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Minor Compounds of Palm Oil: Properties and Potential Applications

Alexis Gonzalez-Diaz and Jesús Alberto García-Núñez

Abstract

The oil contained in ripe fruits produced by cultivars of African oil palm *Elaeis guineensis* Jacq., as well as that obtained from fresh fruit bunches of certain inter-specific hybrid cultivars derived from crossbreeding between *Elaeis oleifera* (Kunth) Cortés and *E. guineensis* Jacq., have shown to be lipid substrates rich in valuable phytochemicals with exceptional biological properties and functional applications for multiple human health tasks. Eight isoforms of vitamin E (four tocopherols and four tocotrienols), α - and β -carotene, squalene, and various phenolic structures, make up the largest group of minor compounds in palm oil and are essential nutrients with physiological functions that include, but are not limited to their antioxidant properties. Vitamin E regulates the redox (oxidation-reduction) balance in the body, and compounds such as squalene and carotenoids are ubiquitously distributed throughout the body, including cell membranes and lipoproteins. Several studies suggest that regular intake of foods rich in this group of phytonutrients minimizes the reactivity of oxidative chemical species at the cellular level and serves as an effective adjunct in the treatment of oxidative stress.

Keywords: vitamin E, provitamin A, carotenes, phenolic compounds, phytochemicals, nutraceuticals

1. Introduction

In palm oil mills, crude palm oil (CPO) is obtained by mechanical pressing ripe fruits produced by commercial cultivars of African palm *Elaeis guineensis* Jacq. D $\times$ P type (i.e., Dura $\times$ Pisifera breed) (D $\times$ P CPO) or by *Elaeis oleifera* (Kunth) Cortés $\times$ *E. guineensis* Jacq. Breeds are commonly known as O $\times$ G interspecific hybrids (O $\times$ G CPO) under specific pressure and temperature conditions. In its natural unprocessed state, CPO is dark red, a distinctive feature that is attributed to the carotenoid fraction contained in its lipid structure, which includes α - and β -carotene (the precursor to vitamin A that gives carrots their characteristic color), and lycopene (which gives fruits and vegetables their red color) to a lesser extent [1, 2].

CPO is a fatty compound comprising an important fraction of biologically active molecules with varied physiological properties that, in appropriate amounts, stimulate the proper functioning of the immune, digestive, and reproductive systems [3–5]; facilitate the recovery of connective tissue [6]; promote the correct development of vision [5, 7]; have positive effects on the cardiovascular health of adults

and the elderly [3]; limit the action of free radicals, provide protection against other reactive oxygen species, and fight oxidative stress [8–14]. A high concentration of tocopherols and tocotrienols, carotenoids, squalene, and phenolic compounds gives CPO its antioxidant power.

Antioxidants are compounds that have the ability to prevent or delay the oxidation of other molecules by inhibiting the initiation or spread of chemical reactions [15]. This allows them to protect the body against the possible effects attributed to the action of free radicals and other reactive oxygen species—ROS—(organic and inorganic oxygen ions and peroxides) [4, 16]. Depending on their source, antioxidants can be classified into two groups, one made up of those synthesized by the body (endogenous) and the other made up of those derived from food intake (exogenous) [17]. Over the last decade, the role of antioxidants in the diet and their impact on human health and the treatment of different diseases have gained significant scientific interest [18–20]. Different studies suggest that antioxidants supplied to the body *via* food intake play a key role in slowing the development of chronic diseases with the greatest impact worldwide, such as neoplastic [21, 22], neurodegenerative [23, 24], and cardiovascular [25, 26] diseases.

Furthermore, CPO is refined and fractioned by physical or chemical processes to obtain refined, bleached, and deodorized (RBD) palm olein (liquid fraction: 65–70% of unsaturated fatty acids) and RBD palm stearin (solid fraction: 30–35% of saturated fatty acids). Refining is the most effective mechanism to remove the natural color, odor, taste, and impurities of CPO [27]. However, about 99% of carotenoids are removed during the bleaching stage of palm oil refining [28], while approximately 36% of vitamin E is degraded during its refining and fractioning [29]. For a few decades now, has minimally processed and refined red palm oil been introduced into Western markets, with varying results in the consumers' perception of the product. In some cases, the natural color of red palm oil proved to be unattractive to some buyers, while for others, this property represented a high nutritional value and the richness in carotenoids of this vegetable oil [30].

