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REVIEW

Characteristics of Specialty Natural Micronutrients in Certain Oilseeds and Oils: Plastochromanol-8, Resveratrol, 5-Hydroxytryptamine Phenylpropanoid Amides, Lanosterol, Ergosterol and Cyclolinopeptides

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Abstract The current concern for health has raised the importance of natural micronutrients in edible oils and fats. Different from common micronutrients, e.g., tocopherols, tocotrienols, stigmasterol and sitosterol, new and emerging specialty micronutrients, such as plastochromanol-8, resveratrol, phenylpropanoid amides of 5-hydroxytryptamine, lanosterol, ergosterol and cyclolinopeptides, are becoming increasingly popular among health-conscious people. The first three are phenolic compounds, the forth and fifth sterols, and sixth a peptide. These micronutrients are usually present in certain oils or oilseed-related byproducts, including rapeseed, peanut, flaxseed, tea seed, and camellia oils, and safflower seed cakes, all of which are the highly valuable products of the lipid industry in China nowadays. The first object of this review is to discuss the characteristics of the micronutrients, mainly including their varieties, structures, and sources. Second, the antioxidant activities and indicative functions for oil quality were also analyzed in detail. Third, refining techniques, breeding programs and extraction methods are suggested. Suitable modification treatments of certain micronutrients are also advocated to make them easy to incorporate in other foods.

Keywords Natural micronutrients · Oils · Fats · Plastochromanol-8 · Resveratrol · Phenylpropanoid amides of 5-hydroxytryptamine · Lanosterol · Ergosterol · Cyclolinopeptides

Introduction

In the present time natural micronutrients, usually extracted from oilseeds, oils and fats and their processing byproducts, are industrially important compounds because of their nutritional and pharmaceutical value. They generally belong to the group of nonglycerolipids that differ from triacylglycerols (TAG, the predominant form in lipids, 95–98 %) and glycerolipids (e.g., diacylglycerols, monoacylglycerols and phospholipids) [1]. Their levels in lipid-based food products enhance lipid quality. Tocopherols and sterols are perhaps the most common micronutrients encountered in lipids, and are usually considered as nutritional supplements for humans, antioxidants for lipids or markers for adulteration detection [1, 2]. In contrast, less attention is paid to some specialty natural micronutrients, such as plastochromanol-8 (PC-8), resveratrol, phenylpropanoid amides of 5-hydroxytryptamine (PAHA), lanosterol, ergosterol and cyclolinopeptides (CL), the first three of which are phenolic compounds, the forth and fifth sterols, and the sixth a peptides. Such micronutrients are usually only present in certain oils (or oil cakes) and fats; for example, PC-8 is detected at elevated amounts in rapeseed and flaxseed oils [3], while resveratrol is detected in peanut

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oils [4], PAHA in safflower cakes [5], lanosterol in tea seed oils [6], and CL in flaxseed oils [7]. These compounds are becoming increasingly popular due to recent studies on human nutrition and health that disclosed the interrelation between natural micronutrients in dietary and the civilization diseases. One of the most famous is the "French paradox". It has been found out and statistically confirmed that, in certain parts of France, the death rate caused by coronary artery diseases is lower despite relatively high fat consumption in the human diet [8, 9]. The consumption of wine is considered as one of the dietary factors that might partially explain this phenomenon because wine contains special micronutrients including resveratrol [10].

During the 1990s and 2000s, numerous studies were carried out to determine the food, health, and nutrition-related functionalities of various micronutrients. Oils that contain high levels of above mentioned micronutrients (e.g., from rapeseed, peanut, flaxseed, tea seed, camellia, and safflower cakes) are also gaining in popularity. It is also worthy of mention that these oils are currently of major interest to the lipid industry in China, which is characterized by an abundant edible oil and fat consumption, reaching 31.7 million tons in 2014 [11].

In addition to the nutritional values for humans, the rare micronutrients possess other positive and indicative functions of potential importance. In this review, their varieties, structures, contents and functions in oilseeds, oils and fats, as well as their applications in other foods will be discussed in order to support the development of fat and oil-based food products with enhanced nutritional value.

Plastochromanol-8

Structure of PC-8

Together with tocopherols and tocotrienols, PC-8 belongs to the group of tocochromanols that contain a chromanol ring that is responsible for their spectral and antioxidant properties [12]. PC-8 is considered to be a third type of tocochromanol (in addition to tocopherols and tocotrienols) [13]. The similarity in structure between PC-8 and γ-tocotrienol suggests that PC-8 is soluble in fats (Fig. 1) [14]. Only photosynthetic organisms such as plant, algae and some cyanobacteria are found to have the ability to synthesize such tocochromanols in nature [15].

PC-8 Content in Oilseeds and Oils

PC-8 has been found to be present in large amounts in the plant families Brassicaceae and Linaceae [3, 16], as well as in minor amounts in seed oils of Fabaceae, Poaceae, Asteraceae, Burseraceae, Capparaceae, and others [3, 16–19].

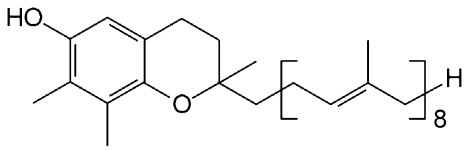

Fig. 1 Molecular structure of plastochromanol-8

Table 1 The levels of plastochromanol-8 and total tocochromanols in common oilseeds and oils

Oilseeds and oils	Content (mg/kg)	
	Plastochromanol-8	Total tocochromanols
Oilseeds		
Rapeseeds [20]	97–128	567–678
Mustard seeds [22]	1.2–1.9	81.7–239.6
Linum seeds [26]	5–72	75–228
Hemp seeds [29]	0–5.3	143.3–340.3
Oils		
Rapeseed oils [3]	85.7–90.8	464.6–541.2
Rapeseed oils [25]	54–68	718–786
Canola oils [21]	28–74	436–681
Modified/transgenic canola oils [2]	16–83	473–1849
Turnip seed oils [16]	20	560
Cabbage seed oils [16]	19–56	483–627
Head cabbage seed oils [16]	64	446
Mustard seed oils [23]	41.30–125.38	425.05–688.57
Camelina seed oils [3]	43	522.3
Camelina oils [24]	9.0–25.2	723–897
Flaxseed oils [3]	170.1–301.5	411.0–726.4
Flaxseed oils [27]	191	747
Linseed oils [17]	257.3	830
Linseed oils [28]	223.0	696.5
Solin oils [21]	43–115	259–375
Soybean oils [17]	12.6	1800
Peanut oils [3]	19.5	248.7
Wheat germ oils [17]	84	5600
Rice bran oils [3]	1.1	278.3
Corn oils [3]	16.9	1128.6
Safflower seed oils [3]	1.2	456.8
Sunflower oils [3]	2.5	690.1
Milk thistle oils [3]	2.4	267.3
Olive oils [3]	4.6	58.2
Grape seed oils [3]	13.1	504.6
Palm oils [17]	14.6	730
Maize oils [17]	36.8	1600
Perilla oils [27]	10	734
Poppy seed oils [3]	1.1	180
Hemp seed oils [3]	1.6	370.7
Evening primrose oils [3]	1.5	355.5

