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Chapter

Oilseeds as Functional Foods: Content and Composition of Many Phytochemicals and Therapeutic Alternatives

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Abstract

Oilseeds composition has been studied extensively, but recently it has been thoroughly investigated considering especially the phytochemicals representing the minor components. This interest is connected with the activity of such compounds against cardiovascular diseases, lipid oxidation, protein cross-linking and DNA mutations and hemostasis function, which prevent the attack of biomolecules by free radicals. This chapter book could aim to give an overview of the different uses of several oilseeds as bioactive foods, focusing on their active constituents (phytosterols, polyphenols, tocopherols, tocotrienols, and carotenoids) and their content in oilseeds. We will also focus on the beneficial aspects of these nutraceuticals in human health.

Keywords: oilseeds, phytosterols, phenolic acids, tocopherols, tocotrienols and carotenoids

1. Introduction

Phytochemicals in plant material have raised interest among scientist, producers, and consumers for their roles in the maintenance of human health and in assessing the protective status of people from chronic degenerative disorders. These biologically active compounds have been reported to elicit several biological effects, including cardioprotective, anti-inflammatory, anticancer, and others. Plant derived phytochemicals have been the focus of recent research due to their health promoting effects [1].

Phytochemicals are bioactive non-nutrient chemical compounds found in plant foods, such as fruits, vegetables and grains which may be potent effectors of biologic processes and have the capacity to influence disease risk via several complementary and overlapping mechanisms. Nowadays, thanks to technological and scientific advances, it is possible to extract, characterize, and evaluate bioactive compounds from foods and medicinal plants [2].

From phytosterols to polyphenols, fat to polyphenols, it is the combination of these components that lead to good health and well-being. Furthermore, many of the characteristic components of oilseeds are known to have positive effects on health, capacity and well-being, and can be used to design functional foods.

Vegetables, fruits and nuts are all rich in phenols, flavonoids, isoflavonoids, phytosterols and phytic acid—essential bioactive compounds providing health benefits. In fact, with the increasing demand for edible oil, plant sources have become the target for research to explore their quality and functional properties. Thus, there are many in vitro, in vivo, randomized, and clinical studies evaluating the ability of bioactive compounds to provide health benefits. Also, their beneficial health effects starting from major diseases and health conditions that are in the first places of death worldwide, including cardiovascular disease, cancer, diabetes, neurodegenerative diseases, and aging [3].

Therefore, this chapter is intended to describe the main bioactive compounds such as sterols, polyphenols, tocopherols, and carotenoids. It will also encourage a large consumption of this species in local and international markets and its possible industrial use, especially in the food.

2. Phytosterols (DESM, MMS, DIM)

Phytosterols also called plant sterols, are minor components of vegetable oils and from a major proportion of the unsaponifiable fraction of lipids which can occur in vegetable oils either in free form or esterified with fatty acids [4]. The individual sterols and their relative proportions can be used to determine the identity of the oil and to detect adulterations. Phytosterol contents in vegetables are known to vary due to different factors such as variety, season, extraction, and other technological procedures [5].

Furthermore, phytosterols are known to lower serum low-density lipoprotein (LDL). Cholesterol levels by reducing intestinal cholesterol absorption. Clinical studies confirmed that phytosterols have hypocholesterolemia, anti-inflammatory and anticarcinogenic effects [5]. Therefore, phytosterols have been added to several functional food products such as yoghurt, milk and some vegetable oils. These types of products are now available on the market and have been scientifically proven to lower blood LDL cholesterol by around 10–15% as part of a healthy diet [5].

2.1 Structure

Phytosterols (PS) are by-products of the isoprenoid biosynthetic pathway via squalene from acetyl-coenzyme A [6]. They are 28 or 29-carbon alcohols and resemble cholesterol in vertebrates in terms of both functions, i.e. by stabilization of phospholipids bilayers in plant cell membranes as in structure, given the four-ring steroid nucleus, the 3β -hydroxyl group and often a 5, 6-double bond (**Figure 1**) [7].