In recent decades, several studies have revealed much of the biological functions of the micronutrients found to some extent in palm oil, such as phenols and tocotrienols, β -carotene, squalene, and phytosterols, which make this fatty constituent a unique and ideal raw material for various food applications given its versatility. This chapter highlights the most relevant properties of the most abundant group of minor compounds in palm oil of different sources while proposing it as a suitable material to formulate and develop functional foods enriched with palm phytochemicals.

2. Palm phytochemicals

In addition to triglycerides (>95%) [31], diacylglycerols, and free fatty acids, CPO contains a significant amount of minor compounds representing at least 1% of their lipid composition by weight (**Table 1**). These compounds can be of two types—glycerolipids such as monoglycerides, diglycerides, and phospholipid; and non-glycerolipids, which include tocopherols, tocotrienols, phytosterols, carotenoids, and other vitamins, proteins and amino acids, phenolic and polyphenolic compounds, and free fatty acids [42, 43]. Hence, the content of biologically active phytochemicals in CPO cannot be overlooked, given the attractive biological properties and the nutritional value attributed to this type of substances, as well as the marked preference of the pharmaceutical and nutraceutical industries for natural raw materials to exploit these phytonutrients [44–47].

Minor compounds	D × P CPO (mg·kg ⁻¹)	Coari La × Mé O × G CPO (mg·kg ⁻¹)	References
Tocopherols and tocotrienols (vitamin E)	500–800	876–1843	[32, 33]
Total carotenoids	988	514–1042 1172.1–1449.6	[33–35]
Total phytosterols	~300	735–1135	[32, 33]
Squalene	200–500	253.86 247.4 ± 3.3	[36–38]
Total phenolic compounds	~61–91	215–224*, †	[28]
Aliphatic alcohols	100–200	N. D	[36]
Phospholipids	20–80 5–130	N. D	[36, 39]
Isoprenoid alcohols	40–80	160.7–251.3 269.3 ± 60.0	[36, 38, 40]
Methyl sterols	40–80	6.9–14.9 12.7 ± 1.5	[36, 38, 40]
Ubiquinones	18–25 10–80	N. D	[36, 41]
Aliphatic hydrocarbons	50	N. D	[36]

N.D: no data.
*Data from Colombian Oil Palm Research Center—Cenipalma.
†Expressed in gallic acid equivalent milligrams.

Table 1.
Minor compounds in crude palm oil from different sources.

However, palm oil refining is the most widely implemented conventional process to remove unwanted compounds such as free fatty acids, residual phospholipids, remaining metals, soap traces, volatile oxidation products, and other contaminants [48–50]. To date, there is no known refining technology on an industrial scale that is effective and selective to remove components considered as harmful or that cause adverse effects on the organoleptic qualities of the final product and that to preserve most of the original phytochemicals of CPO. This brings new opportunities for the palm sector worldwide, considering the current trends in the food market with “functional” characteristics and their influence on consumer behavior. Furthermore, this situation translates into new challenges for the oils and fats industry.

Some of the most relevant properties of the minor compounds group in the CPO of different sources are described below.

2.1 Tocopherols and tocotrienols

Tocopherols and tocotrienols are well-known isoforms of vitamin E (**Figure 1**), which greatly improve the oxidative stability of vegetable oils, thanks to their anti-oxidant properties [52]. In nature, tocopherols are freely found as alcohols, while tocotrienols are found in esterified forms [53]. The term vitamin E refers to eight isoforms of fat-soluble vitamins that can be classified in four tocopherol isoforms (α-, β-, γ-, and δ-Tocopherol) and in four tocotrienol isoforms (α-, β-, γ-, and δ-Tocotrienol) [54, 55], in which the position and number of methyl groups (–CH₃) in the chromanol ring of their structures are unequal (**Figure 1**).

Figure 1.

Tocopherols and tocotrienols in palm oil. Chemical structured developed in ACD/CHEMSktech software [51].

In virgin vegetable oils, the concentration of the different isomeric forms of tocopherols and tocotrienols may depend on the type and quality of the raw material. In some vegetable oils, part of the original vitamin E content is removed involuntarily during refining, especially during the deodorization stage [56]. The main food sources of tocopherols and tocopherols are O × G CPO extracted from the Coari × La Mé cultivar (1316 mg·kg⁻¹) [33]; D × P CPO (914 mg·kg⁻¹) [57]; olive oil (10.4 mg·kg⁻¹) [57]; and barley germ, canola, corn germ, cottonseed, oat bran, peanut, rapeseed, rice bran, rice bran, sesame, soy, sunflower, and wheat germ oils [58, 59].