Table 1 provides the PC-8 and total tocochromanol levels in common oilseeds and oils. Concretely speaking, more than eight kinds of oilseeds listed in Table 1 have been found to be associated with the members of Brassicaceae family: rapeseeds [3, 20, 21], turnip seeds [16], cabbage seeds [16], mustard seeds [22, 23] and camelina seeds [3, 24]. Among them, rapeseeds are the most common oilseeds of Brassicaceae. The levels of PC-8 in rapeseed and canola oils are usually 28.0–90.8 mg/kg, corresponding to 6–20 % of the total tocochromanols [3, 21, 25]. However, the proportion of PC-8 in some transgenic canola oils is lower because the amount of tocopherols, especially the α- and γ-tocopherols, increased in these oils via the genetic engineering technique [2]. In addition, other oils of Brassicaceae such as turnip seed oils, cabbage seed oils, mustard seed oils and camelina seed oils also contain 9.0–125.4 mg/kg of PC-8, accounting for 1–14 % of their own total tocochromanols level [3, 16, 23, 24]. Both the total PC-8 content and the PC-8 content of tocomanols are close to those of rapeseed and canola oils.

The other family that produces PC-8 is Linaceae, mainly linum and solin [21, 26]. The PC-8 levels in flaxseed (linseed) oil can be as high as 170.1–301.5 mg/kg, corresponding to 26–50 % of the total tocochromanols [3, 17, 27, 28]. Similarly, solin oils also contain high level of PC-8, reaching 43–115 mg/kg (17–40 % of the total tocochromanols) [21]. Linaceae seed oils possess the highest PC-8 content.

Other oilseeds and oils contain PC-8 at lower levels, 1.1–84.0 mg/kg (0–8 % of the total tocochromanols) (Table 1) [3, 17, 27, 29].

Positive Properties of PC-8 on Oilseeds and Oils

The Concentration and Antioxidant Activity of PC-8 of Oilseeds and Oils During Storage

PC-8 and other tocochromanols have been originally identified as essential nutrients in mammals based on their vitamin E activity [15]. These compounds also play a significant role in inhibition of auto-oxidative processes that occur in lipid rich products, especially the rapeseeds and their oils, due to their high solubility in lipids and natural antioxidant activity [14, 30]. Theoretically, the tocochromanols possess the ability to scavenge peroxyl radicals, singlet oxygen and peroxynitrite [1]. The antioxidant activity is mainly related to the chromanol ring and the unsaturated side chain; and, the antioxidation activity increases with the number of the methyl groups in the ring and the unsaturated bonds in the side chain [12, 31]. Therefore, an increase of unsaturated bonds in the side chain of PC-8 might enhance its antioxidant ability since PC-8, tocopherols and tocotrienols share the same chromanol ring [12]. The hypothesis is supported by several theoretical studies researches and storage experiments for rapeseeds. Gruszka *et al.* [31] revealed that the singlet oxygen scavenging activity of PC-8 was similar to that of γ-tocopherol and γ-tocotrienol in a polar solvent, while in a hydrophobic environment its activity was considerably higher than that of either tocopherols or tocotrienols. Similarly, the antioxidative activity of PC-8 was found to be similar to α-tocopherol [32, 33]. Furthermore, Gawrysiak-Witulska *et al.* [20] reported that the loss of PC-8 in rapeseeds ranged from 4 to 24 % depending on storage conditions (storage temperature 25–30 °C and moisture levels 10.2–15.5 %), and was almost two times larger than that of tocopherols. Goffman and Möllers [25] also demonstrated that the level of PC-8 in rapeseeds decreased from 85–90 to 50–70 mg/kg at 40 °C after 24 weeks storage; in contrast, the level of tocopherols only slightly decreased under the same conditions. These results suggest that the PC-8 plays an important role in the preventing lipid oxidation for oilseeds during storage.

However, the losses of PC-8 and other tocochromanols in lipids are quite different compared with that occurring in oilseeds. Goffman and Möllers [25] found the degradation of tocochromanols in rapeseed oils was detected after only 4 weeks of storage under 40 °C; after 16 weeks of storage, complete degradation occurred. The extent of degradation was greatest for α-tocopherol, followed by >γ-tocopherol, and then by >PC-8. It can be speculated rapeseeds that remain intact during storage possibly synthesize certain tocochromanols, such as α-tocotrienol and γ-tocopherol during storage, and thus maintain a constant level of tocochromanols [25]. A comparative study found that when PC-8 (300 mg/kg) was added to lard, the latter could withstand 31 days of storage at 60 °C without the occurrence of significant degradation; however, when the same level of α-tocopherol was added, the absence of major degradation occurred for only 21 days [28]. These results suggest that PC-8 is superior for protecting lipids from oxidation during long-term storage compared to other tocochromanols due to the greater amount of unsaturated bonds in PC-8.

Thermal Stability of PC-8 During Flaxseed Oils Usage

In major flax-growing regions in China, flaxseed oils have been used as cooking oil and are favored by the local people over rapeseed or mustard oils [34]. However, in general, flaxseed oils are seldom used for frying when heat is involved because heating causes huge losses of PC-8 and tocopherols (Table 2). But, the decomposition rate of PC-8 is slightly slower than that of tocopherols under comparable conditions [35]. The result is similar to that discussed above for PC-8 change in stored rapeseed oils and lard, i.e., the degradation of PC-8 is lower than that for tocopherol in rapeseed oils and lard. The higher thermal stability of PC-8

Table 2 Losses of plastochromanol-8 and tocopherols under 150 °C pan-heating [35]

Heating time (min)	Content (mg/kg)	
	Plastochromanol-8	Tocopherols
0	42–47	134–203
3	14–25	43–59
6	5–9	12–20

compared to tocopherols might be partially responsible for its slower loss rate in oils and fats; thus, PC-8 may provide enhanced protection from lipid oxidation during storage.

Resveratrol

Varieties and Structures of Resveratrol

Resveratrol (3,5,4′-trihydroxystilbene) and its glycosides, piceid and polydatin, are oil-soluble secondary plant metabolites that belong to the stilbene phytoalexins [4, 36–38]. Both resveratrol and piceid contain phenolic hydroxyls, similar to the PC-8, and exist in *cis* and *trans* isomeric forms (Fig. 2). The *trans*-isomers usually predominate in plants [36].

Resveratrol Content in Oilseeds and Oils

Resveratrol is a well-known component of wine, and has also been found in oilseeds and oils, especially peanuts and peanut oils (Table 3). Peanuts contain resveratrol and piceid (164–1188 μg/kg), with *trans*-resveratrol being the most prominent. A significant variation of total resveratrol and piceid is detected with a sevenfold difference among the accessions, attributable to variation in peanut species, geographical regions, moisture content, and storage conditions [4, 39]. Therefore, there is potential to enhance resveratrol and piceid levels in oilseeds via breeding programs and transgenic techniques [40, 41]. In addition, stilbenes are also found in other oilseeds, e.g., grapes, garlics and gingers [42, 43]. Of note, 98 % of the total stilbenes in garlic and ginger oils are resveratrol [42].