They have been categorized into three subclasses: on the basis of the number of methyl groups at the C₄ position: (4-DEMS) none (4-desmethylsterols or “sterols”), (4-MMS) one (4 α -monomethyl-), and (4-DIMS) two (4,4'-dimethylsterols or triterpenes alcohols) [8, 9]. The main compounds of 4-desmethylsterols class are β -sitosterol, campesterol, stigmasterol and Δ^5 -avenasterol (**Figure 2**). 4,4'-dimethylsterols (triterpenes alcohols) and 4 α -monomethylsterols are metabolic intermediates in the biosynthetic pathway leading to the end-product, 4-desmethylsterols, but they are usually present at lower levels than 4-desmethylsterols in most plant tissues [8–11]. The major components of 4,4'-dimethylsterols are β -amyrin, α -amyrin, cycloartenol and 24-methylencycloartanol (**Figure 2**). In the case of 4 α -monomethylsterols, we evoke mainly Obtusifoliol, gramisterol and citrostadienol (**Figure 2**). Generally, plant sterols are 4-desmethylsterols because they do not contain any methyl groups at the fourth position of the sterol ring structure [12].

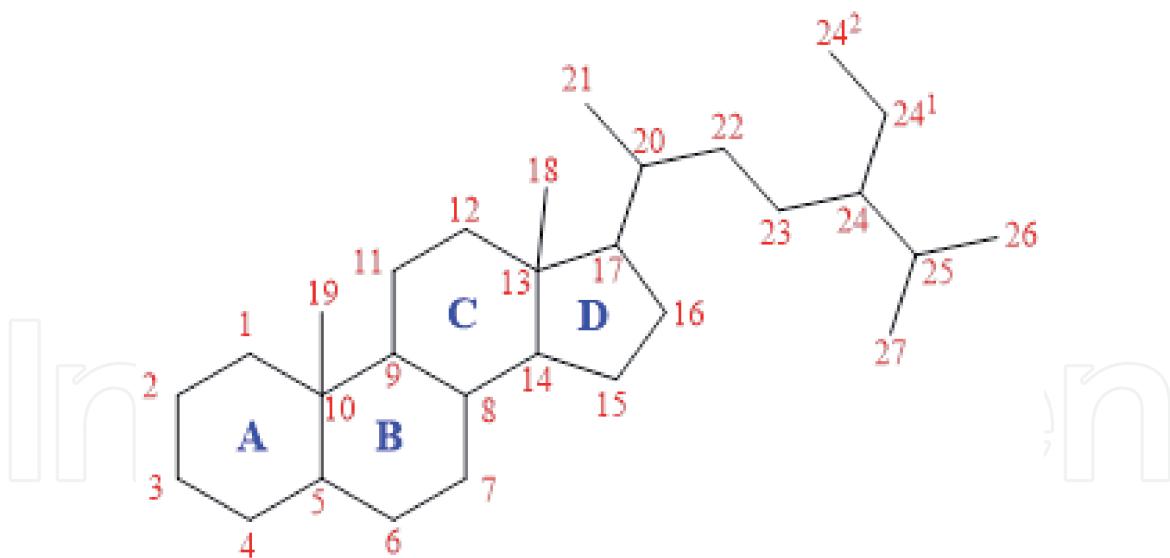


Figure 1.
Steroid structure.