2.2 Provitamin A: carotenoids

Carotenes are pigments with an organic structure found in plants and other photosynthetic organisms [60]. The α - and β -carotenes (**Figure 2**) are tetraterpenes biochemically synthesized from eight isoprene units (methyl-1,3-butadiene) [61] and are part of more than 600 liposoluble carotenoids identified in natural sources around the world [62].

β -Carotene is a biological precursor (inactive form) of vitamin A or retinol (**Figure 2**), also responsible for the biosynthesis of other retinoids (retinol ester, retinaldehyde or retinal, retinoic acids and its analogs) [63]. β -Carotene is

Figure 2.

Molecular structure of the most predominant carotenoids in crude palm oil (α - and β -) and vitamin A (retinol). Chemical structured developed in ACD/CHEMSktech software [51].

considered an indispensable compound for life, which must be obtained from the diet. This substance is capable of producing two retinol molecules thanks to the enzymatic action of β,β -Carotene-15,15'-monooxygenase [13, 64].

Structurally, α - and β -carotene consist of 40 carbon atoms and two rings of β -ionone located at each end of the chain (**Figure 2**) [60, 65]. D $\times$ P CPO contains between 500 and 700 mg $\cdot$ kg⁻¹ of carotenoids, with α -carotene (~ 35%) and β -carotene (~ 56%) being the most prevalent in the matrix [66]. In addition, concentrations between 514 and 1042 mg $\cdot$ kg⁻¹ of these compounds have been found in O $\times$ G CPO extracted from the Coari $\times$ La Mé hybrid cultivar, with β -carotene accounting for approximately 73% of the total carotenoids [33]. The group of foods with high carotenoid content includes vegetables, milk and dairy products, meat and meat products, fish and seafood, eggs and derivatives, fruits, D $\times$ P CPO and O $\times$ G CPO (**Table 1**), and other vegetable fats, sauces, herbs, and spices [67].

2.3 Squalene

Squalene is a polyunsaturated triterpene made up of six isoprene units, resulting in a compound with six double bonds between carbon atoms in its structure. As a result, squalene is classified as the molecule with the highest degree of unsaturation among lipids, which makes it highly sensitive to oxidation [68]. Squalene belongs to the group of natural antioxidants known as isoprenoids, classified as a bioactive compound with the ability to prevent or minimize the negative effects of free radicals on cells in the human body [69, 70]. Some studies suggest that the squalene secreted in the fatty mantle of human skin provides protection against ultraviolet radiation [71]. D $\times$ P CPO has been found to contain between 200 and 500 mg $\cdot$ kg⁻¹ of squalene [36], whereas O $\times$ G CPO of the Coari $\times$ La Mei hybrid cultivar has been found to contain 253.86 mg $\cdot$ kg⁻¹ of squalene on average [37]. Currently, squalene is classified as a component with nutritional and medicinal properties with vast expectations for application in the pharmaceutical industry. Some of these properties include cardioprotective, antioxidant, antibacterial, antifungal, anticancer, and detoxifying effects [72].

2.4 Phenolic compounds: phenols and polyphenols

CPO contains significant amounts of phenolic phytohormones (e.g., p-salicylic acid), phenolic aldehydes (e.g., protocatechuic aldehyde), and phenolic acids (e.g., vanillic acid, protocatechuic acid, gallic acid, and ferulic acid) (**Figure 3**) which together make up the largest proportion of phenolic compounds in this type of oil [73]. In plants, phenolic compounds are secondary natural metabolites that are biologically synthesized by the shikimic acid (shikimate-phenylpropanoid) pathway, resulting in phenylpropanoids [74], or by the acetate-malonate pathway (polyketide route), in which monomeric and polymeric phenols and polyphenols are produced [75].

These compounds have important physiological functions in plants and play a key role as defense compounds when environmental stress, pathogen attack, herbivory, and nutrient deficiency lead to a systematic increase in the production of free radicals and other oxidative chemical species [75]. Furthermore, phenolic compounds are regularly described as bioactive substances with antioxidant properties at the cellular level, partly attributed to their ability to act as chelators of metal ions [76–78].