For peanut oils, the content of *trans*-resveratrol (3–245 μg/kg) and total resveratrol and piceid (114–526 μg/kg) is less than the corresponding levels in peanuts (Table 3). Oil extraction and refining processes might be responsible for this trend. Each step of the refining, such as degumming, deacidification, decoloration and deodorization, causes losses to the stilbenes (Table 4) [4]. In particular, both of resveratrol and piceid disappeared after deodorization, and neither of them was detected in full refined peanut oils. In this regard, the distillates are the ideal sources to recover both of the stilbene phytoalexins. However, for edible oils, the moderate refining technique is extremely important to be developed to remain these nutriments in refined oils. It is worth mentioning that the resveratrol level in peanut oils is similar to or slightly lower than that found in wine (118–1895 μg/kg), but is much higher than that found in other oils [44, 45].

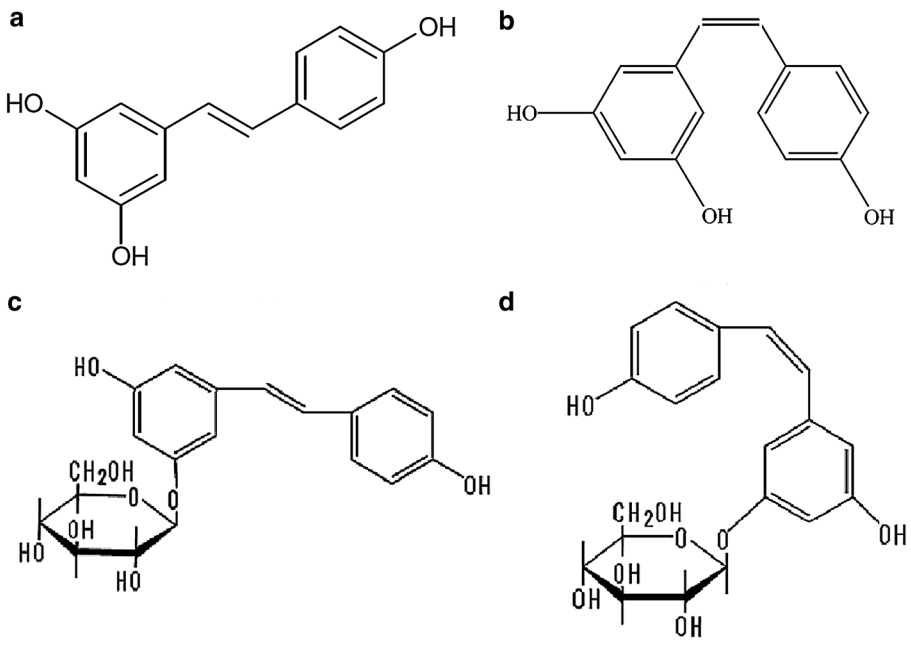

Fig. 2 Four conformational forms of resveratrol and piceid [4]. **a** *trans*-resveratrol, **b** *cis*-resveratrol, **c** *trans*-piceid, **d** *cis*-piceid

Table 3 Resveratrol and piceid content in peanuts and peanut oils

Peanuts and peanut oils	Content (μg/kg)				
	trans-Resveratrol	*cis*-Resveratrol	*trans*-Piceid	*cis*-Piceid	Total
The US peanut mini-core collections [40]	30–260	–	–	–	–
Peanuts [4]	33–685	115–985	ND-822	ND-754	164–1188
Peanuts [58]	22–1792	–	–	–	–
Peanut oils [39]	8–105	–	–	–	–
Peanut oils [44]	3–85	2–51	–	–	–
Peanut oils [4]	29–245	62–224	ND-221	ND-172	114–526

ND, not detected; –, not measured

Table 4 Content changes of resveratrol and piceid during peanut oil refining [4]

Oils in refining process	Content (μg/kg)				
	trans-Resveratrol	*cis*-Resveratrol	*trans*-Piceid	*cis*-Piceid	Total
Crude oils	90	329	ND	233	652
Degummed oils	86	204	ND	ND	290
Deacidified oils	20	49	23	ND	92
Decolored oils	ND	44	ND	ND	44
Deodorized oils	ND	ND	ND	ND	ND
Winterized oils	ND	ND	ND	ND	ND

ND, not detected

Antioxidant Property and Stability of Resveratrol in Oils

Antioxidant Activity of Resveratrol in Oils

Resveratrol in oils, oilseeds and other foods is of interest due to its potential beneficial effects on human health, including skin disorders control, amyloid neurodegenerative diseases prevention, sepsis-induced liver injury protection and cardiovascular protection [46–49]. The beneficial effects of resveratrol may be attributed to its high level of free radical scavenging activity. The hydroxyl group at the 4′-position seems to be relevant to the antioxidant efficiency of resveratrol [50]. Corduneanu *et al*. [51] found that the phenol group of resveratrol was first oxidized irreversibly; subsequently, the resorcinol moiety was irreversibly oxidized. However, Murcia and Martínez-Tomé [52] pointed out that resveratrol does not scavenge hydroxyl radicals or react with H_2O_2, making it an inefficient catalyst of subsequent oxidation. Even so, resveratrol is considered as an ideal antioxidant in oils because its ability of inhibit lipid peroxidation is stronger than that of propyl gallate, vanillin, phenol, butylated hydroxytoluene (BHT) and α-tocopherol and is equal to that of caffeic acid [52, 53]. The enhanced ability of resveratrol to inhibit lipid peroxidation is due to it possessing one additional phenolic ring than propyl gallate, phenol and BHT, and two more –OH groups than α-tocopherol [54].

Resveratrol exhibits different antioxidant capacity in different kinds of oils. *trans*-Resveratrol is a more effective antioxidant for lard TAG than for vegetable oil TAG (e.g., sunflower and rapeseed oils) because vegetable oils possess nearly optimal levels of tocopherols, in contrast to animal fats [36, 53]. On the other hand, the combined antioxidant effects of the micronutrients should not be ignored. Brewer [54] concluded that resveratrol, monophenols, and other micronutrients may act either synergistically or antagonistically depending on their concentrations and the reaction temperature. In agreement, Marinova *et al*. [55] found that the combination of resveratrol with quercetin and of resveratrol with caffeic acid have synergistic effects in preventing lipid oxidation of sunflower oils. However, the combination of α-tocopherol and resveratrol is antagonistic. Thus, the issue that how to keep the resveratrol with stronger antioxidant capability by combining suitable micronutrients requires further study.