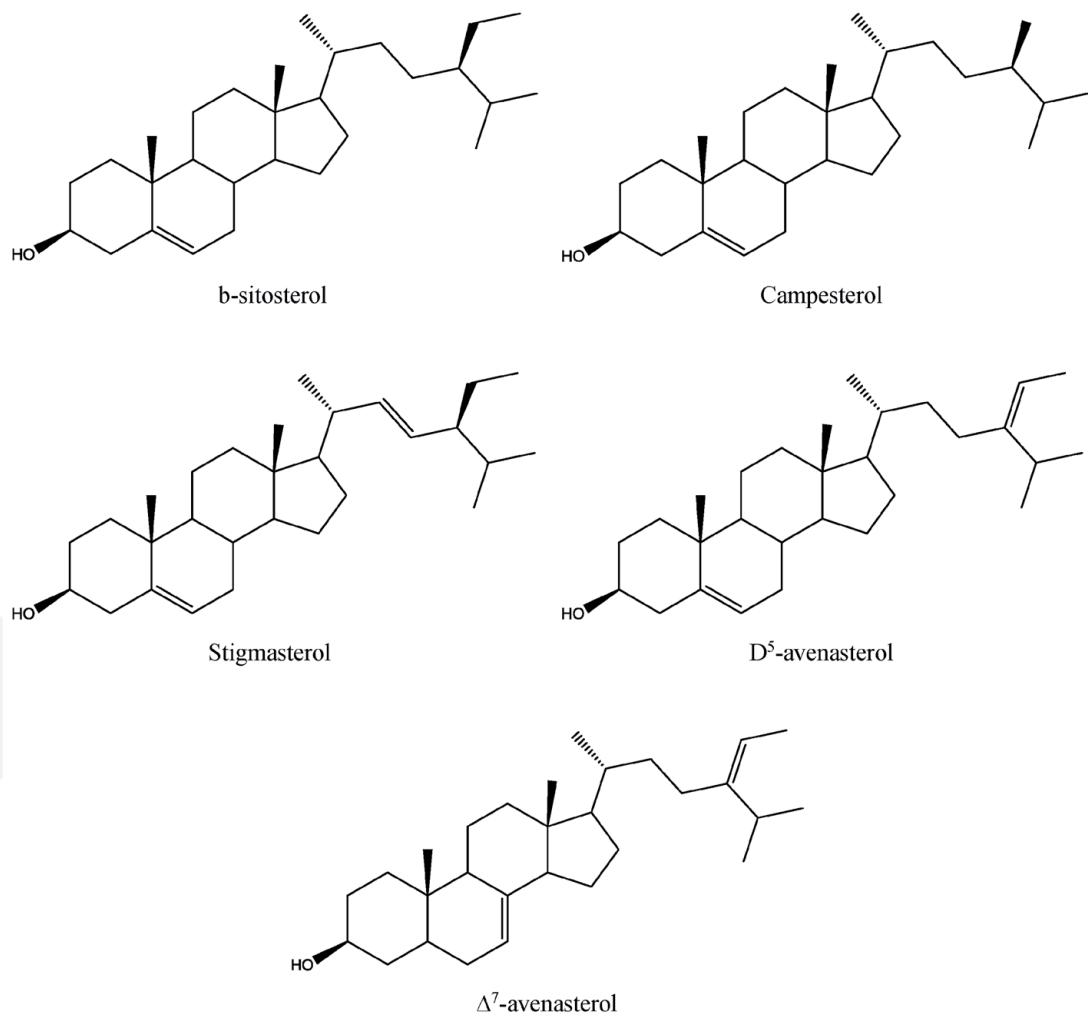


Figure 2.
Detailed chemical structures of β -sitosterol, Campesterol, Stigmasterol, D^5 -avenasterol and D^7 -avenasterol.

2.2 Plants as source of phytosterols

Vegetable oils, oilseeds, and nuts are the richest sources of phytosterols. β -sitosterol (29C), campesterol (28C) and stigmasterol (29C) are the most common sterols [4, 12]. The total PS content and profile can vary according to

variety, agronomic and climatic conditions, maturity, extraction and refining methods [13, 14].

The impact of cultivar on seed oils phytosterols content was demonstrated and many major phytosterols components were identified on some seed oils of commercial importance such as rapeseed, soybean, and sunflower have been regarded as rich sources of phytosterols [15].

2.2.1 Health benefits

Several studies have demonstrated the PS protect against many chronic ailments such as cardiovascular diseases [16, 17], cancer [18], ulcers [19], diabetes [20], and inflammation [21].

4-desmethylsterols contribute to lowering serum cholesterol levels [22]. In fact, it has been reported that they have the capacity to reduce dietary cholesterol absorption in the intestine [22]. They are also considered to have anti-inflammatory, anti-bacterial, anti-atherosclerotic, anti-oxidative, anti-ulcerative, and anti-tumor properties in humans [8–23], as well as contributing to the oxidative and thermal stability and shelf-life of vegetables oils [24]. In vivo studies have shown that diets enriched with PS (2%, w/w) contributed to improve lipid profiles and decreased atherosclerotic lesions in apolipoprotein E-knockout (apoE-KO) mice [20]. In addition, they are useful emulsifiers for cosmetic manufacturers and supply most steroid intermediates and precursors to produce therapeutic steroids [25].

PS have been reported to have a protective effect against various forms of cancer such as breast [21], prostate [26], lung [4], liver and stomach [27], and ovary and colon cancers [28].

Triterpenes compounds are also important bioactive secondary metabolites, due to the wide range of their biological activities. They show mainly antimicrobial, cytotoxic, antitumoral, antiviral, anti-inflammatory- hepatoprotective, antifeedant and insecticidal activities [29].

