Review Article

Peanut oil: Compositional data

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The major fatty acids of peanut oil acylglycerols are palmitic (C16:0), oleic (C18:1), and linoleic (C18:2) acids, and only a trace amount of linolenic fatty acid (C18:3) is present. Thus they have a very convenient oxidative stability and have been considered premium cooking and frying oils. This paper provides information about compositional data of peanut oil taking into account major (triacylglycerols and their fatty acids) and minor (free fatty acids, diacylglycerols, phospholipids, sterols, tocopherols, tocotrienols, triterpenic and aliphatic alcohols, waxes, pigments, phenolic compounds, volatiles, and metals) compounds. Moreover, the influence of genotype, seed maturity, climatic conditions, and growth location on peanut oil chemical composition is considered in the present report. In addition, peanut oils from wild species found in South America as well as from peanut lines developed through conventional breeding are also compared.

Keywords: Fatty acids / Minor compounds / Peanut oil / Triacylglycerols / Wild peanuts

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1 Introduction

Botanically, the peanut, *Arachis hypogaea*, belongs together with soybean to the *Leguminosae* family, but in composition it resembles other nuts rather than most beans or peas [1]. Numerous peanut cultivars and wild species are found and have been collected in South America. The probable centers of origin of *Arachis* species and *A. hypogaea* were in the Gran Pantanal (Mato Grosso, Brazil) and on the eastern slopes of the Bolivian Andes. Peanuts are grown worldwide in the tropics and temperate zones primarily as an oilseed crop. World wide peanut production reached the mark of 5.8 million tonnes during 2008, representing 15.5% of the soybean production. Asia and Africa together contributed 94% of the world's peanut oil production (5.45 million tonnes) while America did with 4%. This has been the tendency for almost 3 years (2006–2008), showing a little increment in the African, Asia, Europe, and South American production, while North American showed the tendency to diminish its production. In trade terms, until 2007 Senegal, Argentina, and India dominated peanut oil exportation, while USA, France, Italy, Belgium, and Germany lead in peanut oil importation [2]. The world trade market for peanuts may be considered a residual market, in the sense that only a small proportion of the world production is devoted to exports and imports, and most of the production is domestically utilized [3].

Peanut seeds make an important contribution to the diet in many countries. They are a good source of proteins, lipids, and fatty acids for human nutrition. They are rich in oil, naturally containing from 47 to 50% [4, 5]. Flavor and quality of peanuts and peanut products are largely functions of lipid chemistry [6].

The chemical and physical properties of fats and oils are mainly determined by the fatty acids that they contain and their position within the triacylglycerol (TAG) molecule. Peanut oil is a pale yellow oil with distinctive nutty taste and odor obtained from the processing of peanut kernel. Its odor is almost removed with refining [5]. It has a high oleic content, what is associated with its good oxidative and frying stabilities. It is a non-drying oil that solidifies from 0 to 3°C [1, 7, 8].

Aflatoxin, a carcinogenic compound associated with proteins, is generally not found in refined oil. However, crude

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Abbreviations: CN, carbon number; **DAG,** diacylglycerol; **FFA,** free fatty acid; **IV,** iodine value; **PA,** phosphatidic acid; **PC,** phosphatidylcholine; **PE,** phosphatidylethanolamine; **PG,** phosphatidylglycerol; **PL,** phospholipid; **PS,** phytosterol; **TAG,** triacylglycerol

or lightly processed oil containing fines may hold some aflatoxin [5].

1.1 Major compounds: Triacylglycerols

1.1.1 Fatty acid composition

The major fatty acids present as acylglycerols in peanut oils are palmitic (C16:0), oleic (C18:1), and linoleic (C18:2) acids. Normally, stearic (C18:0), arachidic (C20:0), eicosenoic (C20:1), behenic (C22:0), and lignoceric (C24:0) acids occur in minor proportions, while a trace of linolenic fatty acid (C18:3) can take place. Cultivars from USA, Argentina, Bolivia, and Poland have presented the following fatty acid distribution: C16:0 = 9.3–13.0%, C18:0 = 1.1–3.6%, C18:1 = 35.6–58.3%, C18:2 = 20.9–43.2%, C20:0 = 0.3–2.4%, C20:1 = 0.7–3.2%, C22:0 = 1.8–4.4%, and C24:0 = 0.4–1.9% [9–14]. Similarly, African peanut oil contains 44.5, 32.3, and 13.9% of C18:1, C18:2, and C16:0, respectively. These fatty acids represented *ca*. 90% of the total fatty acids [15]. The Codex Alimentarius proposed that the arachidic and higher fatty acid content of arachis oil (peanut oil) should not exceed 48 g/kg [16]. The presence of high percentage values of C20:0 and C22:0 in other oils like olive oil could be related to adulteration with peanut oil [8].

Peanut oil is considered a premium cooking and frying oil due to its excellent oxidative stability [1]. Moreover, it has been considered to be superior to soybean oil during frying, developing fewer flavor defects with long-term use [8]. Considerable importance has been ascribed to the role of the oleate/linoleate ratio (O/L) and iodine value (IV) in governing product shelf life. High O/L ratio and low IV have been associated with greatly enhanced shelf life and decreased rancidity of the product [6]. Peanuts exported from Argentina, China, and USA in three crop years presented 1.22, 1.15, and 1.70 of mean O/L ratios, respectively [17]. The IV of crude peanut oil is between 86 and 107 [16], being close to olive oil IV (75–94) and smaller than soybean oil IV (120–143) [7].

