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Original Article

Tocopherol, tocotrienol and plant sterol contents of vegetable oils and industrial fats

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Abstract

The tocopherol and tocotrienol (i.e. tocol) and plant sterol contents of 14 vegetable and 9 industrial fats and oils available on the Finnish market in 2005 were determined using NP-HPLC with fluorescence detection (tocols) and GC-FID (plant sterols). Best sources of α-tocopherol were wheat germ (192 mg/100 g) and sunflower oil (59 mg/100 g). Oils richest in γ-tocopherol were camelina (72 mg/100 g), linseed (52 mg/100 g) and organic rapeseed oil (51 mg/100 g). Total tocol contents were between 4.2 mg/100 g (coconut fat) and 268 mg/100 g (wheat germ oil). Plant sterol contents ranged from 69 mg/100 g in a frying fat to 4240 mg/100 g in wheat germ oil. Organic rapeseed oil, the second best source of plant sterols, contained 887 mg/100 g. The variations of the total tocol and sterol contents in 10 rapeseed oil sub-samples analysed separately were 9.7% for tocols and 9.9% for sterols in refined rapeseed oil, and 6.3% for tocols and 4.2% for sterols, respectively, in cold-pressed rapeseed oil. In addition to the target compounds, plastochromanol-8 could be determined in all plant-based samples with contents ranging from 0.13 (walnut oil) to 18 mg/100 g (linseed oil). The lignans sesamin and sesamolin could be identified in sesame oil.

Keywords: Tocopherols; Tocotrienols; Plant sterols; Vegetable oils; Industrial fats; Chromatographic analysis; Finnish food composition database

1. Introduction

Tocopherols and tocotrienols, together abbreviated as tocols and summarized under the term vitamin E, are a group of fat soluble antioxidants with a chromanol ring and a hydrophobic side chain (phytyl in the case of tocopherols, isoprenyl in the case of tocotrienols). Individual tocopherols (α-, β-, γ-, and δ-tocopherol) and the corresponding tocotrienols differ by the number and positions of methyl substituents on the phenolic part of the chromanol ring. The structural features of tocols govern their metabolic fate and biological activities. Despite similar absorption from the gastrointestinal tract, α-tocopherol (α-T) is preferentially resecreted by incorporation into lipoproteins by the hepatic α-tocopherol transfer protein (α-TTP), resulting in highest plasma and tissue levels. Therefore, the Institute of Medicine defined natural *R*-α-T as the only tocol contributing toward meeting the vitamin E requirement (Institute of Medicine, 2000).

The main function of α-T is that of a radical-chain-breaking antioxidant in membranes and lipoproteins, as well as in foods (e.g. Kamal-Eldin and Appelqvist, 1996). Due to its antioxidant potential and various functions at the molecular level, it is believed to reduce the risk of cardiovascular diseases and of certain types of cancer (Burton and Traber, 1990; Burton, 1994). Despite lower plasma concentrations, other tocols are still capable of exerting antioxidant and biological activities. γ-T, for instance, has been reported to be more potent than α-T in decreasing platelet aggregation, LDL oxidation, and delaying intra-arterial thrombus formation (Li et al., 1999; Saldeen et al., 1999). Likewise, tocotrienols have been shown to inhibit cholesterol biosynthesis (Qureshi et al., 1995) and are discussed in the context of reducing the risk of breast cancer (Schwenke, 2002). Hence, concurrent administration of various tocopherols and tocotrienols

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may result in increased antioxidant, antitumor and hypocholesterolemic potential. In order to take into account the biological activities of other tocols, some nutrient databases still include them in the form of α-T equivalents (e.g. Eitenmiller and Landen, 1999; Bramley et al., 2000).

Plant sterols are isoprenoid compounds with a sterol nucleus and an alkyl chain. Most plant sterols have a double bond in position C-5 in the nucleus, while others are totally saturated and called stanols (Moreau et al., 2002). In this paper, the term "sterols" is used for both sterols and stanols. Plant sterols are of nutritional interest because of their potential to lower both total serum cholesterol and LDL-cholesterol in humans by inhibiting the absorption of dietary cholesterol as well as the reabsorption of cholesterol excreted into the bile in the course of the enterohepatic cycle (Piironen et al., 2000). A meta-analysis of 41 trials showed that a plant sterol intake of 2 g/day reduced LDL-cholesterol by 10% (Katan et al., 2003). Unlike sterols which compete with cholesterol for absorption and are themselves present in serum, stanols are virtually unabsorbable. Still, they are capable of decreasing total and LDL-cholesterol as well as plant sterol serum levels (Piironen et al., 2000). More recently plant sterols have been proposed to have other potential positive health effects (Awad and Fink, 2000; de Jong et al., 2003; Berger et al., 2004), and even plant sterol intakes from baseline diets may have a cholesterol-lowering effect (Ostlund Jr., 2004).

