An Overview
Tocotrienols: Occurrence, Chemistry and Functions in Food

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ABSTRACT

Tocotrienols, the vitamin E of the 21st century, are considered as the other half of the natural vitamin E family. Vitamin E refers to eight different isoforms (α, β, γ and δ of both saturated tocopherols and unsaturated tocotrienols).

Only, a very small fraction of plants contain tocotrienols. Palm oils, barley and rice bran are the most abundant sources of tocotrienols. From the chemical point of view, tocotrienols are unsaturated analogues and possess an isoprenoid side chain.

Recently, attention has been paid towards tocotrienols as high potent antioxidants along with other health promoting properties. Consequently, the tocotrienols rich sources have been utilized to formulate different functional foods. This overview summarizes occurrence and chemistry of tocotrienols along with their functions in foods.

Keywords: ***Palm oil, bread, cookies, biscuits, chocolate spread, salad dressings, antioxidants, functional foods.***

INTRODUCTION

Initially discovered in 1938 as a "fertility factor", vitamin E now refers to eight different isoforms that belong to two categories, four saturated analogues (α, β, γ and δ) called tocopherols and four unsaturated analogues referred to as tocotrienols (Aggarwal *et al.*, 2010).

It is worth to mention that although tocotrienols represent half of the natural vitamin E family, work on tocotrienols accounts for roughly 1% of the total literature on vitamin E. Such a situation can be explained on the basis that the abundance of α-tocopherol in the human body and the comparable efficiency of all vitamin E molecules as antioxidants, led biologists to neglect the non-tocopherol vitamin E molecules as topics for basic and clinical research (Sen *et al.*, 2007).

Members of the vitamin E family are not redundant with respect to their biological functions, α- tocotrienol, γ-tocopherol and δ-tocotrienol have emerged as vitamin E molecules with functions in health and disease that are clearly distinct from that of α-tocopherol (Sen *et al.*, 2006).

Occurrence of tocotrienols

Tocotrienols are present in only a small fraction of plants (Figure 1). Palm oils, barley and rice bran are considered as the most abundant sources of tocotrienols, since they contain 940, 910 and 466 mg/kg of tocotrienols, respectively (Aggarwal *et al.*, 2010).

Barley (*Hordeum vulgare* L.) represents a landmark early discovery highlighting the unique significance of tocotrienols in health and disease (Qureshi *et al.*, 1986). However, palm oils represent one of the most abundant natural sources of tocotrienols.

According to Sundram *et al.* (2003), the distribution of vitamin E in palm oil was 30% tocopherols and 70% tocotrienols. In accordance, El Hadad *et al.* (2010a) analyzed palm olein (POL) and red palm olein (RPOL) for their contents of α, β, γ and δ tocotrienols along with α-tocopherol. Data indicated that POL contained 165.0, 17.9, 167.0 and 49.0 ppm of α, β, γ and δ tocotrienols, respectively. As for, RPOL, it exhibited higher values being 254.0, 26.7, 261.5 and 104.0 ppm of α, β, γ and δ tocotrienols, respectively. Meanwhile, the total tocotrienols + α-tocopherol exhibited values of 504 and 820 ppm for POL and RPOL, respectively.

Rice bran oil, a by-product of the rice milling industry is a major natural source of α-tocotrienols.