The fatty acid composition of peanut oil varies depending on the genotype, seed maturity, climatic conditions, growth location, and interactions between these factors [8]. Lower temperatures during seed development normally are associated with a more unsaturated oil [18, 19]. In general, it has been reported that oleic acid increases and linoleic acid decreases with seed maturity. Hinds [20] found that as seeds progressed from intermediate through nearly-mature to mature stages, palmitic and linoleic acids decreased while oleic acid increased.

In other studies, no influence of different years or planting date was reported [6]. Hinds [20] analyzed the influence of the soil type in Eastern Caribbean finding that seeds grown on volcanic clay loam contained more stearic acid as well as long-chain and total saturated fatty acids but less linoleic and total unsaturated acids than samples from volcanic sandy loam. The influence of genotype on the fatty acid composition of peanuts has been well demonstrated by Worthington *et al.* [21]. Brown *et al.* [18] found that variety affected the composition of peanut oil grown in USA. In general the three major fatty acids (palmitic, oleic, and linoleic) were more affected than the minor fatty acids (Table 1). The authors reported that with increasingly more northern growing locations, the oleate and palmitate contents of all varieties tended to decrease, while the polyunsaturated content tended to increase. Similar results were found by Grosso *et al.* [22] studying the peanut oil grown in Argentina. They reported that higher oleic acid contents and correspondingly the best O/L ratios (1.30–1.46) and IV (101–102) were obtained in zones located southeast of cultivate area, with soils more sandy and higher precipitations than the other localities. Higher temperatures during the last weeks before harvest resulted in higher O/L ratio [23].

Grosso and Guzmán [24] analyzed the fatty acid composition of three peanut varieties cultivated in the province of Córdoba (Argentina) corresponding to the main cultivars used by industry: Florman (runner type), Colorado Irradiado (valencia type), and Virginia Manfredi 5 (virginia type). Virginia Manfredi 5 had the highest O/L ratio and the lowest IV, closely followed by Florman, indicating that these cultivars have better oil quality than Colorado Irradiado.

Fatty acid profiles among various peanut cultivars have been analyzed in different regions. Branch *et al.* [9] and

Table 1. Fatty acid composition of peanuts from 10 varieties and different locations (% w/w methyl esters)[a)]

	Fatty acids						
Type	C16:0	C18:0	C18:1	C18:2	C20:0	C20:1	C22:0
Spanish botanical	10.7–12.2	2.0–3.2	42.5–47.9	33.3–38.7	0.9–2.0	0.7–1.6	2.1–3.1
Virginia botanical	8.8–9.0	1.6–2.1	60.0–61.7	23.4–26.2	0.8–1.4	0.9–1.0	1.5–1.6
Virginia market	9.0–9.1	2.2–2.4	56.4–60.3	24.2–26.8	1.1–1.8	1.0–1.1	1.8–2.4
Runner market	9.0–11.2	1.3–1.9	41.3–59.1	25.8–41.9	0.7–1.2	1.1–1.8	1.8–2.4
Spanish market	10.5–11.5	1.4–1.7	41.1–49.1	33.6–40.1	0.4–1.7	1.1–2.2	1.8–2.6

[a)] Brown *et al.* [18].

Table 2. Fatty acid profile among peanut cultivars (% w/w methyl esters)

	Fatty acids							
Cultivars	C16:0	C18:0	C18:1	C18:2	C20:0	C20:1	C22:0	C24:0
				Several[a)]				
Grown in USA[b)]	10.2–10.9	1.4–1.9	49.2–56.3	24.1–30.6	1.0–1.4	1.3–1.4	2.6–3.1	1.5–1.9
Grown in Argentina[c)]	10.5–13.0	1.9–3.6	37.2–51.3	28.4–43.1	0.3–2.4	0.7–1.7	2.1–2.8	0.4–1.3
				Florunner				
Grown in USA [b)]	10.3	1.5	51.7	29.8	1.1	1.3	2.7	1.7
Grown in Argentina[c)]	11.2	1.9	45.8	35.3	0.4	1.2	2.8	1.3

[a)] Cultivars studied in: USA = Florunner, GK-7, Langley, Okrun, Southern Runner, Sunbelt Runner, Sunrunner, Argentina = Blanco Río II, Blanco Manfredi, Colorado Común, Colorado Correntino, Colorado Irradiado, Florunner, Manfredi, Virgina 3, Manfredi Virginia 5.
[b)] Branch *et al.* [9].
[c)] Pignata and Guzmán [12].

Pignata and Guzmán [12] reported the variation of fatty acid composition in various peanut cultivars grown in USA and Argentina, respectively. They have found significant differences within the fatty acid profile among the studied runner-type peanut cultivars. The variations found in cultivars grown in Argentina were higher than that from USA (Table 2). This fact could be attributed not only to differences between regions (see Florunner cultivar, Table 2), but also to different cultivars studied.