In foods, phenolic compounds influence their appearance, quality, acceptability, and stability because they act as dyes [79], antioxidants [80], and flavorings [81]. Cereals and legumes (e.g., wheat flour, soy, and oats), as well as fruits (e.g., sweet orange, yellow raspberry, and apples) and vegetables (e.g., red cabbage, broccoli,

Figure 3.

Phenolic compounds of major relevance in palm oil. Chemical structured developed in ACD/CHEMSketch software [51].

carrots, tomatoes, and spinach) [82], and some vegetable oils (e.g., palm [28, 83], olive [84], soy and cotton [85], coconut [86], sesame and sunflower [87] oils), are part of the food sources of phenolic compounds.

2.5 Phytosterols and phytostanols

Phytosterols and phytostanols are biologically active compounds regularly found in plants and various foods of plant origin. Phytosterols differ from cholesterol in that they have a different elemental distribution in the side chain that forms their chemical structure (**Figure 4**), whereas phytostanols are 5 α -saturated derivatives of phytosterols [88]. These structural changes, although minimal, make phytosterols, phytostanols, and cholesterol have particular physicochemical characteristics and differentiate them from each other metabolically and functionally.

Phytosterols and phytostanols are not synthesized by the human body [89, 90]; therefore, they must be supplied to the body through the intake of foods rich in these compounds. The main food sources of phytosterols are vegetable oils, fats, and edible fatty derivatives [91, 92], as well as nuts [93], cereals and derivatives [92], and vegetables [94]. The most abundant phytosterols and phytostanols in the human diet are β -sitosterol, campesterol, sitosterol, and campestanol [95].

D $\times$ P CPO contains a substantial amount of natural sterols (325–527 mg $\cdot$ kg⁻¹) [36], mainly constituted by β -sitosterol (46.55 $\pm$ 0.93%), campesterol (31.91 $\pm$ 0.5%), and stigmasterol (21.54 $\pm$ 0.86%) [59]. Similarly, concentrations between 735 and 1135 mg $\cdot$ kg⁻¹ of these compounds have been found in O $\times$ G CPO extracted from the Coari $\times$ La Mé hybrid cultivar, with β -carotene accounting for approximately 63% of the total sterols [33].

Figure 4.

Phytosterols most abundant in palm oil and cholesterol. Chemical structured developed in ACD/CHEMSketch software [51].

3. Oil palm as natural ingredient rich in biologically active constituents

Both D × P CPO and O × G CPO of the Coari × La Mé cultivar are naturally occurring lipid materials with important tocopherols and tocotrienols contents (**Table 1**), with a wide range of uses in various productive sectors. For the pharmaceutical sector, as for the food and nutraceutical industries, palm oil of different sources may be an active component to enrich various edible matrices or to formulate and develop new products. Given the high content of vitamin E in its lipid composition, palm oil can be incorporated into the formulation of products that may be useful to prevent or treat vitamin E deficiency, associated with health disorders such as peripheral neuropathy, retinopathy pigmentosa ataxia, and myopathy [96–98].

Carotenoids in palm oil can be biologically active primary components in the formulation of new products; furthermore, the amount of tocopherols, tocotrienols, and squalene naturally found in this oil could add even more value to products that may contain them [99–102]. Also, the β -carotene in palm oil can serve as an active component in food aggregates for human and animal diets [103–105] due to the properties that have been identified in this compound at the biological level and due to the reported benefits of its consumption for human [106, 107] and animal [108] health.

On the other hand, the phytosterols that make up the complex of minor compounds in palm oil (**Figure 4**) have industrial uses as essential elements required to manufacture various products [109–111]. β -Sitosterol, one of the natural sterols found in greater amounts in palm oil, could be included in food preparations aimed at reducing low-density lipoproteins (LDL), which are closely related to the development of cardiovascular diseases [112, 113].

To another extent, squalene is a constituent of high biological value used as an aggregate in different products. This compound is part of the raw materials used in cosmetics [114] and the formulation of pharmaceutical and food products [115, 116]. In the food and cosmetic industries, squalene is used as an additive due to the several benefits for human health that have been reported in various works [72, 117]. Squalene in palm oil could contribute to the enrichment of diverse food matrices and, together with tocopherols, tocotrienols and carotenoids, could collectively supplement much of the deficiency of these substances in some organisms. In addition to the aforesaid, some research has found that squalene is an effective chemotherapeutic agent for the treatment of colon carcinomas [118], breast cancer [119], and pancreatic tumors [120].