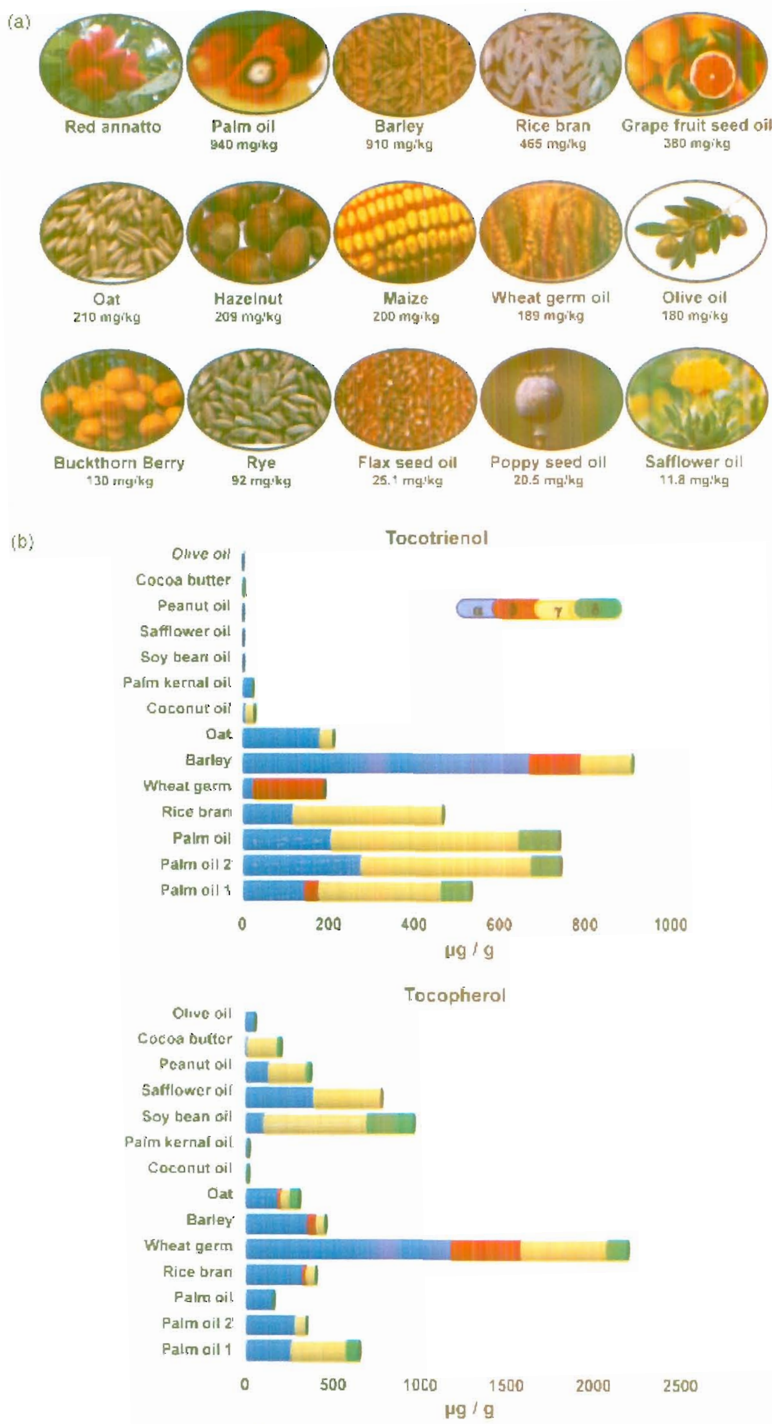


Fig. 1: (a) Natural sources of tocotrienols, (b) Content of tocotrienol and tocopherol isomers from various sources

Source: Aggarwal *et al.* (2010)

Moreover, rice bran oil provides desmethyl tocotrienols. Two novel tocotrienols were isolated from stabilized and heated rice bran, apart from the known α, β, γ and δ tocopherols and tocotrienols (Qureshi *et al.*, 2001 & Iqbal *et al.*, 2005).

Notwithstanding, tocotrienols were found to be (in µg/g.d.m): 76.8 (α), 479 (γ) and 15.4 (δ) in black rice. The corresponding values for red rice were as follows in the same aforementioned order: 197, 439 and 12.3 µg/g.d.m. It is worth to mention that β-tocotrienol was not detectable in both types of rice (Yoshida *et al.*, 2010).

Cereals such as oat and rye contain small amounts of tocotrienols. The α-tocotrienol is the predominant form of tocotrienol in oat (*Avena sativa* L). The β-tocotrienol is the major form of tocotrienol found in hulled and dehulled wheat ranged from 33 to 43 mg/kg on dry weight basis (Panfili *et al.*, 2003).