The genetic manipulation of peanut chemistry has the potential to improve the nutritional quality of peanuts and peanut products. The incorporation of high-oleic genes into peanut breeding lines results in a high-oleic variety and consequently in an oil with extended shelf life. In Table 3, the fatty acid composition range of four high-oleic peanut lines obtained from two middle-oleic cultivars [25] is summarized. These obtained breeding lines, with oleic acid accounted for about 80% of the total fatty acids, had very good agronomic characteristics in Oklahoma (southwestern United States). The largest difference in the fatty acid composition was found to be the replacement of linoleic acid by oleic acid in high-oleic peanut oil.

Aboriginal peanut cultivars contain new sources of germplasm that can be used to increase the variability in the genetic base of cultivated varieties. Numerous wild species of peanut are found and have been collected in South America. Oil fatty acid composition of some wild species of peanut is summarized in Table 4. Significant differences were found within fatty acids among varieties of peanut [26]. The cultivars of the *hypogaea* Subspecie exhibited higher oleic acid content and O/L ratio (1.11–1.46), and lower IV means (98–108) than the *fastigiata* Subspecie (*Fastigiata*, *Aequatoriana*, and *Peruviana varieties*). Grosso and Guzmán [26] found IVs higher than the results obtained by Ahmed and Young [27] to peanut cultivars, attributing the differences to climatic conditions, soil moisture, and air temperature.

Grosso *et al.* [4] characterized the fatty acid composition of aboriginal peanut seeds from Bolivia and found similar results (*hypogaea*: O/L mean ratio = 1.30, IV mean = 100.9). Aboriginal peanut seeds from Ecuador (subspecies *hypogaea*: var. *hypogaea* and *hirsuta*; subspecies *fastigiata*: var. *fastigiata*, *peruviana*, and *aequatoriana*) were studied by Grosso and Guzmán [28] finding that the varieties *hypogaea*, *fastigiata*, and *peruviana* had lower IV (102–106) than the other varieties. The O/L ratio of var. *hypogaea* was higher (1.26) than cultivated runner-type peanut from the same region (1.20). Grosso *et al.* [29–31] studied seeds of different

Table 3. Fatty acid composition (% w/w) of Peanut lines developed through conventional breeding[a)]

	Peanut Lines	
FA	Middle-oleic	High-oleic
10:0	0.18–0.20	0.20–0.23
12:0	0.17–0.19	0.19–0.22
14:0	0.18–0.21	0.20–0.22
16:0	4.85–6.75	3.98–4.26
16:1	0.21–0.23	0.26–0.28
18:0	1.53–1.67	1.52–2.35
18:1n-9	45.6–68.2	79.6-81.0
18:2n-6	15.6-35.9	2.31–4.33
18:3n-3	0.23–0.27	0.25–0.28
20:0	1.01–1.10	1.09–1.35
20:1n-9	1.43–1.80	1.50–1.85
20:3n-6	0.19–0.21	0.21–0.23
20:4n-6	0.17–0.19	0.19–0.22
20:5	0.18–0.19	0.19–0.22
22:0	2.47–2.68	2.33–2.47
22:1n-9	0.33–0.36	0.30–0.39
24:0	1.67–1.68	1.44–1.68

[a)] Jonnala *et al.* [25].

Table 4. Fatty acid composition of wild peanut species (% w/w methyl esters)

	Fatty acids							
Species	C16:0	C18:0	C18:1	C18:2	C20:0	C20:1	C22:0	C24:0
A. appressipila[a]	10.0	2.3	30.8	47.4	1.3	2.1	4.2	2.0
A. batizocoi[b]	11.1	2.1	39.4	41.1	1.2	1.4	2.5	1.0
A. benensis[a]	11.1	2.4	31.6	43.3	1.8	2.3	5.8	1.8
A. cardenasii[b]	11.2	1.7	34.9	43.6	1.3	1.7	3.7	1.4
A. chiquitana[a]	10.2	2.2	36.3	44.9	0.9	1.8	2.4	1.3
A. correntina[c]	10.0	1.9	42.3	39.1	1.0	1.6	3.0	1.1
A. diogoi[a]	10.3	1.6	36.4	44.2	1.0	2.33	3.0	1.2
A. duranensis[c]	10.3	1.9	34.9	45.3	1.3	1.8	3.3	1.3
A. fastigiata[d]	11.8	1.8	35.0	44.1	1.6	1.6	2.3	0.7
A. helodes[a]	10.4	2.2	40.5	40.6	1.3	1.4	2.7	1.0
A. hoehnei[a]	9.6	1.9	38.1	42.1	1.2	1.7	4.0	1.4
A. hypogaea[d]	10.5	1.8	44.2	35.8	1.5	2.3	2.1	1.0
A. kempff-mercadoi[a]	10.4	1.8	37.4	43.3	1.1	2.5	2.1	1.1
A. kretschmeri[a]	9.8	1.9	37.5	40.1	1.3	2.9	4.9	1.7
A. kuhlmannii[a]	10.2	2.0	41.5	37.9	1.3	2.1	3.7	1.4
A. magna[c]	11.9	1.6	38.8	39.3	1.3	1.7	4.0	1.3
A. matiensis[a]	9.6	1.9	30.6	44.6	1.3	3.2	6.2	2.3
A. monticola[b]	10.7	2.6	38.0	42.5	1.4	1.4	2.3	1.0
A. paraguariensis subsp. *capivarensis*[c]	8.3	1.5	31.8	47.5	1.0	3.1	4.9	1.9
A. paraguariensis subsp. *paraguariensis*[c]	9.3	1.6	30.3	48.8	0.9	2.5	4.4	2.2
A. pintoi[a]	9.9	1.7	35.5	44.7	1.3	1.5	4.0	1.5
A. rigonii[c]	10.3	1.8	35.0	43.7	1.6	2.1	3.7	1.8
A. stenosperma[a]	10.5	1.7	38.0	40.8	1.2	2.1	4.1	1.7
A. sylvestris[a]	10.0	1.6	39.5	41.2	1.0	1.9	3.2	1.6
A. trinitensis[a]	10.5	2.6	35.1	45.3	1.0	1.3	2.0	1.9
A. valida[a]	9.8	1.8	41.6	35.7	2.0	2.1	5.4	1.7
A. villosa[a]	10.7	2.5	46.8	34.1	1.3	1.3	2.1	1.1
A. williamsii[a]	11.7	1.8	35.5	39.8	1.5	2.3	5.7	1.7

