

Chapter 5

Virgin Walnut (*Juglans regia* L.) Oil



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Abstract The consumption of nuts (e.g. walnuts, pistachios, almonds) has recently received particular attention due to their high content of unsaturated fatty acids, antioxidants and other biologically active compounds and, thus, their potential beneficial health effects. Apart from nuts, a growing interest towards virgin vegetable oils has also increased recently. The main reasons for this trend are marked by consumers that increasingly appreciate the taste and smell of oils related to the raw materials from which they come from as well as by their potential nutritional properties -resulting in novel healthy oils- with added value for the consumers as compared to the common industrial refined vegetable oils. The purpose of the current chapter is to analyze and discuss the current knowledge on the extraction and processing of virgin walnut oil as well as the composition and properties of major (fatty acid profile) and minor components (tocols, phenolics, sterols, carotenoids, flavour and aroma compounds), which are directly related to their organoleptic and functional traits. Virgin walnut oils are characterized by a high content of linoleic (50–65%) and linolenic (up to 20%) acids, phospholipids (16.5 g/kg), sterols (1.5–2.2 g/kg), and tocopherols (220–650 mg/kg). These bioactive phytochemicals have well known health-promoting impacts, as well as a peculiar sensory properties.

Keywords Gourmet oils · Cultivar · Chemical characterization · Bioactive compounds · Health-promoting effect

Abbreviations

FA	Fatty acids
LDL	Low-density lipoprotein
MUFA	Monounsaturated FA
PUFA	Polyunsaturated FA

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SFA	Saturated FA
TAG	Triacylglycerols
TPP	Total polar phenolics
VWO	Virgin walnut oil

1 Nuts and Their Oils

Walnut (*Juglans regia* L.) is a plant of the Juglandaceae family native to Central Asia, the western Himalayan chain and Kyrgyzstan (Fernández-López et al. 2000; Salas-Salvadó et al. 2011) that was introduced in Europe before Roman times (1000 B.C.), from where spreads to other regions with a Mediterranean type ecosystem throughout the world such as USA and North of Africa. Nowadays, it is in continuous expansion thanks to new cultivars that adapt better to different climatic conditions. Currently, China is the major crop producer (1,785,879 tons) followed by the USA (607,814 tons), Iran (405,281 tons) and Turkey (195,000 tons) (Martínez et al. 2010; FAOSTAT data 2014), although USA and France are the main exporting countries.

Thanks to their potential to improve lipids profile in blood and to reduce the risk of coronary heart diseases (CDH), walnuts have been the focus of intense research studies (Sabaté et al. 2010; Amarowicz et al. 2017). These health benefits could be attributed to the high amount of unsaturated fatty acids in nuts, as well as to the dietary fibre and phytosterols that inhibit the absorption of cholesterol in the digestive tract (Bolling et al. 2011). The high unsaturated/saturated fatty acid ratio (10) found in walnuts (60% of linoleic acid and 15% of oleic and linolenic acid each; Tables 5.1 and 5.2) was the aim of several investigations, showing a good balance of *n*-6 and *n*-3 polyunsaturated fatty acids (PUFA), beneficial in decreasing the incidence of cardiovascular risk and lowering the blood cholesterol (Simopoulos 2002).

Table 5.1 Composition of walnut, its virgin oil and residual cake

Walnut		Virgin Walnut Oil (VWO)		Residual cake	
Moisture (%)	3–5	Fat yield (%)	78–90	Moisture (%)	5.5–6.5
Fat (%)	62–71	TAG (%)	96–98	Fat (%)	6–10
Protein (%)	14–16	SFA (%)	9–11	Protein (%)	26–30
Fibre (%)	6.5–7.5	MUFA (%)	15–24	Fibre (%)	12–15
Phenolics (%)	1.0–1.3	PUFA (%)	66–75	Phenolics (%)	1.6–2.0
		Phospholipids (g/kg)	16.5		
		Sphingolipid (g/kg)	2.9		
		Sterols (g/kg)	1.5–2.2		
		Tocopherols (mg/kg)	220–650		
		Pigments (mg/kg)	7–20		
		Phenolics (mg/kg)	14–26		
		Volatiles (mg/kg)	4–9		

TAG triacylglycerols, SFA saturated fatty acids, MUFA monounsaturated fatty acids, PUFA polyunsaturated fatty acids