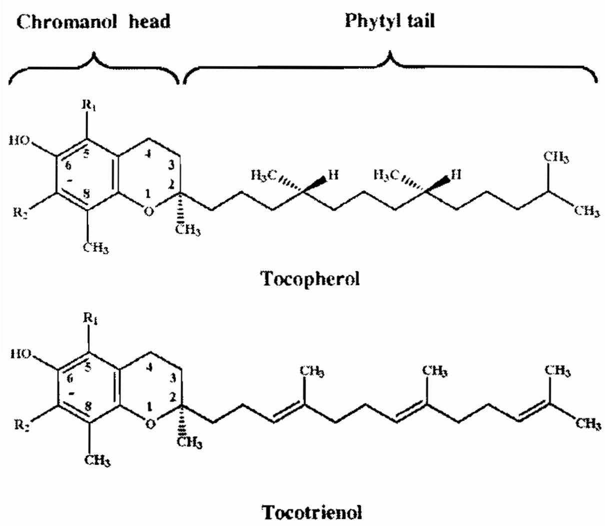
According to Zielinski *et al.* (2007), α-tocotrienol concentration (µg/g.d.m.) in three cultivars of rye ranged between 6.87 and 7.47, while β-tocotrienol content ranged between 4.13 and 6.49 in whole grains. Endosperm with embryo exhibited values ranged from 4.92 to 6.84 of α-tocotrienol and from 4.56 to 6.00 (β-tocotrienol). On the other hand, pericarb with testa had α-tocotrienol ranged between 12.8 and 17.2, while their counterpart values for β-tocotrinol ranged from 7.01 to 11.61 µg/g.d.m.

Chemistry of tocotrienols

Figures (2 and 3) illustrate the structure and chemical composition of tocotrienols as compared to their counterparts belonging to tocopherols. Tochopherols are saturated forms of vitamin E, whereas tocotrienols are unsaturated and possess an isoprenoid side chain. Some evidences suggest that human tissues can convert tocotrienols to tocopherols (Qureshi *et al.*, 2001, 2002).

Tocopherols consist of a chromanol ring and a 15-carbon tail. The presence of three *trans* double bonds in the tail distinguishes tocopherols from tocotrienols. The isomeric forms of tocotrienols are distinguished by the number and location of methyl groups on the chromanol rings: α-tocopherol is 5, 7, 8-trimethyl, β-tocotrienol is 5,8-dimethyl and γ-tocotrienol is 8 monomethyl and δ-tocotrienol is 8 monomethyl as it is shown in Figures (1 and 2) (Ruperez *et al.*, 2001, Aggarwal *et al.*, 2010).

Molecular targets of tocotrienols can



R_1	R_2	Compound
CH_3	CH_3	α
CH_3	H	β
H	CH_3	γ
H	H	δ

Fig. 2: The structure of tocopherols and tocotrienols

Source: Ruperez *et al.* (2001)

be classified as those that are modulated by binding directly and those that are modulated indirectly. Modulation of various targets by tocotrienols may occur at the transcriptional, translational, or post translational levels, or by direct interaction with cellular targets (Van Hoaften *et al.*, 2002; Khanna *et al.*, 2003, Aggrawal *et al.*, 2010).

It is worth to mention that the name "tocotrienol" to denote a tocopherol with a true isoprenoid side chain was first suggested by Bunyan *et al.* (1961), and the tocotrienols were described in *Nature* when isolated from the latex of the rubber plant (*Havea brasiliensis*) in 1964 (Dunphy *et al.*, 1965, Whittle *et al.*, 1966).

Functions of tocotrienols in foods

Tocotrienols attracted no real attention until the 1980s and 1990s when their cholesterol lowering potential and anticancer effects were described (Kato *et al.*, 1985).

Like tocopherols, tocotrienols exhibit antioxidant activeties, and most of its effects can be linked to its antioxidant functions. Moreover, numerous studies indicate that tocotrienols exhibite antican-

