamin A and β-carotene has the highest pro-vitamin A activity (1 mol of β carotene = 2 mols of retinol or vitamin A).

Sterols are also known to exist in all oils and fats. Cholesterol is the major sterol in animal fats but can also occur in edible oils of vegetable origin, albeit in negligible concentrations. Other major plant sterols occurring in edible oils include β-sitosterol, campesterol, stigmasterol, ergosterol and desmosterol. Squalene an intermediate product during the synthesis of sterol from acetate is the predominant hydrocarbon occurring in dietary fats.

Of the minor components, vitamin E and the carotenoids have traditionally been the most important. They not only possess antioxidant properties, important for enhancing the stability of the oils against oxidation but also possess physiological properties that are presently gaining much prominence in biomedical applications.

MINOR COMPONENTS IN PALM OIL

Some of the minor components in palm oil include the carotenoids, tocopherols, tocotrienols, sterols, phosphatides, triterpenic and aliphatic alcohols. Although these minor components account for less than 1% of the oil's constituents, they nevertheless play a significant role in the stability and quality of the oil. In addition some of these minor components especially the carotenoids and vitamin E (tocopherols and tocotrienols) are important nutritionally.

Crude palm oil contains between 500 and 700 ppm of carotenoids. The major components are α–carotene and β-carotene. These carotenoids have pro-vitamin A activity. Unfortunately, in an effort to meet the consumer's perception of a refined oil (golden yellow colour), the carotenoids are often thermally degraded and removed during the deodorization stage of the refining process. In crude palm oil these carotenoids appear to offer some protection against oxidation by themselves being oxidized first prior to the oxidative attack on the triacylglycerols.

Crude palm oil is also a rich source of vitamin E (600–1000 ppm). Unlike the seed oils the vitamin E content in palm oil is represented largely as the tocotrienols. The vitamin E content of palm oil is partially lost as a result of processing. It has been reported that refined, bleached and deodorized (RBD) palm oil, palm olein and palm stearin retain approximately 69%, 72% and 76% of the original level of vitamin E in the crude oils respectively. However, there is a large variation in these estimates within the refining industry because differences in the plant conditions as well as the plant design influence the amount of vitamin E lost during refining. It has been observed that vitamin E tends to partition preferentially into the olein fraction during fractionation of RBD palm oil. For example, the concentrations of vitamin E in RBD palm olein and RBD palm stearin were 104%–135% and 58%–75% respectively of the original level of vitamin E in the source RBD palm oil.

The sterol fractions in palm oil have also been characterized. These are largely constituted by sitosterol, campesterol, stigmasterol and cholesterol. As in the case of all other edible oils of vegetable origin, the cholesterol content in palm oil is very negligible indeed and the sterol levels are further reduced on refining.

THE BIOLOGICAL SIGNIFICANCE OF MINOR COMPONENTS: THEIR ROLE AS VITAMINS, ANTIOXIDANTS AND FREE RADICALS

Traditionally doctors have advised patients that all vitamins can be obtained through a balanced diet. Taking vitamins just creates expensive urine and ordinary daily doses sufficient to ward off acute deficiencies were considered the norms. There is a fundamental shift in the way the medical world views vitamins today. Recent studies suggest that vitamins might play unexpected roles in maintaining human health. New evidence suggests that consuming reasonable quantities of certain vitamin supplements may ward off maladies, amongst them, birth defects, heart disease, cataracts, cancer, aging and other chronic ailments.

The vitamins that have generated the most interest among the scientific community are the β-carotenes, along with vitamin C and E. These are collectively also known as the biological anti-oxidants. These antioxidants are considered safe with no serious side effects. Basically these deactivate free radicals, which can otherwise damage other healthy molecules.

PRODUCTION OF FREE RADICALS

An adult consumes on the average 600 g of oxygen every day and 90%–95% is converted to water by mitochondrial respiration. Approximately 5%–10% undergoes various changes, resulting in production of chemically reactive forms of oxygen (superoxide free radical, hydroxyl radical). Free radicals result naturally from normal metabolism in cells, but exposure to sunlight, X-rays, and carcinogens such as tobacco smoke and car exhaust fumes promote their formation. Production of oxygen free radical can be either beneficial or harmful in the body. Production of oxygen free radicals by the macrophages is crucial in the destruction of harmful bacteria.

FREE RADICALS AND DISEASE

Free radicals can damage cells directly by reacting with fatty acids, proteins, enzymes, and DNA. Lipid peroxidation in cell membranes alters the structure and function of the cells and renders the lipoprotein LDL more atherogenic. The process may contribute to the development of various diseases as well as aging. Free radicals have been implicated in some 60 age related afflictions including cancer and heart disease. They are also implicated in cellular damage, inflammation and thrombosis.