3. Phenolic acid

Phenolic phytochemicals are the most abundant secondary metabolites and the most widely distributed in the plant kingdom. The three most important groups of dietary phenolics are flavonoids, phenolic acids, and polyphenols (tannins, stilbenes and lignans) [30].

Phenolic are hydroxyl group (-OH) containing class of chemical compounds where the (-OH) bonded directly to an aromatic hydrocarbon group. Phenol (C_6H_5OH) is considered the simplest class of this group of natural compounds. Phenolic compounds are a large and complex group of chemical constituents found in plants [31]. They are plant secondary metabolites, and they have an important role as defense compounds. Phenolics exhibit several properties beneficial to humans and its antioxidant properties are important in determining their role as protecting agents against free radical-mediated disease processes.

3.1 Structure

They are defined as chemical substances possessing one or more aromatic rings with one or more hydroxyl groups in their structures [32].

The term “phenolic acids” (PA), in general, designates phenols that possess one carboxylic acid functional group. Naturally occurring phenolic acids contain two distinctive carbon frameworks: the hydroxycinnamic and hydroxybenzoic

structures (**Figure 3**). Hydroxycinnamic acid compounds are produced as simple esters with glucose or hydroxy carboxylic acids. Plant phenolic compounds are different in molecular structure and are characterized by hydroxylated aromatic rings [33]. These compounds have been studied mainly for their properties against oxidative damage leading to various degenerative diseases, such as cardiovascular diseases, inflammation, and cancer. Indeed, tumor cells, including leukemia cells, typically have higher levels of reactive oxygen species (ROS) than normal cells so that they are particularly sensitive to oxidative stress [34]. Many papers and reviews describe studies on bioavailability of phenolic acids, emphasizing both the direct intake through food consumption and the indirect bioavailability deriving by gastric, intestinal, and hepatic metabolism [35]. In addition, Phenolic acid compounds and functions have been the subject of a great number of agricultural, biological, chemical, and medical studies. In recent years, the importance of antioxidant activities of phenolic compounds and their potential usage in processed foods as a natural antioxidant compounds have reached a new level and some evidence suggests that the biological actions of these compounds are related to their antioxidant activity [36].

3.2 Plants as source of phenolic acid

The hydroxycinnamic acids are more common than are the hydroxybenzoic acids and consist chiefly of *p*-coumaric, caffeic, and ferulic. Indeed, caffeic acid, both free and esterified, is generally the most abundant phenolic acid and represents between 75 and 100% of the total hydroxycinnamic acid content of most fruit. Concentrations generally decrease during ripening but increase as the fruit increases in size [37]. The hydroxybenzoic acid content of edible plants is generally very low, except for certain red fruits, black radis and onions, which can have concentrations of several tens of milligrams per kilogram fresh weight [37]. Tea is important source of gallic acid; tea leaves may contain up to 4.5 g/kg fresh wt [37]. It has been stated that the most important PA derivatives are in the rape-seed oil including 2.6 dimethoxy-4-vinylphenol (257 µg/100 g) and ferulic acid (5.6 µg/100 g), while vanillic acid (11.4 mg/100 g) is in pumpkin seed oil and ferulic