Thermal and Photosensitive Stabilities of Resveratrol

Resveratrol acts as a defense agent to counteract stresses such heat and ultraviolet (UV) radiation [41, 56]. In particular, resveratrol and piceid have different thermal stabilities, and the stabilities of *trans*-resveratrol and *trans*-piceid are higher than that of their corresponding *cis*-isomers [4]. Moreover, during 10 days of storage at 60 °C, levels of *trans*-resveratrol and *trans*-piceid decreased by only 5 %, while

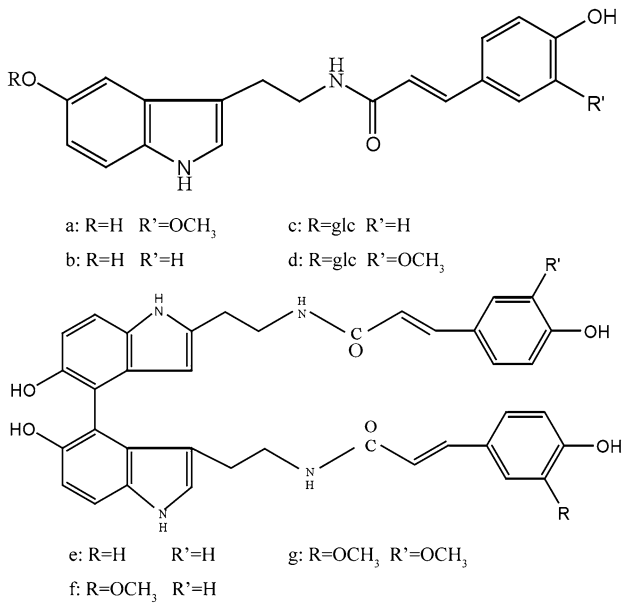

Fig. 3 Molecular structures of seven main compounds in phenylpropanoid amides of 5-hydroxytryptamine [5]. **a** *N*-feruloylserotonin (FS), **b** *N*-(*p*-Coumaroyl)serotonin (CS), **c** *N*-(*p*-coumaroyl)serotonin 5-*O*-β-D-glucopyranoside (CSG), **d** *N*-(feruloylserotonin) 5-*O*-β-D-glucopyranoside (FSG), **e** 4,4″-bis(*N*-*p*-coumaroyl)serotonin (CS–CS), **f** [4-*N*-(*p*-coumaroyl)serotonin-4″-yl]-*N*-feruloylserotonin (CS-FS), **g** 4,4″-bis(*N*-feruloyl)serotonin (FS–FS). *glc* glucose

the levels of *cis*-resveratrol and *cis*-polydatin decreased by 20–40 % under the same conditions [4]. At lower temperature, such as room temperature, the resveratrol level remained almost unchanged in a long-term study [57].

In addition, resveratrol, especially *trans*-resveratrol, remains stable for several months when stored in the dark. However, resveratrol is very sensitive to UV radiation [43, 58]. Sanders *et al*. [58] found that *trans*-resveratrol can be easily isomerized to its *cis*-form when exposed to 366 nm UV light. Zhang [4] reported that *cis–trans* isomerization of resveratrol and piceid occurred under 254 or 365 nm UV radiation. The amounts of resveratrol and piceid remained almost unchanged during exposure to 365 nm UV light, but decreased by 36 % during 254 nm irradiation [4]. However, the UV process is necessary for peanut oil refining to accelerate the photodegradation of the aflatoxin B_1 which is characterized by huge toxicity and carcinogenicity. Thus, in order to prevent the degradation of resveratrol and piceid (especially the *trans*-compounds) in oilseeds and oils from photodegradation and thermal decomposition to some extent, selecting suitable process conditions is particularly important, and the refined oils should be stored in the dark and at low-temperatures.

Although resveratrol has also been added to foods, its increased use is currently limited by its abovementioned instabilities as well as its poor aqueous solubility [38]. Numerous studies are therefore, committed to addressing these deficiencies. In particular, encapsulation of resveratrol by cyclodextrins or nanoemulsions may serve as an ideal method to resolve the problems [38, 56].

Phenylpropanoid Amides of 5-Hydroxytryptamine

Varieties and Structures of PAHA

Phenylpropanoid amides of 5-hydroxytryptamine (PAHA), synthesized biochemically from hydroxycinnamoyl-CoA thioesters and serotonin, are a class of polyphenol compounds with phenolic hydroxyls that belong to the family of *N*-hydroxycinnamic acid amides (HCAA) [5, 59, 60]. There are 7–10 PAHA types, all of which consist of a serotonin moiety bound to a phenylpropanoid substrate through an amide bond [59]. *N*-feruloylserotonin (FS), *N*-(*p*-Coumaroyl)serotonin (CS), *N*-(*p*-coumaroyl)serotonin 5-*O*-β-D-glucopyranoside (CSG), *N*-(feruloylserotonin) 5-*O*-β-D-glucopyranoside (FSG), 4,4″-bis(*N*-*p*-coumaroyl) serotonin (CS–CS), [4-*N*-(*p*-coumaroyl)serotonin-4″-yl]-*N*-feruloylserotonin (CS-FS) and 4,4″-bis(*N*-feruloyl)serotonin (FS–FS) (Fig. 3).

Particularly, CS and FS are the most well-known and possess the simplest structures among the PAHA types, and both of them contain both *cis*- and *trans*-isomers. The content of *trans*-isomers in plants is usually much higher than the content of *cis*-isomers [61].

PAHA Content in Safflower Seeds and Cakes

PAHA commonly exists in various plants; but, for oil crops, they occur in only a few species: safflower (*Carthamus tinctorius* L.) seeds, peppers and rice [62–64]. However, the levels of PAHA in the latter two are low; for example, hot pepper, green onion, wild type rice and transgenic rice contain only 0.35, 0.69, 2.50 and 48.00–424.00 mg of CS and FS per kg, respectively [63, 64]. In contrast, the amounts of CS, FS, CSG and FSG in safflower seeds are much higher (Table 5) [62, 65]. The PAHA content of safflower seeds is >4500 mg/kg, depending on the variety and harvest time. Jin *et al*. [66] reported that CSG and FSG accounted for >20 % of the total amount of PAHA in safflower seeds. Kim *et al*. [62] found that CS and FS accounted for ~60–80 % of the total PAHA content in the seeds. Moreover, CS and FS were the only PAHA detected in the hull of the seeds [67] (Table 5).

Most PAHA transfer into cakes when safflower seeds are subjected to solvent extraction of oil [5]. The cakes

Table 5 Contents of CS, FS, CSG and FSG in harvestable safflower seeds

References	Content (mg/kg)			
	CS	FS	CSG	FSG
[62][a]	1528–1920	2341–2604	841–959	493–582
[65][a]	2338	1739	–	501
Whole seeds [67]	4110	7290	–	–
Hull [67]	4450	8340	–	–
Kernel [67]	0	0	–	–

CS, *N*-(*p*-Coumaroyl)serotonin; FS, *N*-feruloylserotonin; CSG, *N*-(*p*-coumaroyl)serotonin 5-*O*-β-D-glucopyranoside; FSG, *N*-(feruloylserotonin) 5-*O*-β-D-glucopyranoside; –, not measured

[a] Safflower seeds were directly harvested in early August

are becoming an increasingly important source of value-added biobased products in the lipid industry, for oil cakes are usually used as animal feed, a low-value product [68]. There is increasing research focused on isolation, extraction and purification of PAHA from safflower seed cakes [5, 68, 69]. CS–CS, CS–FS and FS–FS, which typically account for a lesser proportion of PAHA, were found in cakes, reaching 41, 63 and 13 mg/kg, respectively [68].