[a] Grosso *et al.* [29].
[b] Grosso *et al.* [31].
[c] Grosso *et al.* [30].
[d] Grosso and Guzmán [26].

species (Table 4) from different origin (Argentina, Brazil, Bolivia, Paraguay, Peru, and Uruguay) concluding that the chemical quality and stability of oils from these wild peanuts were not better than those of cultivated peanuts, except for *A. villosa* and *A. valida* that exhibited better O/L ratio (1.37 and 1.17, respectively). Some species showed concentration of behenic acid (C22:0) higher than 5% (*A. matiensis*, *A. valida*, *A. Kretschmeri*, and *A.Williamsii*). IV was lower in *A. valida* (98.5–99.8).

No data have been found reporting any influence of post-extraction process over fatty acid composition of peanut oil. Since fatty acid composition of the TAG fraction is similar to that of the whole oil [5], it would be reasonable that the latter would not be affected significantly by processing, in accordance with findings to other oils [32, 33]. Sanders [5] reported that no *trans*-fatty acids had been detected in major US brands of peanut butter.

The intermediate content of saturated fatty acids and high linoleic/linolenic acid (L/Ln) ratio observed in peanut oil (more than the recommended by some organizations of different countries that is *ca.* 10% of saturated fatty acids and 5 or less of L/Ln ratio) disqualify it to be used as the principal oil of the human diet, being an alternative to use it in mixes with oils or fats providing other fatty acids [34].

1.1.2 Triacylglycerol composition

Most of the peanut oil fatty acids are present as TAGs (93.3–95.8 wt%) [5, 7]. Sanders [5] demonstrated that seed maturation influences over TAG content of the obtained oil showing an increment of *ca.* 10% from an early maturation stage accounting for 25.3% of oil (TAG content 85.3%) to a fully stage with 48.2% of oil (TAG content 95.8%). Working on African peanut oil, Sempore and Bezard [15] identified 30

TAG by HPLC-RID reporting the major TAG as: OOL (17%), PLO (13%), LLO (12%), OOO (10%), POO (8%) (P = palmitic, O = oleic, S = stearic, and L = linoleic acids). In the above-mentioned study, the very long-chain saturated fatty acids were always found associated with unsaturated fatty acids, preferably with two molecules of linoleic acid. In contrast, the analysis by HPLC combined with atmospheric pressure chemical ionization MS (APCI-MS) of two samples from peanuts of unknown origin revealed the following main TAG: OOO (34–46%), OOL (13–17%), POO (10–12%), and LLO (7–9%) [35]. It is supposed that these samples were of high-oleic cultivars. Similarly, main TAG from polish peanut oil analyzed by HPLC-UV technique were: OOO (31.2%), POP (18.4%), OOL (15.9%), POO (11.6%), LLP (6.9%), and LLO (6.4%) [14]. The great diversity between the samples analyzed was probably due to differences in the peanut origins. Manganaro *et al.* [36] found differences in the TAG structure of genetic varieties of North American, African, and Argentinean origin. The major differences reside in the linoleic/oleic acid ratios in the TAG, especially in the *sn*-2 position, and in the proportions these acids are combined with the long-chain fatty acids. However, the three oils possess closely similar GLC elution profiles and carbon number (CN) proportions (CN50 = 3.0–3.7%, CN52 = 21.1–24.2%, CN54 = 54.7–59.5%, CN56 = 7.4–7.9%, CN58 = 5.7–6.9%, and CN60 = non-detected up to 3.4%).

In comparison with other common vegetable oils (*i.e.*, olive, soybean, or sunflower oil), the high percentage (>12%) of TAG with CN higher than 54 is remarkable. TAG from 56 to 60 CNs mainly represent combinations of two C18 and one long-chain (C20–C24) fatty acid *per* TAG molecule [36]. The presence of these TAG molecules could be used to identify adulterations of other oils with peanut oil. The occurrence of this higher melting fraction with non-crystalline properties generally hinders the use of peanut oil as salad oil [8, 37].