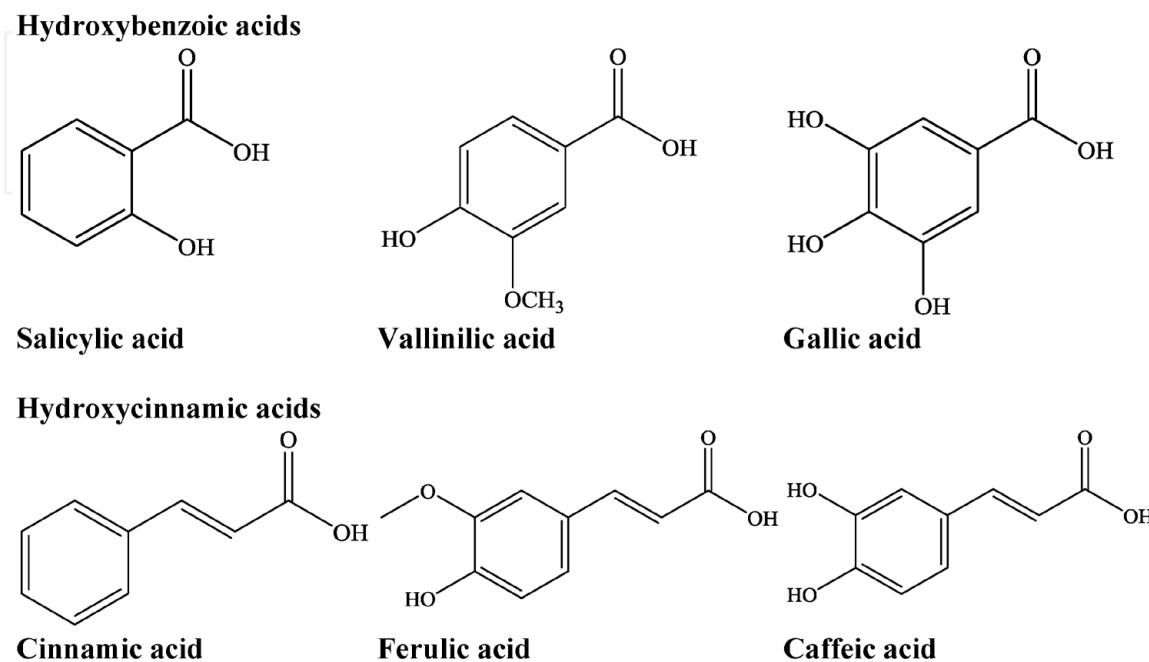


Figure 3.
Structure of the important naturally occurring phenolic acids.

acid (5.8 mg/100 g) is in corn oil. The total amount of PA was determined as 79 mg gallic acid/kg oil in soy oil, 124 mg gallic acid/kg oil in canola oil, 8397 mg gallic acid/100 g oil in palm fruit, and 20–43 mg synapic acid/100 g oil in rapeseed oil [38]. PA content and profile in plant oil generally depends on the variety, environmental conditions, extraction methods, and storage conditions [39].

3.3 Health benefits

Phenolic compounds are famous group of secondary metabolites with wide pharmacological activities. Phenolic acid compounds and functions have been the subject of a great number of agricultural, biological, chemical, and medical studies. Phenolic compounds in many plants are polymerized into larger molecules such as the proanthocyanidins (PA; condensed tannins) and lignins. Moreover, phenolic acids may arise in food plants as glycosides or esters with other natural compounds such as sterols, alcohols, glucosides, and hydroxy fatty acids. Increases bile secretion, reduces blood cholesterol and lipid levels and antimicrobial activity against some strains of bacteria such as *Staphylococcus aureus* are some of biological activities of phenolic acids [40]. Varied biological activities of phenolic acids were reported. Phenolics acid possesses diverse biological activities, for instance, antiulcer, anti-inflammatory, antioxidant, cytotoxic and antitumor, antispasmodic, and antidepressant activities [41]. Moreover, a phenolic compound can interrupt the radical chain reaction by donating a hydrogen atom to the free radicals and therefore converting itself to a radical. PA can also act as metal chelators and oxygen scavenger and helps then against diseases associated with oxidative stress [42].

4. Tocols

4.1 Structure

Tocopherols and tocotrienols, together abbreviated as tocols, are natural lipophilic antioxidants that protect oxidation in vegetable oils [43]. Tocopherols

