Fatty Acid Profile of Phytosterol Esters and Total Lipids Fractions from Cold Pressed Nonrefined Sesame and Walnut Oil

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Abstract

Vegetable oils are mainly constituted by triacylglycerols (95-98%) and complex mixtures of minor compounds (2-5%) of a wide range of chemical nature (sterols, pigments, tocopherols, fatty alcohols, etc.) Sesame oil is of vegetable origin and is obtained from sesame seeds by pressing. Walnut oil is used to a limited extent in food preparation, though not as extensively as other oils due to the fact that it is still an expensive specialty product.

The aim of our study was to identified the fatty acid profile of phytosterol esters and total lipids fractions from cold pressed nonrefined sesame and walnut oil. The profiles of fatty acids from total lipids and phytosterol esters fraction was determined by GC-FID. Transesterification procedures were used for derivatization of fatty acids for GC analysis. The main fatty acids from the studied oil samples were: oleic, linoleic and palmitic fatty acids.

Key words: phytosterol esters, fatty acids, GC-analysis, sesame oil, walnut oil

Introduction

Sesame is one of the oldest cultivated plants in the world. The tiny seeds of sesame have been known as a highly prized source of food oil in Babylon, Assyria and many other eastern countries for at least 4,000 years. The sesame oil as edible oil lowered blood pressure, decreased lipid peroxidation, and increased antioxidant status in hypertensive patients (Sankar et al., 2006). Cold pressed nonrefined sesame oil is high in polyunsaturated fat. When used in moderation, this type of fat can benefit the heart by helping the body to eliminate newly made cholesterol. The significant reduction in lymph cholesterol and fatty acids due to sesame oil feeding may be an important factor in reducing hypercholesterolemia (Satchithanandam et al., 1993).

Walnuts (genus Juglans) are plants in the family Juglandaceae. The best-known member of the genus is the Persian Walnut (Juglans regia), native from the Balkans in southeast Europe, southwest & central Asia to the Himalaya and southwest China. Walnuts have received considerable interest because they are excellent sources of omega-3 fatty acids which possess plasma cholesterol-lowering effects (Sabate et al., 1993; Savage et al., 1999). The nuts are rich in oil, and are widely eaten both fresh and in cookery. Walnut oil (extracted from walnuts) is expensive and consequently is used sparingly; most often in salad dressing. The beneficial action of walnut oil on skin is known for centuries and it is widely used in cosmetic manufacturing industry. The walnut oil is a component of dry skin creams. It has good moisturizing, anti-aging and regenerative properties as well as free radical scavenging capacity (Tsamouris et al., 2002). The use of the walnut oil for cosmetic purposes may be due to its high content in Omegra-3 and Omega-6 fatty acids (essential fatty acids), in particular linoleic and alpha-linolenic acids (Karleskind, 1996; Lunn et al., 2006).

Essential Fatty Acids (EFAs) are necessary fats that humans cannot synthesize, and must be obtained through diet. EFAs are long-chain polyunsaturated fatty acids derived from linolenic and linoleic acids.
There are two families of EFAs: Omega-3 and Omega-6. Omega-3 fatty acids are derived from linolenic acid, Omega-6 from linoleic acid. The ideal intake ratio of Omega-6 to Omega-3 fatty acids is between 1:1 and 4:1, (Simopoulos, 2003).

Phytosterols (PS) are compounds present in all plants and in food products with plant origin. They occur in five common forms as the free alcohol (FS), as fatty-acid esters (SE), as steryl glycosides (SG) and as acylated steryl glycosides (ASG). The last three forms (SE, SG and ASG) are generically called “phytosterol conjugates” (Moreau et al., 2002).

Our studies are focused on identification and quantification of fatty acids found in phytosterol esters and total lipids fractions from cold pressed nonrefined sesame and walnut oil. The fingerprint of fatty acids was determined by gas chromatographic techniques, using flame ionization detection (FID).

**Materials and methods**

**Sampling and Reagents**

Cold pressed, non-refined sesame oil was purchased from the market. The walnut oil was obtained by cold pressing of the walnut kernels which were collected in Transylvania (Romania). Methanol, petroleum ether, hexane, chloroform and other reagents were analytically grade and purchased from Merck- Germany.