Table 5.2 Fatty acid (FA) and triacylglycerols (TAG) composition (%) of VWO

P-C16:0	Po-C16:1	S-C18:0	O-C18:1	L-C18:2	Ln-C18:3	References
Virgin oil						
6.6–7.8	–	1.5–2.2	17–28	50–59	1.9–19	Martínez et al. (2006)
6.3–7.5	0.0–0.4	1.7–1.7	16–24	58–65	9.1–11	Rabrenovic et al. (2011)
6.7–7.3	0.1–0.1	2.4–2.7	15–16	60–62	13–15	Ojeda-Amador et al. (2018b)
6.0	0.1	2.4	14.5	61.5	14.1	Rabadán et al. (2018)
Solvent-extracted oil						
6.3–7.5	0.1	2.2–2.8	14–18	58–63	9.6–13	Amaral et al. (2003)
7.1	0.1	2.3	13.5	63	0.05	Arranz et al. (2008)
5.9	0.0	2.3	18	63	10	Derewiaka et al. (2014)
LLL	LOL/OLL	LLLn	OOL	Total		References
Virgin oils						
25–29	14–16 ^a	15–18	–	–		Bada et al. (2010)
Solvent-extracted oil						
135	111	97	–	–		Holčapek et al. (2005) ^b
–	–	–	–	97		Miraliakbari and Shahidi (2008)
31	29	14	10	–		Tu et al. (2016)

P palmitic, Po palmitoleic, S stearic, O oleic, L linoleic, Ln Linolenic

^aOLL+PoLO

^bIndividual triglycerides expressed as mg/kg

Moreover, the PREDIMED study (Prevention with Mediterranean Diet) as well as other clinical trials, have confirmed that a high intake of walnuts can lower the incidence of hypertension, diabetes, cancer and other inflammatory conditions (Salas-Salvadó et al. 2008; Mohammadifard et al. 2015; Amarowicz et al. 2017). The US Food and Drug Administration (FDA) approved in 2003 a health claim regarding the recommended consumption nuts (42 g, 1.5 oz daily) that may reduce the risk of heart disease.

On the other hand, minor compounds (i.e., tocopherols, phenolics and phospholipids) can act as antioxidants, reduce oxidative damage of cellular biomolecules such as lipids, proteins, and nucleic acids and protect against certain types of cancer (Aruoma 1998), apart from improving the oil oxidative stability (Wang et al. 2002; Alasalvar et al. 2003) due to their radical scavenging function. Due to the high energetic value of nuts, studies showed that the intake of nuts not only does not increase the body weight but also promotes satiety (Vadivel et al. 2012; Souza et al. 2017).

Apart from nuts, a growing interest towards their virgin vegetable oils has appeared in recent years, which goes beyond the olive virgin oil. The main reasons for this trend are marked by consumers that increasingly appreciate the taste and smell of the raw materials from which the oil is extracted as well as by their potential nutritional properties, resulting in novel gourmet oils. These possess an added value for the consumers as compared to the common industrial refined vegetable oils (Kamal-Eldin and Moreau 2010), being the denominated “virgin” or “cold-pressed” oils (as defined by FAO-WHO Codex Stan 210 1999) generally recognized

as a synonym of quality and enjoyment by consumers (Matthäus 2008). A recent project for amending the standard for named vegetable oils FAO-WHO Codex Stan 210 (CX/FO 15/24/11 2015) is under consideration with the purpose of incorporate composition standards for cold-pressed oils including virgin nut oils (e.g. walnut, pistachio and hazelnut). These virgin oils obtained from nuts are considered as specialty oils due to their flavor and healthy properties and are generally produced in small size mills with a low production and sold in healthy markets mainly employed in gastronomy (Kamal-Eldin and Moreau 2010). Virgin walnut oil (VWO) is used for edible purposes, mainly as salad dressing, and in the cosmetic industry as a component of dry skin creams, antiwrinkle and anti-aging products (Martínez et al. 2010).

More attention has also been focused on the valorization of food processing by-products (Nyam et al. 2009). In this sense, the pressing process of walnut oil extraction produces a residual partially defatted cake, which could result as a disposal problem for the industry. However, this by-product retains nutrients and bioactive compounds (Table 5.1) that may be used as a natural source of phytochemicals and antioxidants for dietary supplements as well as ingredients for functional foods.

2 Extraction and Processing of Nut Oils

The production and consumption of edible virgin oils date from 8000 years ago. More than one century ago, the development of a production technology by means of organic solvents extraction led to an important increase in the yield of this industry, although implies the requirement of a refining of the raw extracted oil, that led to the disappearance of the virgin oils from market (except the virgin olive oil). However, a recent interest for consuming less processed foods appeared among consumers, which demand the production of virgin oils produced in small amounts with a simple production technology (Matthäus 2008). Nevertheless, the industrial production of VWO is still searching for appropriate procedures to rich higher performances and to prevent oxidative degradation during oil extraction due to the high unsaturated fatty acid content (Martínez et al. 2010).