DAMAGE TO HEART AND BRAIN

When tissues become ischaemic, normal cell components breakdown and these then become the substrate in reactions producing free radicals when oxygen is added during reperfusion. That is why addition of antioxidants protects the myocardium during reperfusion. Vitamin E also preserves heart muscle after ischaemia. There is also evidence that free radicals are involved in the damage to the brain during ischaemia/reperfusion. The brain is vulnerable because it contains large amounts of fatty acids, which can be oxidized to lipid peroxides. Moreover the brain contains relatively low levels of protective enzymes. The protective effects of the biological antioxidants has given rise to possible new and exciting therapies for preservation of brain function in diseases such as stroke.

REMOVAL OF FREE RADICALS

Ordinarily free radicals are eliminated by scavenging enzymes such as superoxide dismutase, catalyse or glutathione peroxidase. There is a search for substances that will scavenge radicals during reperfusion. The low molecular weight scavengers are of interest and these include the α-tocopherols and ascorbate. α-tocopherol is lipid soluble and therefore easily crosses the blood brain barrier and enters cell membranes.

ANTIOXIDANTS AND CORONARY HEART DISEASE

Epidemiological studies have revealed an increased risk of CHD and strokes in those with low plasma concentrations of antioxidants. A lower risk of CHD has been documented with high levels of vitamin E intake in a study involving 87 245 female nurses and 39 910 male professionals in the US over a period of eight years. Antioxidants such as the carotenoids, vitamin C and E are part of the body's natural defense against lipid peroxidation and its subsequent damage. Oxidation is what makes cholesterol so harmful to the coronary arteries. Oxidized LDL particles are atherogenic. They are chemotactic and so attract circulating monocytes. They may be cytotoxic to circulating endothelial cells and they may increase vasoconstriction in arteries. Vitamin E is a potent fat soluble antioxidant and is carried within the LDL particle and has been shown to increase the resistance of LDL to oxidation. Intakes of anti-oxidant nutrients including Vitamin E should be increased in line with increased intakes of long chain polyunsaturated fatty acids (PUFA) as they are particularly susceptible to oxidation, a potentially harmful process. Vitamin E supplements as well as green vegetables consumption have also been shown to reduce risk of lung cancer in men and women. Vitamin E protects key molecules against peroxidative damage triggered by free radicals. Researchers at Harvard have found preliminary evidence that 50 mg of β-carotene supplements taken every other day can half the risk of heart attack among men with histories of cardiovascular disease. Crude palm oil is a very rich source of the carotenoids, containing as much as 500–700 ppm. Since 1988, the US market for β-carotene soared from 7 million to 82 million US dollars and vitamin E sales from US$260 to 338 million.

NUTRITIONAL EFFECTS OF PALM OIL MINOR COMPONENTS: TOCOTRIENOLS AND CAROTENOIDS

There is now a growing interest in the nutritional and physiological properties of vitamin E in palm oil especially the tocotrienols. Qureshi *et al.*(1986) first isolated tocotrienols from barley and suggested that α-tocotrienol in barley exerted a dose dependent inhibition of HMG-CoA reductase (HMGR) activity which regulates cholesterol synthesis in the liver. Parker *et al.*(1990) suggested that alpha-, gamma- and delta-tocotrienols act post transcriptionally to lower the mass of HMGR in HepG2 cells.

Subsequently, Qureshi *et al.*(1991) used tocotrienol-rich fractions (palmvitee) from palm oil to evaluate a possible hypocholesterolaemic effect in humans. In a double-blind cross-over study using 20 hypercholesterolaemic subjects (Total Cholesterol, TC > 6.2 mmol/L) palmvitee supplementation caused a significant reduction in TC and LDL-C. Apolipoprotein B decreased by 9%–11%, serum thromboxane by 25% and platelet factor PF4 by 16% in comparison to the corn oil placebo capsule supplementation. Tan *et al.*,(1991) demonstrated that administration of just one palm vitee capsule containing 18 mg tocopherols and 42 mg tocotrienols significantly lowered TC and LDL-C in their hypercholesterolaemic subjects. Hypercholesterolaemic pigs with inherited hyperlipemias fed palm tocotrienol rich fractions also showed significant decreases in TC, LDL-C, apolipoprotein B, TxB2 and PF4 (Qureshi *et al.*,1991). It has been proposed that a combination of gamma-tocotrienol and alpha-tocopherol in a ratio similar to that present in palm oil deserves further evaluation as a potential hypolipaemic agent for people at atherogenic risk.

Although both tocopherols and tocotrienols are isomeric forms of vitamin E, d-α-tocopherol has the highest biopotency. Indeed its activity is the standard against which all other vitamin E isomers are compared to. In rat resorption-gestation studies, the activity of d-α-tocotrienol was only 30% of the activity of d-α-tocopherol. However, α- tocotrienol has now been reported to exhibit greater protection of red blood cells against oxidative hemolysis than α-tocopherol. It also showed a higher inhibitory effect on rat liver microsomal lipid peroxidation induced by adriamycin than α-tocopherol (Kato *et al.*,1985).