Antioxidative Capacity of PAHA in Oils

PAHA has been implicated to an array of biological activities including antioxidative, antifungal, antiviral, cardiovascular risk reduction, and antiinflammatory (inhibition of cytokines) [60, 70–73]. Takii *et al*. [72, 74] found that CS present in safflower oils possessed antioxidative activity. The authors of the cited study suggested that the hydroxyl group in serotonin was essential for this activity. In addition, the antioxidative activities of CS, FS, CS–CS, CS–FS and FS–FS were found to be at least comparable to those of α-tocopherol, butylated hydroxyanisole (BHA) and BHT [68, 75–77]. However, the biological activities of CSG and FSG were lower than those of CS and FS [77]. In summary, PAHA is a potentially valuable natural antioxidant additive for edible oils, fats and other foods, to delay the onset of rancidity.

Lanosterol and Ergosterol

Structures of Lanosterol and Ergosterol

Lanosterol (5α-lanosta-8,24-dien-3β-ol) and ergosterol (ergosta-5,7,22-trien-3β-ol) are triterpene compounds belonging to the sterol family, which make up the greatest proportion of the unsaponifiable fractions of vegetable oils [1]. Their structures are based on a steroidal alcohol framework comparable with that of cholesterol (Fig. 4). Lanosterol is a 4,4-dimethyl sterol with two double bonds and ergosterol is a desmethyl sterol with three double bonds.

Lanosterol and Ergosterol Content in Oilseeds, Oils and Fats

Lanosterol and Ergosterol Content in Oils and Fats

Sterols such as β-sitosterol, stigmasterol and campesterol generally occur in various oils; however, lanosterol only exist in certain oils and fats, e.g., tea seed, camellia seed, manketti nut, and black cumin seed oils and milk fats [6, 78–82] (Table 6). In particular, the first two oils listed above are potential targets for nutritional oils exploitation in China. Tea and camellia seed oils contain large amounts of lanosterol: 1026–2920 mg/kg (32–74 % of the total sterols) and 731–1572 mg/kg (31–55 % of total sterols), respectively [6, 78, 82]. Both plant species belong to the same family: Theaceae; suggesting other members of this family may serve as valuable sources of lanosterol. The lanosterol concentration in manketti nut oils, black cumin seed oils and milk fats, are less than 350 mg/kg, accounting for less than 3.5 % of their respective total sterols [79–81].

Because ergosterol does not naturally occur in most oils and fats but serves as the principal sterol of fungi. The ergosterol level in oils and fats usually reflects the degree of deterioration by fungi in oil crops (discussed in detail below). Pronyk *et al*. [83] reported that initial ergosterol content in canola oil was only 1.46–1.67 mg/kg. A limited number of articles describe the presence of ergosta-7,22-dien-3-ol, a compound related to ergosterol which contains only two double bonds, in corns, cottonseeds, peanuts, linseed oils and tea seed oils [78, 84, 85].

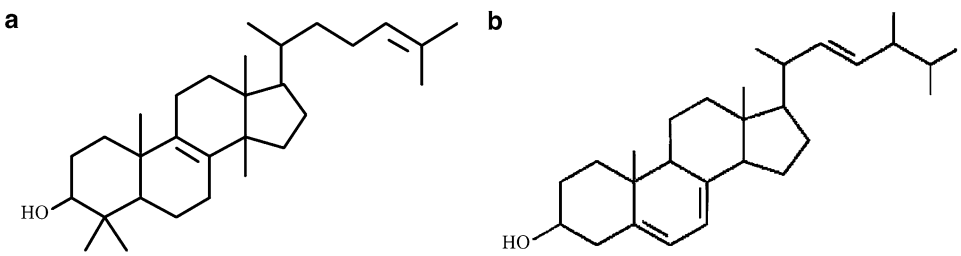

Fig. 4 Molecular structures of lanosterol (**a**) and ergosterol (**b**)

Table 6 Lanosterol and the total sterol content of selected oils

Oils and fats	Content (mg/kg)	
	Lanosterol	Total sterols
Tea seed oils [6]	2476–2920	3573–4252
Tea seed oils [78]	1026–1530	2812–3817
Camellia seed oils [82]	731–1572	1868–3382
Manketti nut oils [79]	60–343	33,534–95,485
Black cumin seed oils [80]	106–114	3326–3662
Milk fat globule membranes [81]	tr-200	80,000–159,000

tr, <50 mg/kg

Table 7 Lanosterol and the total sterol content of selected oils from solvent, supercritical fluid, hot press and cold press extraction

Oils	Sterol content (mg/kg) of different extraction methods			
	Solvent[a]	Supercritical fluid	Hot press	Cold press
Tea seed oils [6]				
Lanosterol	–	2854–2920	2476	2678
Total sterols	–	4169–4251	3573	3596
Camellia seed oils [82]				
Lanosterol	882	–	896–911	853
Total sterols	2794	–	2670–3019	2621
Manketti nut oils [79]				
Lanosterol	–	151	343	–
Total sterols	–	95,485	38,144	–
Sea buckthorn seed oils [86]				
Lanosterol[b]	6730	7874	–	4622
Total sterols	13,265	16404	–	8794

–, not measured or listed

[a] Hexane

[b] This value is the sum of lanosterol and sitosterol

Table 8 Content changes of lanosterol and the total sterols during the refining of camellia seed oils [82]

Sterols (mg/kg)	Camellia seed oils for different refining processes			
	Crude oils	Degumming and alkali oils	Bleaching oils	Deodorization oils
Lanosterol	1210	1103	918	828
Total sterols	2874	2558	2280	1916

Lanosterol Content Changes During Oil Extraction

Table 7 demonstrates that the lanosterol and total sterol contents differ largely depending on the extraction methods. The effects of hot press and cold press on the amounts of lanosterol and total sterol were similar; however the sterol levels extracted from the press were lower than that extracted from the solvent and supercritical fluid extraction [6, 79, 86]. Supercritical fluid extraction is usually considered as the most effective method for extracting the sterols from the oilseeds. For industrial production, the cakes obtained from the oil extraction may be re-treated with supercritical fluid or solvent to fully recover the sterols.

Lanosterol Content Changes of Camellia Seed Oils During the Refining Process

Sterol levels change during degumming, alkali refining, bleaching and deodorization (Table 8). Significant decreases in lanosterol (from 1210 to 828 mg/kg) and total sterols (from 2874 to 1916 mg/kg) during the refining processes were also reported [82]. In particular, the adsorption of sterols during bleaching and the removal of sterols during the vacuum distillation step of deodorization are considered as the main sources for the losses. Similar trends for the loss of sterols in tea seed oils were also reported in a previous refining study [78]. There is no doubt that such losses are undesirable, and the moderate refining techniques (especially the decoloration and deodorization) of camellia seed and tea seed oils therefore received increasing concerns in current factories. The distillates resulting from the deodorization are idea industrial materials to isolate and enrich lanosterol and other sterols.

Positive Effects of Lanosterol and Ergosterol on Oilseeds and Oils

Lanosterol and ergosterol differ from other common sterols in that their contents are associated with membrane related function, cell viability for fungi such as yeast, and for ergosterol, an important vitamin D_2 precursor [87–89]. In particular, both sterols in oils and oilseeds are closely related to the oxidation resistance mechanisms, and for ergosterol fungal spoilage defense mechanisms.