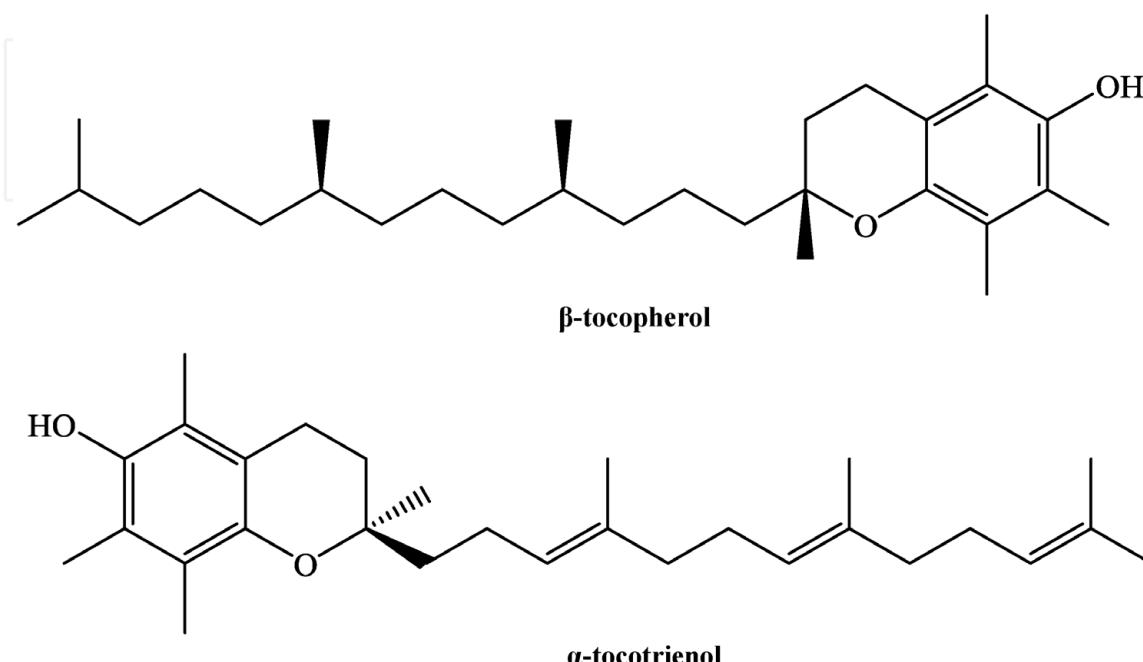


Figure 4.
Structure of the important naturally occurring tocols.

(vitamin E) are the most important and effective lipid-soluble compounds constituting a family of antioxidants with several health benefits [44]. Vit E comprise a chromanol ring with a C16 phytol side chain and are reclassified in two types according to which the side chain is either saturated (tocopherols) or contains three double bonds at carbons 3, 7 and 11 (tocotrienols). The presence of methyl (-CH₃) group in the aromatic ring of tocopherol (**Figure 4**) makes this compound stable to heat, alkali, or acid. However, this vitamin undergoes degradation and isomerization under certain stress conditions, such as oxidizing agents or UV light, yielding four major vitamers: isomers (i.e., α-, β-, γ-, and δ-tocopherols) (**Figure 4**) and differ in the matylation pattern of the benzopyran ring with three methyl groups (at C-5, C-7, and C-8) [45].

Among these homologs, α-tocopherol exhibits 100% biological activities, 30, 15, and 5% for β-, γ-, and δ-tocopherols, respectively. Seeds often dominate other plant parts in terms of the abundance of total-tocopherols (T-tocopherol), although α-tocopherol, a form of vitamin E that is most biologically active, is often only a minor component [44].

4.2 Plants as source of tocopherols

For tocopherols, the richest dietary sources are vegetable oils and the products made from these oils. Genetic factors and cultivars differences predominantly drive the expression of tocopherol compounds in seed oil exist. Vegetable oils contain not only α-tocopherol but also other tocopherols, especially γ and Δ tocopherol [46]. The soybean and corn oils are usually dominated by γ-tocopherol while in olive oil the more abundant form is α-tocopherol [47]. The tocopherol contents in seed oils range from 2 to 8 mg/100 g of coconut oil to 113 to 183 mg/100 g of corn oil [48]. The amounts of tocopherols in vegetable oils vary according to variety, extraction method, and refining [49].

4.3 Health benefits

Plant lipids containing high level unsaturated fatty acids are prone to oxidation, therefore lipophilic antioxidants such as tocopherols are often found to co-exist with plant lipids, protecting the integrity and vitality of the plant [50]. Tocopherols and tocotrienols are vitamin E homologs, serving as strong antioxidants and having many essential physiological functions such as anticoagulant, essential regulator of metabolic processes including inflammation and cancer in humans [51]. Vit E is also indispensable for immune defense. It has been suggested that tocopherols, acting as hormones or as secondary donors of genetic information, control the expression of some genes [48]. Vit E deficiency causes the damage of cellular membranes resulting from oxidation of the unsaturated fatty acids in lipids, and vitamin E deficiency can also display itself as muscular pain and progressing muscular disorder [48].

Meanwhile, the importance of tocotrienols in human health both as vitamin E and bioactive components has received renewed recognition in recent years. Tocotrienols have hypocholesterolemic, anti-cancer and neuroprotective properties.