**Sample preparation for fatty acids analysis**

**Total fatty acids**

For total fatty acids analysis, fatty acid methyl esters (FAMEs), were prepared by transesterification of the oil samples by sodium methoxide (CH3ONa) catalysis (Christie, 1982)

**Fatty acids from sterol esters (ES) fraction**

The FAMEs from sterol esters fraction were obtained in the same way like for the total fatty acids after the esterified sterols were separated by column chromatography from the oil samples (this fraction was eluted whit petroleum ether= diethyl ether= 95:5 solvent mixture). The dried organic phase (wit FAMEs) was purified then by column chromatography. The column was packed with Silica gel 40 (0.063-0.200 mm) (Merck- Germany). The FAMEs was eluted with petroleum ether: diethyl ether = 90:10(v/v) solvent mixtures and the free sterols were eluted with petroleum ether: diethyl ether = 50:50(v/v). After the fractions of the FAMEs were collected, the solvent mixtures were evaporated and the separated fractions were re-dissolved in hexane and submitted to GC analysis.

**GC-FID analysis**

The FAMEs obtained by transesterification of oils samples and esterified sterols fractions were analyzed by GC-FID. A SHIMADZU GC-17-A gas-chromatograph with FID detector was used. The FAMEs were separated on a CHROMPACK WCOT 25M×0.25mm ID, 0.2μm film thickness capillary column, using a temperature program from 150°C / 5 min, 4°C/min until 235°C and 5 min at 235°C. Were respected the following conditions: injector temperature 260°C; FID temperature 260°C and the carrier gas – Helium. All analyses were carried out in triplicate and the mean values and standard deviation were calculated.

**Results and discussion**

The chromatograms of the fatty acids obtained from the studied vegetable edible oils (total lipids and esterified sterols fractions) are shown in Fig. 1 and Fig 2. These results are useful for fingerprinting oils and detecting adulteration by comparing peaks and peak heights. The results of the compositional determinations based on the normalized peak area are listed in Table 1. Vegetable oils have characteristic fatty acids compositions that are useful for evaluating product quality and authenticity. The fatty acids compositions may be influenced not only by species or strain, but also by regional, climate, degree of ripeness, harvesting and processing conditions, etc. The fatty acids composition of the studied two vegetable oils was in a good agreement with the values previously reported in the literature (Lee et al., 1998; Tsamouris et al., 2002).

In Table 2 are presented the ratio between ω-6/ ω-3 fatty acids in total lipids and esterified sterol fractions.
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Figure 1. GC-FID chromatograms of FAMEs in walnut oil: (a.)-total lipids fraction; (b.)-esterified sterols fraction

Figure 2. GC-FID chromatograms of FAMEs in sesame oil: (a.)-total lipids fraction; (b.)-esterified sterols fraction

Table 1. The fatty acid composition of edible vegetable oils determined in this study