Oxidation Resistance of Lanosterol and Ergosterol

Lanosterol exhibited a better antioxidant activity than other sterols (e.g., stigmasterol, β-sitosterol and amyrin) during oil extraction of camellia seed, especially via hot pressing at 100–130 °C [82]. Similarly, in a high temperature study of deep-fat frying, ergosterol showed higher anti-polymerization activity than stigmasterol, fucosterol and brassicasterol when added to soybean oil at 0.5 % [90]. Winkler and Warner [90] concluded that the anti-polymerization

Table 9 Main cyclolinopeptides in flax [96–98]

Code	Old name	New name	Amino acid sequence[a]
CL**1**	CLA	[1-9-N*a*C]-CLA	Ile-Leu-Val-Pro-Pro-Phe-Phe-Leu-Ile
CL**2**	CLB	[1-9-N*a*C]-CLB	Met-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile
CL**3**	CLC	[1-9-N*a*C],[1-MetO]-CLB	MetO-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile
CL**4**	CLK	[1-9-N*a*C],[1-MetO2]-CLB	$MetO_2$-Leu-Ile-Pro-Pro-Phe-Phe-Val-Ile
CL**5**	CLD', CLK, CLO	[1-8-N*a*C]-CLD	Met-Leu-Leu-Pro-Phe-Phe-Trp-Ile
CL**6**	CLD	[1-8-N*a*C],[1-MetO]-CLD	MetO-Leu-Leu-Pro-Phe-Phe-Trp-Ile
CL**7**	CLE', CLJ, CLP	[1-8-N*a*C]-CLE	Met-Leu-Val-Phe-Pro-Leu-Phe-Ile
CL**8**	CLE	[1-8-N*a*C],[1-MetO]-CLE	MetO-Leu-Val-Phe-Pro-Leu-Phe-Ile
CL**9**	CLJ	[1e8-N*a*C],[1-MetO2]-CLE	$MetO_2$-Leu-Val-Phe-Pro-Leu-Phe-Ile
CL**10**	CLF, CLL	[1-8-N*a*C]-CLF	Met-Leu-Met-Pro-Phe-Phe-Trp-Val
CL**11**	CLI	[1-8-N*a*C],[3-MetO]-CLF	Met-Leu-MetO-Pro-Phe-Phe-Trp-Val
CL**12**	CLT	[1-8-N*a*C],[1-MetO]-CLF	MetO-Leu-Met-Pro-Phe-Phe-Trp-Val
CL**13**	CLF	[1-8-N*a*C],[1,3-MetO]-CLF	MetO-Leu-MetO-Pro-Phe-Phe-Trp-Val
CL**14**	CLG, CLM	[1-8-N*a*C]-CLG	Met-Leu-Met-Pro-Phe-Phe-Trp-Ile
CL**15**	CLH	[1-8-N*a*C],[1-MetO]-CLG	MetO-Leu-Met-Pro-Phe-Phe-Trp-Ile
CL**16**	CLN	[1-8-N*a*C],[3-MetO]-CLG	Met-Leu-MetO-Pro-Phe-Phe-Trp-Ile
CL**17**	CLG	[1-8-N*a*C],[1,3-MetO]-CLG	MetO-Leu-MetO-Pro-Phe-Phe-Trp-Ile
CL**18**	GLQ	[1-9-N*a*C]-CLQ	Met-Leu-Lys-Pro-Phe-Phe-Phe-Trp-Ile
CL**19**	GLR	[1-9-N*a*C],[1-MetO]-CLQ	MetO-Leu-Lys-Pro-Phe-Phe-Phe-Trp-Ile
CL**20**	GLS	[1-9-N*a*C]-CLR	Gly-Ile-Pro-Pro-Phe-Trp-Leu-Thr-Leu

[a] Abbreviations are Met for methionine, MetO for methionine S-oxide and $MetO_2$ for methionine S,S-dioxide

activity appeared to be more dependent on the number and location of double bonds in the ring structure rather than on the presence of an ethylidene group in the sterol side chain. In terms of structures of sterols including ergosterol, stigmasterol, fucosterol and brassicasterol, ergosterol contains two double bonds in the ring while other three only have one. However, the practical use of the sterols in other foods has been greatly limited by their poor solubilities [1, 91]. Esterification of ergosterol is, therefore, performed to make it fat-soluble and easy to incorporate into food products [91, 92].

Ergosterol Content Related with Identification of Fungal Spoilage in Oilseeds and Oils

Ergosterol is found almost solely in fungi and is often used as a biomarker of deterioration in oil seeds caused by fungal growth [83, 88]. As'wad *et al*. [93] demonstrated that the amount of spoilage can be determined through monitoring the ergosterol content and early detection would permit culling of infected oil palm before the disease could spread. Pronyk *et al*. [83] found that the ergosterol content in canola was >2 mg/kg, attributable to a significant level of spoilage. Furthermore, Ruibal-Mendieta *et al*. [94] concluded that ergosterol from the total sterol content in Spelt and Winter Wheat was not a cereal sterol. Therefore, it is more likely that ergosterol will serve as an exogenous antioxidant and nutrient in oils and fats rather than be present as an inherent component.

Cyclolinopeptides

Varieties and Structures of CL

Cyclolinopeptides (CL) are a group of naturally occurring hydrophobic cyclic peptides found in flax (*Linum usitatissimum* L.) that contain proteinogenic amino acids and their oxidized products [95, 96]. Currently, approximately 20 kinds of CL were identified from flax [96]. These peptides were formerly named to reflect the order of their discovery (Table 9). However, the old naming system is confusing and therefore not recommended by the International Union of Pure and Applied Chemists (IUPAC). Hence, a new nomenclature system based on structures of CL was established (Table 9) [96–98].

CL usually consist of eight or nine amino acid residues with molecular weight 960–1100 Da (Fig. 5) [97, 99]. The nonoxidized CL are divided into three groups based on their number of methionine residues: 0 (e.g., CL**1** and CL**20**), 1 (e.g., CL**2**, CL**5**, CL**7** and CL**18**), or 2 (e.g., CL**10** and CL**14**). CL with one methionine, upon oxidation (undergoing the reaction pathway