More than 160 TAG were identified in peanut oil by HPLC-tandem MS [38] most of them being di- and triunsaturated (POO, SOO, PLO, OOO, OLO, LLO, and LLL). Natural peanut oils possess markedly non-random enantiomeric structures of highly asymmetric positional placement of the long-chain saturated fatty acids [5, 7, 18, 34, 36]. The long-chain saturated fatty acids (C20–C24) are confined almost exclusively to the *sn*-3-position, whereas the palmitic and stearic acids are more predominant in the *sn*-1 and *sn*-3 positions. Moreover, oleic acid is distributed almost evenly in the three positions, while the linoleic acid is preferably found in the *sn*-2 position [8]. Yoshida *et al.* [39] noticed that those unsaturated fatty acids located in *sn*-2 position are significantly protected from oxidation during peanut seed microwave roasting.

Concentrations of specific TAG species may vary with variety and location [5]. Moreover, Sanders [5] concluded that the environment affects not only fatty acid composition of peanut oil but also, although apparently in an indirect way, the spatial arrangements of those acids on the TAG. Generally, a higher percentage of oleic or linoleic acid in the TAG resulted in a greater proportion of the particular fatty acid in the *sn*-2 position.

From the nutritional point of view, not only the oil fatty acid profile is important, but also the distribution of the fatty acids in the three positions of the glycerol skeleton. It is known that the *sn*-2 position is conserved during the whole digestive process while fatty acids from *sn*-1 and *sn*-3 are released by pancreatic lipase. Moreover, long-chain saturated fatty acids present preferentially at these positions and with melting points higher than human body temperature (C18:0, C20:0, C22:0, and C24:0) remain free and solid in the intestinal lumen presenting weak intestinal absorption and no effect on plasma lipids [34].

1.2 Minor saponifiable compounds

1.2.1 Free fatty acids (FFAs) and diacylglycerols (DAGs)

FFAs and DAGs are present in raw peanut oil. Crude oil can have a FFA content as low as 0.3%, but most of the commercial oil is in the range 0.5–1.5% [7]. FFA and DAG levels vary considerably according to peanut maturity. As peanuts of the Florunner variety mature from the flattened and white immature stage to full maturity, FFA content decreases from 4.5 to 0.7%, and DAG content drops from 2.4 to 0.5% [40]. In addition, the degree of damage to the kernels also affects FFA content. Sound mature peanuts generally have an FFA content of less than 0.5%. On occasions, if the peanuts are high in mold damage and/or very immature kernels, levels up to 5% are encountered [40]. As a result, high percentages of FFA may indicate poor handling, immaturity, mold growth, or other ester hydrolysis activity [17]. Whereas FFA are eliminated during various processing steps, DAG are only partially removed; hence, they constitute an important index not only for the original quality of the oil but also for the resulting refined oil. DAG with 34 and 36 CNs are commonly present in peanut oil as 1,2- and 1,3-isomers, being the reported DAG the following: 1,2-PO, 1,2-PL, 1,3-PO, 1,3-PL, 1,2-OO, 1,2-OL, 1,3-OO, 1,3-OL, and 1,3-LL [41].

1.2.2 Phospholipids (PLs)

PLs in peanuts are the major constituents of cell membranes, and they have a high degree of unsaturation [42]. The PL content (0.3–0.7%) is low in peanut oil. The major PL in conventional peanut oils are the following: phosphatidylcholine (PC: 38.3–66.4%), phosphatidic acid (PA: 2.2–11.8%), phosphatidylethanolamine (PE: 13.3–21.9%), phosphatidylinositol (PI: 15.7–30.9%), and phosphatidylglycerol (PG: non-reported up to 2.5%) [40, 43, 44]. Table 5 shows PL composition ranges of high-oleic peanut cultivars,

Table 5. PL composition and total PL content of high-oleic peanuts developed through conventional breeding[a)]

	PL distribution (%)				
Oil Samples	PC	PE	PA	PI	Total PL (mg/100 g oil)
Parental lines[b)]	38.3–38.6	20.2–21.9	10.7–11.8	27.7-30.9	472.1–556.5
Breeding lines[c)]	42.1–48.3	20.8–24.7	10.4–14.1	19.1–22.0	362.2–708.6

[a)] Jonnala *et al.*[43].
[b)] SunOleic and Tamrun 96.
[c)] Tamrun OL 01, Tamrun OL 02, TX 977164, TX 977239.

comparing breeding lines with their parental lines [43]. Although the authors found statistical differences among the PL contents and the composition of breeding lines and parent lines, these variations were within the range reported for traditional peanut varieties.

Changes in PL concentration may occur when peanuts are harvested prematurely, cured at a high temperature, and/or exposed to freezing temperatures [44]. In many cases, the quality is affected and the oil becomes increasingly difficult to refine. Singleton and Stikeleather [44] studied the effects of these stress events founding that immature seeds presented higher total PL content and higher concentrations of PA, PE, and PC than mature peanuts. The decrease in concentration of PA and PC with maturation was explained on the basis that these PL are the precursors to the formation of the other PL. All PL increased in concentration in the heat-damaged sample (at 40°C), except for PG. In contrast, in the freeze-damaged sample, a significant increase in concentration was observed for PA and PG, whereas the concentrations of PC and PE decreased to very low levels when compared to the control sample. The authors also determined the major PC molecular species. In mature peanuts, 40.7 and 59.3% of C18:2 + C18:2 and C18:2 + C18:1 were found, respectively. Immature peanuts presented greater concentrations, but equal proportions of the above mentioned species. In contrast, molecular species found in the high temperature cure sample had a higher degree of saturation due to the presence of C18:1 + C16:0 molecular species (72.8%). This fact was attributed to the oxidation of the more unsaturated molecular species by heat stress.