5. Carotenoids

5.1 Structure

Carotenoids are natural pigments with yellow, orange, and red colors. More than 600 carotenoids have been identified in nature. Their physiological functions

in promoting health are as pro-vitamin A and as antioxidants quenching singlet oxygen radicals (**Figure 5**). Carotenoids generally have a 40-carbon skeleton of isoprene units cyclized at one or both ends [11]. The majority of carotenoids that occur in nature are in trans-form. Because of the long series of conjugated double bonds in the central part of its chemical structure, carotenoids exhibit light absorbing and unique singlet oxygen quenching capability [52]. Carotenoids can be classified as carotenes and xanthophylls, based on their chemical structure. α -carotene, β -carotene and lycopene are the predominant non-polar functional carotenoids and lutein is the primary polar functional carotenoids [53] (see **Figure 5**). Carotenes contain only a parent hydrocarbon chain without any functional group, while those bearing oxygen-containing functional group are called xanthophylls (e.g. astaxanthin, lutein, zeaxanthin). Carotenoids can even be classified as pro-vitamin A (e.g. α -carotene, β -carotene, and β -cryptoxanthin) and non-provitamin A compounds [53]. Actually, carotenoids present various substitutions: terminal ring systems joined by the chromophore-bearing chain of conjugated double bonds (e.g. β -carotene), hydroxyls at the terminal rings (e.g. zeaxanthin, lutein), ketone-groups with or without additional hydroxy groups (e.g. astaxanthin and canthaxanthin), aromatic rings (e.g. synechoxanthin), and the rare monocyclic carotenoids (e.g. torulene). There are over 700 carotenoids, from which 40 are ingested in human diet from fruits and vegetables.

5.2 Plants as source for carotenoids

Carotenoids distribution in plants is associated with the de novo synthesis that occurs in the differentiated plastids of roots, flowers, fruits, and seeds. Their accumulation can be subdivided as chloroplasts (green plastids), chromoplasts (yellow, orange, and red plastids), amyloplasts (plastids containing starch), elaioplasts (lipid containing plastids), leucoplasts (colorless plastids), and etioplasts (dark-matured precursors of the chloroplast) [53].