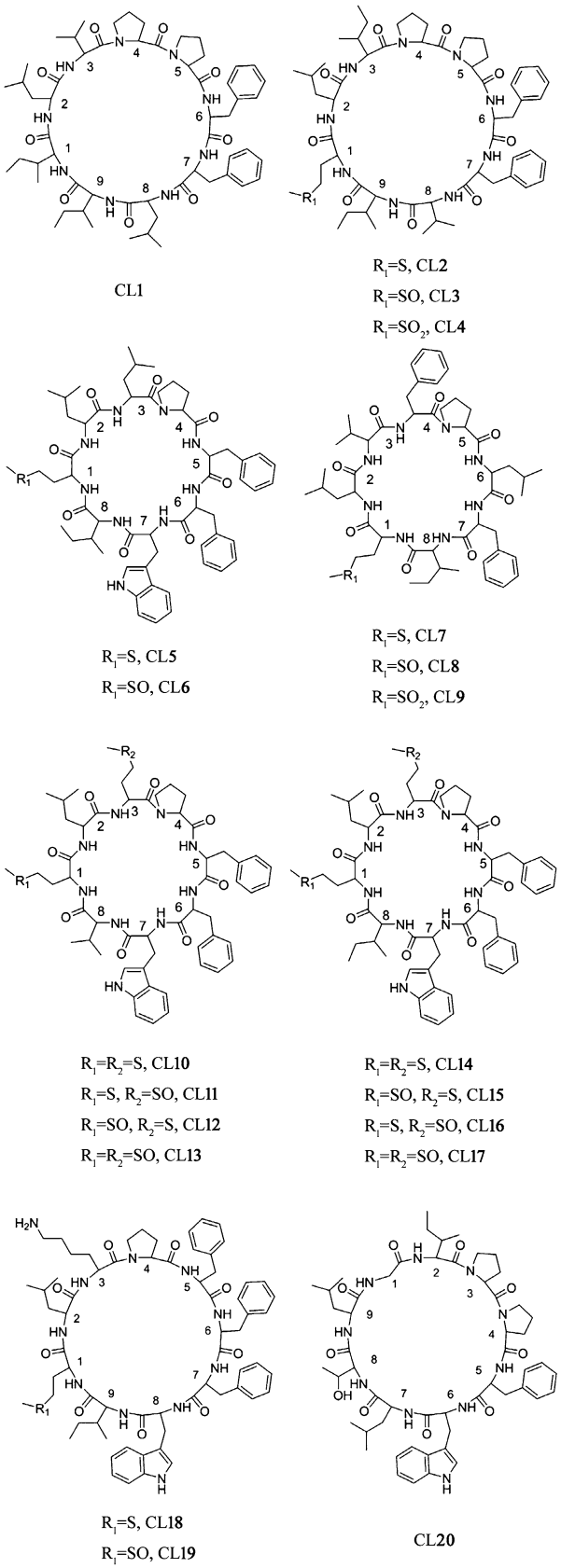

Fig. 5 Molecular structures of cyclolinopeptides in flax [98]

methionine → methionine S-oxide → methionine S,S-dioxide), yield one or two products: CL**2** → CL**3** + CL**4**, CL**5** → CL**6**, CL**7** → CL**8** + CL**9**, and CL**18** → CL**19**. CL with two methionines can be converted into two positional isomers each with one or two methionine S-oxide groups (CL**11**, CL**12**, CL**15** and CL**16**; and CL**13** and CL**17**, respectively) (Fig. 6). Traditionally, CL**1** is usually considered the most stable CL due to its lack of methionine residues in its primary structure; moreover, other CL that containing methionines may produce more oxidized forms depending on the extent of oxidation [99, 100].

CL Content in Oilseeds and Oils

Flaxseeds and flaxseed oils are excellent commercial sources of CL, because these peptides dissolve in oils after seed processing. Therefore, CL levels in flaxseed oils are generally higher (656.1–1972.5 mg/kg) than that in flaxseeds (188.6–302.8 mg/kg) (Table 10). Of interest is that the distribution of CL in flaxseeds is significantly different from flaxseed oil. As shown in Table 10, the cotyledon has the highest concentration of CL, whereas coat has lower levels [7]. It is found that CL**2** is absent in flaxseeds but occurs in oils, suggesting that CL**2** is oxidized to a lesser extent during oil extraction and therefore is present in CL at a higher percentage after oil extraction [7, 95]. Furthermore, CL in crude flaxseed oils are present at much higher concentrations than that observed in commercially available flaxseed oils after immediate pressing, i.e., 1894.6–1972.5 *vs* 656.1–1260.9 mg/kg [7]. The lower levels in some commercially available oils might be caused by the refining processes, especially chemical refining.

Gui *et al.* [7] found that acid degumming more readily caused the loss of CL. As shown in Table 11, CL**2**, CL**3**, CL**6**, CL**13** and CL**17** were not detected in acid degummed oils, and the total CL levels decreased from 1894.6 (crude oils) to 193.5 mg/kg. The decrease might be caused by hydrolysis of CL under the strong acidic conditions that accompany degumming and losses during filtration [7]. Comparatively speaking, alkali deacidification is a more moderate degumming treatment that retained more peptides (Table 11). The presence of free fatty acids might be responsible for the improved results. Free fatty acids are amphiphilic compounds and may stabilize CL in oils through formation of a complex or aggregate, which also may increase their oil solubility, and the CL could be released from the complexes during alkali effect [7]. There could be other underlying causes involved, such as the adsorption of CL onto colloids and soapstocks.

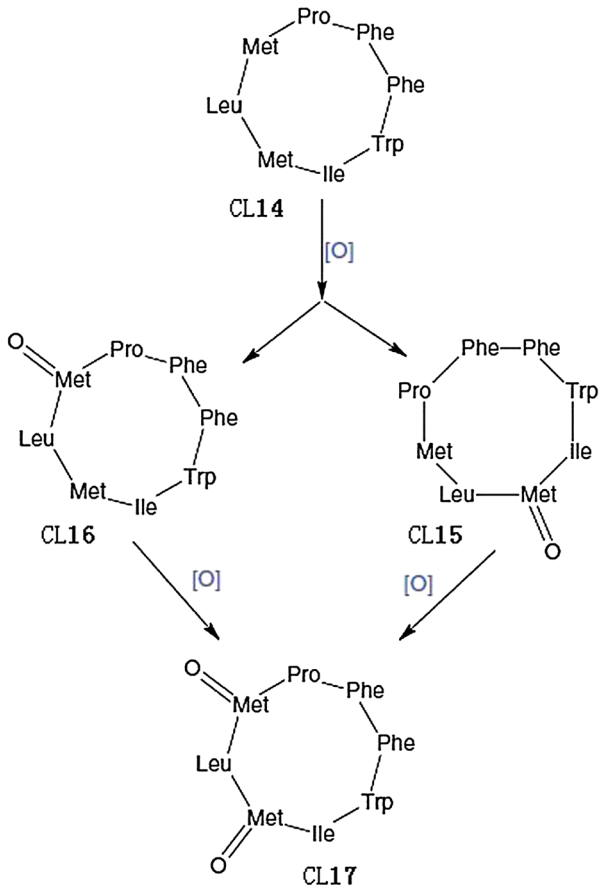

Fig. 6 Sequential oxidation of cyclolinopeptide **14** containing two methionine residues [100]

Positive Influences of CL on Flaxseed Oils

Organoleptic Effects of CL on Stored Flaxseed Oils

The primary organoleptic effect of CL on edible oils is a bitter taste. CL in fresh flaxseed oils are oxidized during storage, leading to deterioration of organoleptic properties of the oils, hence to the bitter flavor. It is widely known that flaxseed oils stored for a few days would develop a bitter off-taste while freshly pressed oils show a delicate nutty flavor. This off-taste might be related to the oxidation of methionine to methionine S-oxide or methionine S,S-dioxide in CL. The oxidation reaction could be a good indicator of deterioration of oils during storage since the reaction occurs slowly over a period of time [101, 102]. As shown in Table 12, a significant decrease in the amounts of CL that contain methionine, namely CL**2**, CL**5**, CL**7**, CL**10** and CL**14**, and a commensurate increase in the amounts of methionine S-oxide containing CL, such as CL**3**, CL**6**, CL**8**, CL**13** and CL**17** were observed [100]. In particular, Brühl *et al*. [103] noted that the degree of the bitterness correlated mostly with the concentration of CL**8**, which was formed via oxidation of CL**7**. However, the CL**8** level was found to decrease after 100 days, from 485 to 415 mg/kg, due to the further oxidation of CL**8**, perhaps forming CL**9** [103]. In addition, Brühl *et al*. [102] found that the threshold concentration of CL**8**, the CL strongly associated with bitterness, was 12.3 μmol/L in water.