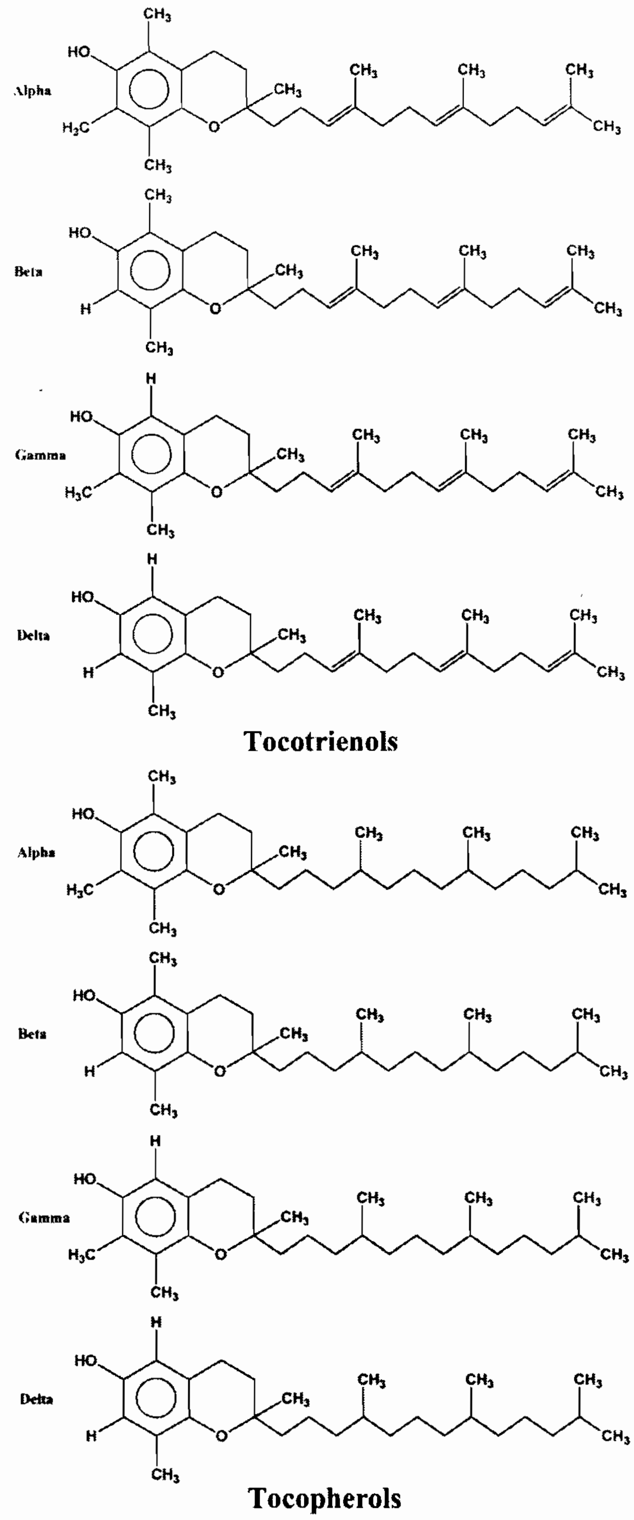


Fig. 3: Chemical formulas of tocopherols and tocotrienols

Source: Aggarwal *et al.* (2010)

cer, antiproliferative, proapoptotic, antiangiogenic and anti-inflammatory activities (Sen *et al.*, 2006, 2007, Nesaretnam, 2008, Aggarawal *et al.*, 2010, Frank *et al.*, 2011). Accroding to Aggarwal *et al.*

(2010), tocotrienols are considered as the vitamin E of the 21st century.

The antioxidant activities of tocotrienols are mediated through industry of antioxidant enzymes such as superoxide dismutase (Newaz & Nawal, 1999, Lee *et al.*, 2009), NADPH: quinine oxidoreductase (Hsieh & Wu, 2008) and glutathione peroxidase (Adam *et al.*, 1996), which quench free radicals such as superoxide radical (Renuka Devi & Arumughan, 2007).

Due to the antioxidant potency of tocotrienols, they have been added to a variety of foods for the sake of formulation "functional foods". Recent years have seen growing interest of the part of consumers and the food industry to provide functional food ingredients and the way in which it may help maintain human health. The important role that diet plays in preventing and treating illness is widely accepted. The basic concepts of nutrition are undergoing a significant change. The classical concept of "adequate nutrition" that is, a diet that provides nutrients in sufficient quantities to satisfy particular organic needs, is being replaced by the concept of "optimal nutrition", which includes, besides nutrients the potential of food to prove health, improve general well-being and reduce the risk of developing certain illness. This is where functional foods, also known as designer foods, therapeutic foods or medicinal foods, play their part (Nagai & Inoue, 2004, Ramadan & Al-Ghamdi, 2012).

Utilization of tocotrienols as antioxidants in foods can be reviewed under three main headings, namely, bakery products, chocolate spreads and salad dressings.