4. Available technologies to extract, concentrate, and/or purify palm phytochemicals

Several mechanisms have been developed to extract, fraction, and refine the phytochemicals, which are found in CPO. Such processes include, but are not limited to, extraction with supercritical fluids [121], molecular distillation and crystallization [122], and molecular distillation with prior esterification/transesterification of oil [123]. In general, these technologies are repeatedly used to produce oily extracts rich in squalene, carotenoids, tocopherols, and tocotrienols.

By means of solid-phase extraction and fractionation in polar phase mobile bed, a product rich in α -tocotrienol free of other isomers of tocotrienols, tocopherols, and carotenoids was obtained from CPO [124]. Squalene, vitamin E, and phytosterols were fractioned from CPO through a process that included esterification, transesterification, vacuum distillation, saponification, crystallization, and

exclusion of organic solvents stages [125]. On the other hand, the implementation of supercritical fluids was useful in the production of extracts rich in tocopherols and carotenoids from CPO.

According to several authors, the vitamin complex composed of tocopherols and tocotrienols can be extracted, fractioned, and purified from various biomaterials by using technologies such as solvent extraction (direct extraction [126], Soxhlet extraction [127], and pressurized fluid extraction (PLE) [128]), supercritical fluid extraction (SFE) [129], enzyme extraction [130], extraction with prior chemical modification of the oil's lipidic matrix (saponification [127] and esterification [131]), absorption [132], sequential adsorption-desorption [133], molecular distillation [134], microwave-assisted extraction (MAE) [135], and membrane filtration [136].

On the other hand, some of the most widely implemented methodologies to extract carotenoids from different vegetable materials include processes such as liquid extraction at atmospheric pressure with maceration [137], Soxhlet extraction [138], MAE [139], ultrasound-assisted extraction (UAE) [140], accelerated solvent extraction (ASE) [141], pulsed electric field-assisted extraction (PEF) and moderate electric field extraction (MEF) [142], SFE [143], complex enzyme-assisted extraction [144], PLE [145], and extraction with green solvents [146]. After an additional separation stage, the analysis of carotenoids has been carried out using instrumental techniques such as high-efficiency liquid chromatography with diode array (HPLC-DAD), thin-layer chromatography, and gas chromatography coupled to mass spectrometry [147].

Currently, fractions rich in phenolic compounds from biomaterials are obtained by implementing technologies such as solid-liquid extraction (SLE) [148], PLE [149], ASE [150], SFE [151], UAE [152], MAE [153], ultrafiltration (UF) [154], and complex enzyme-assisted extraction [155]. These processes have guaranteed the extraction of phenolic compounds with good yields. Likewise, the purification of these compounds by implementing liquid and solid phases has guaranteed the acquisition of extracts with abundant phenol and polyphenol contents with high levels of purity [156].

Finally, squalene and phytosterols have been extracted from natural sources using supercritical carbon dioxide (CO₂) (SFE) [157]. In addition, high levels of these same substances have been found in deodorization distillates during the refining of some vegetable oils, such as palm and olive [158, 159]. Furthermore, the most widely used techniques to quantify the compounds mentioned above include gas chromatography with flame ionization detector (FID) and gas chromatography coupled to mass spectrometry [72].

5. Conclusions

D × P CPO and O × G CPO Coari × La Mé are natural oils derived from ripe fruits of the African palm *Elaeis guineensis* Jacq., and from one of the interspecific hybrid cultivars between the species *Elaeis oleifera* (Kunth) Cortés and *E. guineensis* Jacq., respectively, with a significant content of tocopherols and tocotrienols, α- and β-carotene, phytosterols, squalene, and phenolic structures that, when incorporated into the human diet in appropriate doses, promote the correct physiological functioning of organisms. According to the various works mentioned in this chapter, the above components are considered biomolecules indispensable for life due to their biological functions and nutritional attributes.

At present, different processes have been developed to extract, recover, and purify the phytochemicals contained in palm oil with good yields and high

concentration values in the extracts obtained as final products. Currently, there is a marked trend toward obtaining phytochemicals from various natural sources by means of green technologies. Furthermore, the number of companies engaged in this work is increasing.

This chapter aims to show the attributes and benefits of including D × P CPO and Coarí × Me O × G CPO in the human diet and seeks to propose them as raw materials to produce functional food rich in phytochemicals of nutritional value.

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