1.3 Minor unsaponifiable compounds

Sterols are the predominant compounds in the unsaponifiable material of vegetable oils, typically accounting for 60–80%. Hydrocarbons, tocopherols, and others comprise the remaining 10–25%.

Vegetable oil sterols, known as plant sterols, can be divided into three groups: (i) 4-desmethylsterols (the cholestane series), *i.e.*, normal phytosterols (PSs); (ii) 4-monomethylsterols (usually known as methylsterols); and (iii) 4,4′-dimethylsterols (the lanostane series, also known as triterpene alcohols). The three sterol groups differ in the conformation of carbon 4 in the steroid skeleton. The desmethylsterols have no methyl group at position 4, while the 4-monomethyl- and 4,4′-dimethylsterols have one and two methyl groups there, respectively. The desmethylsterols (or normal PSs) typically account for more than 50% of the unsaponifiable material, while 4-monomethylsterols and 4,4′-dimethylsterols together constitute 10–30%. Sterols occur mainly as free molecule or sterol ester forms, but they also can occur as sterol glucosides and acylated sterol glucosides [45]. Table 6 compares minor unsaponifiable compounds found in peanut oil with those from soybean oil.

1.3.1 Sterols (4-desmethylsterols or phytosterols)

Peanuts and its products, such as peanut oil, peanut butter, and peanut flour, are good sources of PSs. Roasted peanuts contain 61–114 mg PS/100 g depending on the peanut variety, 78–83% of which is in the form of β-sitosterol [46]. Typical sterol composition of crude peanut oil is exposed in Table 6, showing that peanut oil can have a higher percentage of Δ-5-avenasterol than soybean oil. Peanut and soybean oils present similar proportion of their principal sterol, β-sitosterol.

The unsaponifiable fraction of peanut oil includes 0.15–0.90% hydrocarbon sterol esters and 0.59–1.22% free sterols [40]. Worthington and Hammons [47] examined steryl ester and free sterol components of two commercial peanut varieties finding that free PSs of both Florunner- and Star-type peanuts consisted of about 65% of the total sterols in the oil. Unrefined peanut oil contains up to 434 mg PS/100 g, value similar to that of unrefined soybean oil. Refining these oils results in reduction in PS concentration in the oil [8]. Further refining, such as deodorization, results in significant loss in PSs, but hydrogenation after refining has a minimal effect on PS loss [46]. It has been reported that conventional refining does not significantly affect sterol composition expressed as percent of total sterols. The relative proportions of the major sterols remain constant throughout the process [45].

Table 6. Minor unsaponifiable compounds of crude peanut oil and soybean oil

Components	Peanut oil	Soybean oil
Total unsaponifiable compounds (g/kg)[a)]	≤10	≤15
Sterols (mg/kg)[a,b)] (% of total sterols)	900–4344	1800–4500
Cholesterol	ND[c)]–3.8	0.2–1.4
Brassicasterol	ND–0.4	ND–0.3
Campesterol	11.4–19.8	15.8–24.2
Stigmasterol	4.8–13.3	14.9–19.1
β-Sitosterol	47.4–69.0	47.0–60.0
Δ-5-Avenasterol	5.0–19.0	1.5–3.7
Δ-7-Stigmasterol	ND-5.2	1.4–5.2
Δ-7-Avenasterol	ND–6.6	1.0–4.6
Others	ND–1.4	ND–1.8
4-Monomethylsterols (mg/kg)[b)]	157	658
Triterpene alcohols (mg/kg)[b)]	360	845
Squalene (mg/kg)[b,d,e)]	270–1296	ND–170
Total Tocopherols (mg/kg)[a,d,e)]	137–934	993–3370
(% of total tocopherols)		
α – Tocopherol	18–57	3–10
β – Tocopherol	ND–2	ND–2
γ – Tocopherol	36–78	35–64
δ – Tocopherol	ND–6	6–27
Tocotrienols (mg/kg)[a,d)]	ND–474	ND–173
Chlorophylls (mg/kg)[e)]	1.4–1.6	11.9–12.1
β-Carotene (mg/kg)[e)]	0.1	0.2–0.4

[a)] CODEX [16].
[b)] Padley *et al.* [7].
[c)] ND: non-detectable (≤0.05%).
[d)] O'Brien [1].
[e)] Tuberoso *et al.* [14].

Conventional breeding is widely used for modification of various crop and oilseed traits such as fatty acid composition and disease resistance. The effect of breeding on the nutritionally beneficial bioactive plant components in new high oleic peanut cultivars, particularly in Oklahoma grown peanuts crossed from SunOleic and Tamrun 96, was examined by Jonnala *et al.* [43]. They found that a high oleic peanut line (Tamrun OL 01) had higher total PS content (725 mg/100 g oil) than those for the parent lines (670 and 350 mg/100 g oil). In all samples, β-sitosterol was the major PS (75–90% of the total PSs). The other PS found were campesterol (6–14%) and stigmasterol (3–11%).

Genetic engineering offers great potential for developing peanut cultivars resistant to a broad spectrum of pathogens that pose a recurring threat to peanut health. Transgenic peanut lines with increased resistance to fungal diseases, as compared to the parent line, showed no major changes in the PS content with respect to non-transformed cultivars [48].