1- Bakery products

Al-Saqer *et al.* (2004) formulated functional pan bread and sugar-snap cookies by using red palm olein (RPOL) and red palm shortening (RPS) with the objective of providing higher amounts of antioxidants mainly tocotrienols (about 81-84%, of the total tocols in PROL and RPS). Data indicated that the total tocopherol and total tocotrienol contents (325.0 and 468.0 mg/kg fat, respectively) were significantly higher in bread made with control shortening than in that made with a 75% replacement level of RPOL (192 and 407 mg/kg fat) or RPS (101.4 and 300.0 mg/kg fat). Similar trends were observed in the white bread and the brown bread made with RPOL and RPS. The tocotrienol contents in cookies made with varying replacement levels of RPS ranged from 229.1 to 317.8 mg/kg fat, compared with 379.4 to 672.3 mg/kg fat in cookies made with RPOL. The tocotrienols were found to be the predominant fraction in cookies made either with RPS (58.0 to 68.0%) or with PROL (about 69.0 to 83.0%) of the total vitamin E. It was obvious that cookies, being higher in fat content would be better providers of these desirable phytochemicals and antioxidants than breads.

Holtekj Ølen *et al.* (2008) made bread by replacing 40% of wheat flour with barley flour. Data indicated that the incorporation of barley increased the antioxidant properties of the bread, compared to the control bread. It is worth to mention that the measured antioxidant activities FRAP (Ferric reducing/ antioxidant power) were relatively stable during the baking process.

Novel functional biscuits were formulated by replacing white shortening (WS) by red palm olein (RPOL) at 20, 40, 60, 80 and 100%. Sensory evaluation of fresh biscuits revealed that all RPOL levels were significantly acceptable as or superior to the control. Biscuits made from 40% WS + 60% RPOL exhibited significantly the lowest values in terms of water loss during baking, volume, specific lightness, water activity and shearing force. These biscuits contained 1.8 times more tocopherols and tocotrienols and 10.4-14.8 times more carotenes than the control. Moreover, packaged biscuits were able to be stored at room temperature in the light for not less than 6 months without any deterioration in their quality (El-Hadad *et al.*, 2010b).

2- Chocolate spreads

El-Hadad *et al.* (2011a) formulated novel functional chocolate spreads by replacing butter fat in conventional chocolate spread by red palm olein (RPOL) at 20, 40, 60, 80 and 100%. Sensory evaluation revealed that chocolate spreads made from 20% RPOL and 80% butter fat were accepted as the conventional chocolate spread (100% butter fat). Data revealed that the replacement of butter fat in functional chocolate spread led to a significant increment in tocopherols and tocotrienols (3.7 folds) and carotenes (19.8 folds), as compared to the control. The functional chocolate spreads could be stored at room temperature for 6 months without any deteriorative effects on their quality.

3- Salad dressings

Novel functional salad dressings were formulated and evaluated by El-Hadad *et al.* (2011b). Corn oil in conventional salad dressings was replaced by red palm olein (RPOL) at 5, 10, 15, 20, 40, 60 and 80% levels. Data revealed that salad dressings made from 15% RPOL and 85% corn oil was quite acceptable by panelists as the conventional salad dressings (100% corn oil). Data showed that the replacement of corn oil in functional salad dressing by RPOL resulted in significant increments in α, γ, and δ tocotrienols (29 folds) and carotenes (15 folds) as compared to the control.

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نظــرة شــاملة

التوكوثلاثي إينولات: تواجدها، تركيبها الكيماوي، وظائفها في الأغذية

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تعتبر التوكوثلاثي إينولات- وهي فيتامين E القرن الحادي والعشرين – بمثابة النصف الأخر من عائلة هذا الفيتامين، والتي تتكون من ثمانية مشابهات (ألفا، بيتا، جاما، دلتا، لكل من التوكوفيرولات المشبعة والتوكوثلاثي إينولات غير المشبعة).

تجدر الإشارة إلى أن تواجد التوكو ثلاثي إينولات مقصور على عدد محدود جداً من النباتات. وتعتبر زيوت النخيل والشعير ورجيع الكون أعلى المصادر النباتية من حيث محتواها من التوكوثلاثي إينولات. من الناحية الكيماوية فإن هذه المركبات تحتوي على سلسلة أيزوبروينويد جانبيه.

في الحقبة الأخيرة تنامى الاهتمام بالتوكوثلاثي إينولات لكونها مضادات أكسدة عالية الفاعلية فضلاً عن تميزها بفوائد صحية أخرى متعددة، ومن ثم فقد استخدمت المصادر ذات المحتوى العالي من التوكوثلاثي إينولات لتوليف أغذية وظيفية مختلفة.

تلخص هذه المقالة مصادر تواجد مركبات التوكوثلاثي إينولات وتركيبها الكيماوي ووظائفها في الأغذية.