CL were also associated with the viscosity of the oils during the lipid products usage. Treatments that removed the CL from flaxseed oils accelerated the rate of viscosity increase when the oil was heated [7].

Antioxidant Capacity of CL in Flaxseed Oils

CL, especially CL**1**, are known for their wide range of pharmacological activities, such as immunosuppressivity, antimalarial activity and inhibition of cholate uptake into hepatocytes [7, 104, 105]. In addition, CL have also been associated with the longer shelf life of lipid products. The addition of a polar fraction containing a mixture of

Table 10 Comparison of cyclolinopeptide levels in flaxseeds, crude flaxseed oils and retail oils

Flaxseeds and oils	Concentrate of cyclolinopeptides (mg/kg)							
	CL**1**	CL**2**	CL**3**	CL**6**	CL**8**	CL**13**	CL**17**	Total
Flaxseed fractions [7]								
Mucilage	ND	ND	ND	ND	ND	ND	ND	ND
Cotyledon	25.2	ND	98.8	13.1	80.2	19.6	55.0	291.9
Coat	19.3	ND	31.0	15.6	30.7	6.7	19.8	123.1
Whole seed	63.1	ND	78.7	9.9	70.2	13.1	33.3	268.3
Flaxseeds [95]	44.0–65.9	ND	53.5–79.7	12.4–42.5	46.4–71.3	8.3–16.6	24.0–51.0	188.6–302.8
Fresh crude oils [7]	454.0–466.7	90.5–98.0	358.3–368.6	214.1–277.5	445.5–462.7	82.4–86.3	249.7–262.7	1894.6–1972.5
Retail oils [7]	169.1–310.5	ND-122.0	112.4–286.0	21.0–179.7	173.7–293.6	14.6–35.0	16.4–101.2	656.1–1260.9

ND, not detected

Table 11 Degumming and alkali deacidification effects on cyclolinopeptides in flaxseed oils [7]

Oils for different refining processes[a]	Concentrate of cyclolinopeptides (mg/kg)							
	CL**1**	CL**2**	CL**3**	CL**6**	CL**8**	CL**13**	CL**17**	Total
Crude flaxseeds oils	454.0	90.5	358.3	214.1	445.5	82.4	249.7	1894.6
Acid degumming oils	ND-193.5	ND	ND	ND	ND-24.7	ND	ND	ND-193.5
Alkali deacidification oils	135.8–277.2	ND	33.6–253.6	ND	47.4–231.8	ND	ND-21.8	271.5–746.4

ND, not detected

[a] Acid degumming and alkali deacidification were conducted with the material of crude flaxseeds oil respectively

Table 12 Content changes of cyclolinopeptides in flaxseed oils during the storage

Reference	Concentrate of cyclolinopeptides (mg/kg)									
	CL**2**	CL**3**	CL**5**	CL**6**	CL**7**	CL**8**	CL**10**	CL**13**	CL**14**	CL**17**
[100][a]										
Start	390	70	95	35	310	110	40	2	110	10
30 days	90	300	60	48	55	315	10	11	30	19
[103][b]										
Start	–	–	–	–	–	0–53	–	–	–	–
100–150 days	–	–	–	–	–	485–925	–	–	–	–
150 days	–	–	–	–	–	415–925	–	–	–	–

[a] Samples were stored in darkness at 65 ± 1 °C for up to 30 days

[b] Samples were stored at room temperature for 150 days

CL, such as CL**1**, CL**6**, CL**8**, CL**13** and CL**17** successfully improved the oxidative stability of peptide-free oils [106].

Due to the remarkable biological and antioxidant activities of CL and the difficulty of their synthesis *de novo*, isolation of these compounds from flaxseeds or flaxseed oils is desirable to allow their use as food preservatives [7, 95].

Conclusions

Specialty natural micronutrients, i.e., three phenolics (PC-8, resveratrol, and PAHA), two sterols (lanosterol and ergosterol) and a cyclic peptide, have been found in certain oilseeds and oils that are highly valuable in China, because they are of considerable practical importance and of particular theoretical interest. Besides the utility of their biological activities for humans, the specialty lipids are valuable for basic research studies of lipid oxidation. Numerous studies have proven that the activities of PC-8, resveratrol, lanosterol, ergosterol and PAHA were at least comparable to that of common antioxidants, such as α-tocopherol, stigmasterol or BHT. The hydroxyl groups (especially the phenolic hydroxyls) and double bonds in their structures are likely responsible for the excellent antioxidant-related abilities. In particular, oils and fats containing PC-8, lanosterol and ergosterol are more suitable for use during heating because of their higher thermal stabilities or anti-polymerization activities under high temperature. Important issues that deserve further attention are the antioxidative mechanism and the combined antioxidant effects of these micronutrients in different food systems. CL and ergosterol can be used as biomarkers to convey the deterioration information of oils and fats to consumers. The former is able to reflect the presence of a bitter off-taste in stored lipids, and the latter reflects the presence of fungal contamination.

The important roles and behaviors of these natural micronutrients are gaining increased attention, and further investigations are needed to enhance their concentration and stability in lipids and other foods: Related, refining techniques during lipid processing should be moderated to retain more micronutrients in refined oils and fats by using more green approaches such as supercritical fluid extraction. Moreover, the concentration of resveratrol, CL and lanosterol, often become decreased or even approach zero during the refining steps, especially via adsorption onto clays (or soapstocks) and vacuum distillation. Breeding and transgenic programs are another technique to improve the micronutrient levels in oils and fats; however, corresponding studies were seldom carried out on the enrichment of these micronutrients. As for tocochromanols, the widely developed crops are rich in α- or γ-tocopherols and therefore have not been studied as sources of PC-8. By-products coming from oil extraction and refining, i.e. oil cakes, deodorizer distillates and soapstocks, are the ideal sources to

isolate and recover the micronutrients, because synthetic methods for their manufacture are more difficult and provide lower product yields, especially for CL and PAHA. It is also important to further investigate the incorporation of in other foods; but, their applications is often limited by their stability or solubility. Suitable modification methods, therefore, need to be developed. For instance, encapsulation techniques are being studied to reduce the photosensitivity and to improve the aqueous stability of resveratrol, and the covalent attachment of lipophilic groups onto ergosterol via esterification are being developed to increase the micronutrient's lipophilicity.

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