Analysis of tocols is usually performed by normal phase high performance liquid chromatography (NP-HPLC) with fluorescence detection (FLD) (Abidi, 2000; Kamal-Eldin et al., 2000; Rupérez et al., 2001). Capillary gas chromatography with flame ionization detection (GC-FID) is most frequently applied in plant sterol analysis (Dutta and Normén, 1998; Toivo et al., 2001; Lampi et al., 2004; Piironen et al., 2003). Both the food matrix and the native forms in which tocols and sterols occur in foodstuffs determine the choice of sample preparation method prior to chromatographic analysis. Vegetable oils contain tocols mainly in unconjugated form and can be directly injected into the NP-HPLC-system after dilution. Spreads and many industrial fats, however, contain water, emulsifiers and possibly added α-T esters. Their analysis therefore requires saponification under carefully chosen conditions in order to avoid degradation of tocols in alkaline solution (Rupérez et al., 2001; Ryynänen et al., 2004). Plant sterols occur mainly as free or esterified sterols in oils and fats, the forms accumulated in the membranes and in oil droplets, respectively (Piironen et al., 2000). Prior to the GC analysis, sterols have to be liberated from their conjugates, extracted and silylated. There are several approaches to deconjugate plant sterols in different plant food matrices including alkaline, acid and enzymatic hydrolyses (Piironen et al., 2002b, 2003; Toivo et al., 2000, 2001). Since fats and oils contain free and esterified sterols only alkaline hydrolysis (i.e. saponification) is required, and acid hydrolysis that is needed to hydrolyse glycosylated forms could be omitted (Toivo et al., 2001).

Fats and oils and derived products are a major source of tocols and plant sterols in the Western diet. They contribute to 20% and 41% of the total α-T equivalent intake in the US and in Finland, respectively (Murphy et al., 1990; Heinonen and Piironen, 1991), and to 26%, 39% and 50% of the total plant sterol intake in the Netherlands, Finland and Spain, respectively (Normén et al., 2001; Valsta et al., 2004; Jiménez-Escrig et al., 2006).

An extensive study on the tocol contents of vegetable oils and fats consumed in Finland was conducted in the 1980s, and most of the data of the Finnish food composition database (Fineli, 2006) derive from that (Syväoja et al., 1986). In the meantime, the market situation has changed dramatically. Soybean oil, corn oil and peanut oil have disappeared almost completely from the market, appearing currently at the same level as apricot kernel- or grape seed oil in speciality shops. On the other hand, items like organic rapeseed oil, sesame oil, linseed oil, camelina oil and wheat germ oil have found their way into the shelves of retail stores. There has also been a major change in the raw materials of industrial fats. Rapeseed and palm oils and fats are now the major constituents, whereas soybean oil can hardly be found in any product. Plant sterol data on the vegetable oils and fats used in Fineli (Fineli, 2006) have only been published in Finnish (Salminen, 1997). The aim of this work was to provide up to date and validated data on the contents of the individual tocopherols and tocotrienols as well as of plant sterols in vegetable oils and industrial fats currently available on the Finnish market in order to enable an update of the Finnish food composition database.

2. Materials and methods

2.1. Standards, reagents and solutions

Ethanol of Aa-grade (purity ⩾ 99.5%) was purchased from Altia (Altia Oyj, Rajamäki, Finland), ethanol of spectroscopic grade (AaS, purity ⩾ 99.5%) from Primalco (Primalco, Finland), *n*-heptane (HPLC-grade) from Rathburn Chemicals Ltd. (Walkerburn, Scotland) and 1,4-dioxane (HPLC-grade, stabilized) as well as diethyl ether (p.a.) from Riedel-de Haën (Sigma-Aldrich, Helsinki, Finland). Milli Q water was of HPLC-grade. Ascorbic acid, potassium hydroxide pellets, sodium chloride, anhydrous pyridine and *N*,*O*-bis(trimethylsilyl)trifluoracetamide (BSTFA) were from Merck (Darmstadt, Germany). Trimethylchlorosilane (TMCS) was purchased from Fluka (Buchs, Switzerland) and anhydrous sodium sulphate was provided by Prolabo (Paris, France).

2.1.1. Tocopherols and tocotrienols

α-, β-, γ- and δ-tocopherol were purchased as an isomer kit from Merck (Art. 15496). Tocomin® (cf. Section 2.2.2) was obtained from Carotech Inc. (Talmadge Village, Edison, NJ, USA). Standard stock solutions of tocopherols were prepared in ethanol (AaS). The exact concentrations