Grosso and Guzmán [24] analyzed three varieties of peanut oils (runner, valencia, and virginia types) grown in Argentina. They found that β-sitosterol was prominent in all three cultivars according to data reported by Codex [16] (see Table 6).

Wild peanut variety oils from Peru (*Hypogaea*, *Fastigiata*, *Aequatoriana*, and *Peruviana* varieties) [26], from Ecuador (*Hipogaea*, *Hirsute*, *Fastigiata*, *Peruviana*, and *Aequatoriana* varieties) [28], from Bolivia (*Hypogaea*, *Fastigiata*, and *Peruviana* varieties) [4], from Bolivia and Argentina (*A. correntina*, *durannensis*, *monticola*, *batizocoi*, and *cardenasii* species) [31], and from Bolivia, Argentina, Brasil, Paraguay, and Uruguay (*A. duranensis*, *A. rigonii*, *A. magna*, *A. diogoi*, *A. appressipila*, *A. Kuhlmannii*, *A. valida*, *A. Hoehnei*, *A. paraguariensis* subsp. *capivarensis*, *A. paraguariensis* subsp. *paraguariensis*, *A. correntina*, *A. Williamsii*, *A. villosa*, *A. Kretschmeri*, and *A. pintoi*) [30] showed similar PS compositions to peanut cultivars. Significant differences were observed for campesterol (14.73%) and Δ-5-avenasterol (9.66%) compositions of the Ecuadorian origin varieties and for β-sitosterol (53.3%) in the *A. paraguariensis* subsp. *paraguariensis* specie from Paraguay. They showed lower values than the other species. Brassicasterol was not detected. Grosso *et al.* [29] studied the composition of 17 wild peanut species concluding that sterol composition does not permit characterization of the section of wild peanut.

1.3.2 Methylsterols and triterpenic alcohols

The 4-monomethylsterols are intermediate products of the biosynthesis of PSs. The methylsterol content in peanut oil (157 mg/kg) is appreciably lower than in soybean oil, being the main compounds identified obtusifoliol (25.5%), gramisterol (28.0%), and citrostadienol (24.2%) [7].

The composition of terpene fractions vary markedly from one oil to another. Triterpenes in peanut oil represent the 0.14% of the oil [49]. Typical triterpene alcohol composition of peanut oil is: cycloartanol (1.9%), β-amyrin (6.9%), cycloartenol (33.1%), 24-methylene cycloartenol (46.1%), and cyclobranol (8.1%) [7].

Squalene is a triterpene hydrocarbon with secondary antioxidant activity compared to that of phenols and tocopherols. It has been detected in peanut oil in significant higher concentration than in soybean oil (see Table 6), representing more than the 20% of the olive oil content [14].

Kolhe *et al.* [50] reported that 3-oxo triterpenes are not present in peanut oil, being the practical significance of this fact that oxo triterpenes could be used to detect contamination with other oils or fats.

1.3.3 Tocopherols and tocotrienols

Tocols, natural antioxidants found in plant oils like peanuts, include four tocopherol and four tocotrienol isomers, each designed as α, β, γ, and δ, on the basis of the chromanol ring. These antioxidants inhibit lipid peroxidation in foods by stabilizing hydroperoxids and other free radicals. The natural antioxidant content decreases during each stage of processing. Caustic chemical refining can remove as much as 10–20% of the tocopherols and tocotrienols, but 30–60% can be

lost with deodorization or steam distillation [1]. Ayres [40] reported a considerable level of tocopherols in refined peanut oil with a total tocopherol content of 53 mg/100 g and mostly as α- and γ-tocopherol.

Crude peanut oil has only 30–40% of the soybean oil content of tocopherols, but shows almost three times more tocotrienols than soybean oil (see Table 6). Codex [16] reported no detectable amount of α, γ, and δ tocotrienols in arachis oil. Casini *et al.* [51] found total tocopherol levels between 199 and 815.6 ppm to crude type runner peanut oil from Argentina considering four harvest periods and concluded that tocopherol content increases with higher precipitations and lower soil temperatures.

Hashim *et al.* [52] found significant differences within the tocopherol profile among maturity stages of runner- and virginia-type peanut cultivars. α-Tocopherol and γ-tocopherol decreased or increased with maturation, depending on the peanut cultivar type. Comparing the content of tocopherols in peanut oils from Argentina, China, and United States, Sanders *et al.* [17] found they were higher in peanuts originated from USA (210.1–243.8 ppm) and lower in that from China (102.9–183.9 ppm).

Tocopherol composition of peanut lines from conventional breeding was reported by Jonnala *et al.* [43]. One of the parental lines (Tamrun 96) had the highest total tocopherol content (32.2 mg/100 g oil). For all the peanut lines, over 50% of the total tocopherols were in the form of α-tocopherol, being γ-tocopherol the next most abundant tocopherol in peanut genotypes (24–33%). The differences in the tocopherol content were not substantial enough to cause any nutritional concerns. Similar results were found by Jonnala *et al.* [48] studying transgenic peanut lines and by Hashim *et al.* [52] for runner-type peanuts.

1.3.4 Pigments

Color is an important quality parameter of edible oil, both in the refining process and in the marketplace. Primarily owing to naturally occurring polyphenolic pigments, gossypol, chlorophyll, and carotenoids, each oil has its own characteristic color. Peanut oil of the first grade for cooking should not exceed 2 Lovibond red with fixed Lovibond yellow 20 according to Chinese National Standard, and peanut oil of the first grade for salad use should be no more than 1.5 Lovibond red with fixed yellow 15 [53].