<table>
<thead>
<tr>
<th>Fatty Acids</th>
<th>Abbreviations</th>
<th>Fatty acid composition of oils (% of total fatty acids)</th>
<th>Retention Times (Rt) (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sesame oil Total lipids fraction</td>
<td>Esterified sterols fraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
</tr>
<tr>
<td>Palmitic 16:0</td>
<td>16:0</td>
<td>10.86 ± 0.18</td>
<td>13.55 ± 0.21</td>
</tr>
<tr>
<td>Stearic 18:0</td>
<td>18:0</td>
<td>4.77 ± 0.10</td>
<td>9.29 ± 0.18</td>
</tr>
<tr>
<td>Oleic 18:1</td>
<td>18:1</td>
<td>27.80 ± 0.24</td>
<td>21.63 ± 0.22</td>
</tr>
<tr>
<td>Linoleic 18:2 ω-6</td>
<td>18:2 ω-6</td>
<td>51.20 ± 0.29</td>
<td>45.57 ± 0.26</td>
</tr>
<tr>
<td>α-linolenic 18:3 ω-3</td>
<td>18:3 ω-3</td>
<td>4.90 ± 0.12</td>
<td>4.50 ± 0.10</td>
</tr>
<tr>
<td>Arachic 20:0</td>
<td>20:0</td>
<td>0.36 ± 0.06</td>
<td>4.63 ± 0.11</td>
</tr>
<tr>
<td>Gadoleic 20:1</td>
<td>20:1</td>
<td>0.09 ± 0.01</td>
<td>0.80 ± 0.04</td>
</tr>
<tr>
<td>Total (%)</td>
<td></td>
<td>99.98 ± 1.00</td>
<td>99.97 ± 1.12</td>
</tr>
<tr>
<td>Σ SAFAs1</td>
<td></td>
<td>15.99 ± 0.34</td>
<td>27.47 ± 0.50</td>
</tr>
<tr>
<td>Σ UNSAFAs2</td>
<td></td>
<td>83.99 ± 0.66</td>
<td>72.51 ± 0.62</td>
</tr>
<tr>
<td>UNSAFAs / SAFAs ratio</td>
<td></td>
<td>5.25</td>
<td>2.6</td>
</tr>
<tr>
<td>Σ MUFA3</td>
<td></td>
<td>27.89 ± 0.25</td>
<td>22.43 ± 0.26</td>
</tr>
<tr>
<td>Σ PUFA4</td>
<td></td>
<td>56.10 ± 0.41</td>
<td>50.07 ± 0.36</td>
</tr>
<tr>
<td>PUFA3/MUFA3 ratio</td>
<td></td>
<td>2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

1Saturated fatty acids; 2 Unsaturated fatty acids; 3 Monounsaturated fatty acids; 4 Polyunsaturated fatty acids;
The main fatty acids from the studied samples were: linoleic, oleic, and palmitic fatty acids. In both of the studied fractions of the analyzed edible oils the most abundant fatty acid was linoleic acid. It represents 51.20% in total lipids fraction and 45.57% in esterified sterol fraction from the sesame oil, and 61.05% in total lipids fraction and 37.27% in esterified sterol fraction of the walnut oil, respectively. Trace fatty acids such as arachic acid (20:0) and gadoleic acid (20:1) were detected only in sesame oil. The concentration of the arachic acid was considerable higher (4.63%) in esterified sterols fraction than in the total lipids fraction (0.36%). It was observed that the amounts of the saturated fatty acids from the esterified sterols fractions of the studied oils (27.47% in sesame oil and 25.95% in walnut oil respectively) were higher than in total lipid fractions (15.99% in sesame oil and 8.62% in walnut oil respectively). The values of the unsaturated / saturated ratios in the esterified sterols fractions were similar: 2.6 for sesame oil and 2.9 for walnut oil. For the total lipids fractions these values were different: 5.25 for sesame oil and 10.6 for walnut oil respectively. The polyunsaturated fatty acids were the most abundant of the unsaturated fatty acids of total lipids and also among the esterified sterols fractions in both of the analyzed oils (Table 1). The PUFAs / MUFAs ratios were 2.2 and 2 in esterified sterols fraction and total lipids fraction respectively, from sesame oil. For walnut oil these ratios were different: 1.8 for esterified sterols fraction and 3.9 for the total lipids fraction respectively. The ratios between ω-6 / ω-3 fatty acids in walnut oil only ( 5.3 / 1 in total lipids fraction and 3.5 / 1 in esterified sterols fraction) are closed to ideal ratio of 4 / 1, mentioned in literature (Simopoulos, 2003).

Conclusions

Vegetable oils have characteristic fatty acids compositions that are useful for evaluating product quality and authenticity. The relative ratio of unsaturated fatty acids over saturated fatty acids can be a useful index for distinguishing the vegetable edible oils. The pattern of (18:1)/(18:2 ω-6)/ 18:3 ω-6/18:3 ω-3 and their ratios can be considered useful bio-markers of GC-fingerprint, an appropriate method for oil authenticity. The walnut oil can be considered good sources of ω-6 / ω-3 fatty acids because the ratio between these acids is closed to the ideal one, mentioned in literature. This ratio of fatty acids has been shown to be beneficial for the prevention of heart disease and cancer, especially omega 3 fatty acids. Sesame oil is rich in omega-3 fatty acids, which are very useful to maintain the integrity of the skin.

References


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