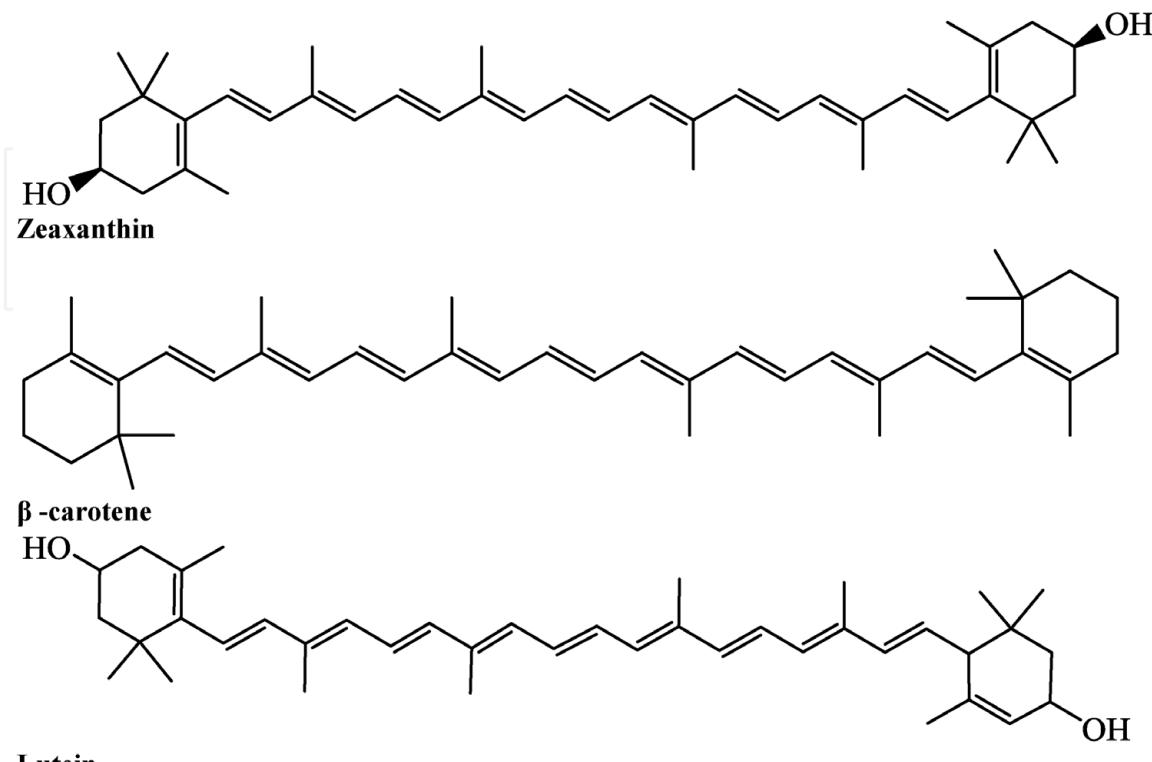


Figure 5.
Structure of the important naturally occurring carotenoids.

Because plants can synthesize carotenoids de novo, they are widely distributed in plant-derived foods and the composition is enriched by the presence of small amounts of biosynthetic precursors and derivatives of the major carotenoids. In general, the level of carotenoids is directly proportional to the intensity of color. Egg yolks, dairy products, fruits, vegetables, legumes, grains and seeds are their major food sources. In green leafy vegetables, β-carotene is predominant while in the orange-colored fruits and vegetables such as carrots, apricots, mangoes, yams, winter-squash, other carotenoids typically predominate. Yellow vegetables have higher concentrations of xanthophylls with a low provitamin A activity, but some of these compounds, such as lutein, may have significant health benefits. The red and purple vegetables and fruits such as tomatoes, red cabbage, berries, and plums contain a large portion of non-vitamin A active carotenoids. Tomato and watermelon are major sources of lycopene [53].

Higher plant usually contains similar carotenoids; however, their distribution differs quantitatively. It is known that the oil with the highest carotenoid content is crude palm oil (500-700 mg/100 g of oil). Carotenoid's content of the other crude vegetable oils is below 100 mg/100 g of oil [38].

5.3 Health benefits

Carotenoids, another group of lipid-soluble compounds synthesized by plants, are also strong antioxidants in addition to functions in plants' photosynthesis. Carotenoids are also essential to human health. More than 700 carotenoids have been identified in plant foods and human body, but the overwhelming majority (90%) in human diet is represented by β-carotene, α-carotene, lycopene, lutein, cryptoxanthin and zeaxanthin [51].

Carotenoids are characterized by a high reactivity due to their system of conjugated double bonds. They can readily suffer chemical transformation being oxidized by reactive species to a number of compounds. After ingestion, carotenoids suffer a series of modifications in the organism, namely through the reaction with reactive oxygen and nitrogen species (ROS and RNS, respectively). Interestingly, the way carotenoids react with ROS and RNS seems to depend on different factors, namely concentration of carotenoids, oxygen pressure, presence of other antioxidants, etc. Moreover, these factors may imply variations of the redox properties of carotenoids and of the oxidation products formed. These compounds, designed as oxidation products, are not yet fully studied and/or identified in biological tissues, but there are some studies relating them with the growth of several cancer cells and to oxidative effects. The increase of knowledge in this field seems to be truly important to establish the real impact of carotenoids and their oxidation products in human health [53]. Studies have shown that antioxidant carotenoids have protective effects against skin disorders, eye disorders, cancer, and cardiovascular diseases [54].

Carotenoids in oils play important role in the stability of the oil as a singlet oxygen quencher in addition to their coloring properties [55]. Carotenoids, together with PA and tocopherols, are involved in the oxidative stability of oils and have synergist antioxidant effects [56].

6. Conclusion

Oilseeds, like other plant sources, provide an important reservoir of myriad of phytochemicals. However, little has been researched about the relationship between ripening index of the seed bearing and oil fatty acids, bioactive compounds, and

antioxidant activity. This should be considered to have a clearer understanding of the preharvest effect on seed oil nutritional qualities and antioxidant properties. For instance, the drying time of seeds would have a considerable effect on extracted oil quality. In view of the thermolabile nature of bioactive compounds such as tocopherols and polyphenols, the effect of seed drying and pretreatments for seed drying on oil antioxidant compounds and capacity deserves more research. This would assist in quantifying losses of bioactive compounds losses and instituting preventive measures at this stage of seed oil processing.

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