Pattee *et al.* [54] suggested that carotenoids are in areas separated from the oil containing spherosomes of the peanut kernel, so the lighter color of the pressed oil compared to the solvent extracted oil might be due to quantitative leaching of carotenoids by the oil instead of the solvent. Comparison of the increase in oil content with the very slight increase in carotenoid content during peanut maturation shows that the reduction in carotenoid concentration is due to a dilution effect by the oil.

Kornsteiner *et al.* [55] reported that the total amount of carotenoids (α- and β-carotene, zeaxanthin, lutein, cryptoxanthin, and lycopene) in peanut oil was marginal. Moreover, Tuberoso *et al.* [14] reported low concentration of β-carotene and chlorophylls in peanut oil, remarking the difference in chlorophylls content with soybean oil (see Table 6).

1.3.5 Aliphatic compounds

Peanut oil has shown a chromatogram of the crystallizable wax fraction similar to that of the soybean oil and contains only 50 ppm of C34–C42 soluble esters, almost one third of the refined soybean oil content. These soluble esters are monounsaturated waxes with the same fragment 278 in their mass spectrum as in sunflower and soybean oils [56].

Free primary alcohols such as hexacosanol and octacosanol have been found to be feeding stimulants for silkworm larvae. Peanuts have shown to have a content of octacosanol of 23.4 μg/g of oil in seed coat and 9.2 μg/g of oil from germ [57].

1.3.6 Phenolic compounds

Resveratrol (3,4′,5-trihydroxystilbene) is a phenolic compound found naturally in fruits, nuts, flowers, seeds, and bark of different plants. Peanut is one of the potent natural sources of resveratrol [58]. It exhibits a wide range of biological effects, including antiplatelet, anti-inflammatory, anticancer, antimutagenic, and antifungal properties. It is also a potent antioxidant, ROS scavenger, and metal chelators. Resveratrol reduces lipid peroxidation as well as oxidation and nitration of platelet and plasma proteins [59].

In peanuts, resveratrol is usually found in fresh kernels or in peanuts products like butter or roasted nuts. The content of resveratrol varies widely, depending on varieties, peanut product, and processing. For fresh peanuts content varies from 0.01–1.79 μg/g [60] up to 2.3–4.5 μg/g [58]. Studies have shown an important increase (four to six-folds) in resveratrol production after peanut germination, incubation for 48 h of fully imbibed peanut kernels, exposure to UV light or grinding [58, 60–62]. Until now, no scientific data have been reported about resveratrol content in peanut oil. No phenolic compounds were detected in cold-pressed peanut oil [14].

1.3.7 Volatile compounds

The pleasant nut-like flavor associated with peanuts fractionates with the oil rather than with the meal during separation. The flavor is accentuated with oxidation but does not become offensive as quickly as some other vegetable oils [1]. The most important volatile compounds found in peanut oil are 2,4-decadienal, hidrocarbons, menthol, nonanal, and 2-nonenal [63], whereas in raw peanut hexanal and 1-methylpyrrole were the volatiles found mainly [64].

1.3.8 Trace metals

Trace amounts of metals are absorbed by plants during the growing season and introduced during fat and oil processing. Heavy metal amount in commercial refined peanut oils, particularly cadmium and lead are very low and close to ones found in literature for seeds [65]: 65–110 μg/kg of Cu, 5–14 μg/kg of Pb, 1–3 μg/kg of Cd, and 53–500 μg/kg of Zn. Sanders *et al*. [17] analyzed pressed cake of peanuts from different countries and different crop years reporting values between 6.15 and 21.22 ppm for copper and between 37.87 and 80.28 ppm for iron.

2 Conclusions

Peanut and soybean belong to the same legumes family. This fact could be the explanation for finding similarities in the chemical composition of both oils, like sterols and crystallizable waxes. However, other compounds are present in peanut oil in different amounts than in soybean oil. Its chemical composition makes peanut oil an alternative to be taken into account for human consumption. This oil has intermediate saturated fatty acids content, especially in palmitic acid. However, most saturated fatty acids are confined almost exclusively to the *sn*-1 and *sn*-3 positions of the TAG, letting them be less harmful to human health than their location in the *sn*-2 position. Peanut oil seems to be a good choice to be used in cooking because of its high oxidative stability and the presence of minor components with antioxidant and nutritional properties. In this paper, we presented the variability of composition found in peanut oils linked to different parameters. Some of them show a clear direction, as the increment in TAG and O/L ratio with maturation, while others need to be analyzed in each specific case, as environment, variety, or combination of different parameters. In addition, the enhancements reached in oxidative stability with genetic manipulation should be mentioned. Genetic manipulation is an important key to achieve possible improvements over peanut cultivars and their oils. Progress in genetics and breeding research to obtain new varieties is a strong justification for increasing investment in peanut-breeding programs. Moreover, the possibility of using wild *Arachis* species as a genetic resource could be utilized to improve resistance to some plant diseases like spots and virus. Development of enhanced breeding lines/cultivars would result in economic gains to peanut farmers, with the possibility of putting peanut cultivars in a better position to compete with other productions.

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