Serbinova *et al.*(1993) demonstrated that palm oil vitamin E afforded greater protection against ischemia/reperfusion injury of isolated Langendorff hearts than tocopherols. This was manifested through a complete suppression of LDH enzyme leakage from the ischemic hearts, decrease in adenosine triphosphate (ATP) and creatine phosphate levels and inhibition of the formation of endogeneous lipid peroxides by palm vitamin E. The palm tocotrienols also demonstrated higher recycling efficiency and greater uniformity of distribution in membrane layers. These properties were therefore said to offer a much high anti-oxidant potency for the tocotrienols (especially d-α-tocotrienol) than the tocopherol isomers.

The non-promoting effects of palm oil on certain types of experimental carcinogenesis may in part also be related to the minor constituents present in the oil. Of these, the carotenoids and tocotrienols are of interest. β-carotene has long been postulated to be beneficial as an anti-cancer agent. Crude palm oil is one of the richest natural sources of carotenoids and through improved processing techniques much of the original carotenoid content can be retained in the processed red palm oil.

β-carotene has recently gained considerable attention for its novel properties. It is increasingly being recognized that the solution to vitamin A deficiency, a scourge in many developing countries, lies in changing dietary behaviour. This involves the promotion of the optimal use of carotenoids rich foods. In this respect, the carotenoids in palm oil have a tremendous potential, as they are well utilized as a pro-vitamin.

Apart from its pro-vitamin activity, it has been suggested that β-carotene is involved in possible cancer prevention, in stimulation of the immune system, in suppression of arteriosclerosis and in the prevention of cataracts. These actions are mediated by its conversion to retinol or through antioxidant activity. Even though the exact role of α-carotene in cancer prevention has not been elucidated, preliminary studies indicate that β-carotene increases cell – cell communication by influencing gap junctions which serve as conduits for the passage of growth regulatory molecules between communicating cells.

Capitalizing on a traditional use of crude palm oil in many African countries, Stich *et al.*(1989) proposed that β-carotene from palm oil could potentially reduce the risk of oral cancer in tobacco chewing populations. Laboratory studies of carotene isolates from palm oil for their possible anti-cancer properties are also apparent. Nishino *et al.*(1989) isolated carotenes from crude palm oil into their individual fractions. α-carotene rather than β-carotene was more effective in suppressing the proliferation of human malignant tumour cells. They also reported that both α- and β-carotene inhibit skin tumour promotion in mice. Tan and Chu (1991) showed that in the presence of palm oil carotenoids, benzo(α)pyrene metabolism in rat hepatocytes (used as a probe for carcinogenesis) could be inhibited. In a follow-up study, the effect of palm oil minor components on the development of papilloma and lymphoma in genetically recessive HRS/J female hairless mice was evaluated. 0.3% palm carotenoid concentration in the diet was found to overcome the development of subcutaneous lymphoma and to exhibit the strongest antitumour effect with respect to mortality.

Apart from the carotenoids, the tocotrienols in palm oil have also been suggested to have possible anti-cancer activities. It was demonstrated that mice injected with mixtures of tocopherols and tocotrienols extracted from palm oil had significantly improved survival rates following intra-peritonial transfer of IMC carcinoma cells. On the other hand, α-tocopherol produced only a modest increase in the survival time. Komiyama *et al.* (1989) hypothesised that the antitumour effects of the palm tocotrienols may be mediated through a direct cytotoxic activity or through an ability to stimulate the host immune system.

The effects of palm oil tocotrienol-rich fraction (TRF) on the proliferation of MDA-MB-435 human breast cancer cells has also been examined. Inhibition of cell proliferation up to 50% (measured as incorporation of ^{3}H thymidine into DNA) was achieved by the addition of 180 µg/ml TRF to the cell cultures. On the other hand tocopherol administration alone did not inhibit cell proliferation. It was concluded that the inhibition of the human breast cancer cells was due to the presence of tocotrienols in TRF rather than tocopherols.

CONCLUSION

It is evident from the information presented, that the minor constituents in palm oil possess many beneficial properties, particularly in terms of health promotion. It is likely that further extension of studies on the role of minor constituents in palm oil would be rewarding and as such there would be an increasing focus on these minor components.

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Lion Oleochemical : Development of Purified Natural Carotenes from Palm Oil

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INTRODUCTION

The technology of extracting pure natural carotenes on an industrial scale is another new development from the laboratories of LION Corporation in Japan. LION uses the most advanced extraction and purification technology to perfect the world's first commercially available process for extracting carotenes from palm oil.

LION Oleochemical Co., a 100% subsidiary of LION Corporation which is one of the biggest manufacturers of toiletries and household products in Japan, was established with a view to produce various kinds of raw materials derived from natural alternatives. For many years the LION Corporation has been seeking substitutes for petroleum based raw materials which should be renewable and stable in terms of supply. They found the alternative in palm based oleochemicals. Lion Oleochemical Sakaide Factory is a sophisticated and efficient factory producing raw materials from natural fats and oils. One of the product a produced by the factory is natural carotenes.