Nut oils can be extracted using pressure systems (expelling by screw press or pressing by hydraulic presses), obtaining virgin oils with a high nutritional value, or employing solvents that require a later refining process. Mechanical systems are considered as cold extraction methods since only pressure is applied, although the screw press system requires the heating of the barrel to obtain satisfactory extraction yields like in the case of virgin pistachio oils (Sena-Moreno et al. 2015; Ojeda-Amador et al. 2018a) or pumpkin seed oils (Rezig et al. 2018). Such heating produces pleasant sensory characteristics with great acceptance by consumers (Álvarez-Ortí et al. 2012). According to Martínez and Maestri (2008), the nut moisture may be more important than heating in terms of oil recovery employing a screw press. The pre-treatment of seed and nuts before extraction is one of the most relevant parameters that influence the process yield. VWO is often produced

in small-scale artisanal mills and sold in gourmet and health markets promoted by their sensory characteristics (color, smell and taste) as well as bioactive compounds with functional properties (Ramadan and Elbanna 2017; Ojeda-Amador et al. 2018a).

The oil extraction process generates a partially defatted by-product (denominated residual cake) which retains nutrients and bioactive compounds present in their kernels, being of great interest their valorization as potential functional ingredients (Santos et al. 2013).

The industrial edible vegetable oils are mainly manufactured by solvent extraction, which requires a refining process that removes a great amount of the minor components like antioxidants and aromatics, reducing therefore the quality of this kind of edible oils. In the case of walnut oil, the solvent extraction method seems to be not suitable on an industrial scale due to the great amount of solvent needed to extract the high lipid content of this nut (Martínez et al. 2010); although, this system could be used to deplete the residual cake obtained after pressing.

Finally, supercritical fluid extraction is an alternative extraction method that usually employs compressed carbon dioxide for the extraction of the oil; in the case of walnut oil, the highest oil recovery (12% of residual oil content in the cake) was obtained employing a pressure of 400–500 bar (Salgin and Salgin 2006).

3 Lipid Composition of Walnut Virgin Oil

Walnut is one of the highest oil-rich nut (Table 5.1; Venkatachalam and Sathe 2006). Different studied cultivars showed an oil range between 62% and 71% (Ozkan and Koyuncu 2005; Dogan and Akgul 2005; Gharibzahedi et al. 2014). As concerned the partially defeated cake obtained after screw pressing, its residual oil content was 6–10% (Table 5.1; Ojeda-Amador et al. 2018b).

The fatty acids profile of VWO is shown in Table 5.2, being remarkable the high amount of essential linoleic acid (50–65%; Amaral et al. 2003; Martínez et al. 2006; Rabrenovic et al. 2011; Ojeda-Amador et al. 2018b; Rabadán et al. 2018), which is higher than other seed and nut oils (e.g. 9–12% palm oil; 48–59% soy oil; 16–37% pistachio oil; 15–34%, almond oil; FAO-WHO Codex Stan 210 1999, and its project for amending CX/FO 15/24/11 2015). VWO from Sejnovo variety had the highest and Franquette the lowest linoleate content. Oleic and linolenic acids were the second and third in abundance (14–28% and 9–19%, respectively), showing Franquette the highest proportion in oleic acid, whilst Chandler contributes with a major proportion of linolenic acid. It is important to remark that walnuts are the only tree nut containing a significant amount of α -linolenic acid (C18:3 ω -3, Derewiaka et al. 2014).

The major components of tree nut oils are triacylglycerols (TAG, 96–98%; Table 5.1), with smaller amounts of diacylglycerols (DAG), monoacylglycerols, free fatty acids and minor unsaponifiable compounds (Kamal-Eldin and Moreau

2010). In VWO, TAG is constituted mainly by LLL (25–31%; Table 5.2) and LOL/OLL (14–16%) followed by LLLn (15–18%) and OOL (10%) (Bada et al. 2010; Anqi et al. 2016).

On the other hand, 96 isomers of phospholipids (PL) were identified in walnuts with a total content of 16,457 mg/kg nut (Table 5.1). Phosphatidylinositol (PI) is the group with the highest concentration (5335 mg/kg) formed by 18 different species such as C16:0/C18:2 (2164 mg/kg) and C16:0/C18:3 (790 mg/kg) as the main contributors. Phosphatidylethanolamine (PE) represents the second most important component (4309 mg/kg) with 17 species, accounting the species C16:0/C18:2 (1714 mg/kg) and C18:2/C18:2 (1024 mg/kg) the high concentration. Furthermore, phosphatidylcholine (PC) and phosphatidic acid (PA) content 15 (3133 mg/kg) and 9 (2439 mg/kg) species, being for PC the most important one C16:0/C18:2 with 1103 mg/kg and C18:2/C16:0, the principal for PA with 896 mg/kg. Other groups such as phosphatidylglycerol (PG, 670 mg/kg) and phosphatidylserine (PS, 109 mg/kg) were also detected. Walnut oils phospholipids (PL) have been also studied by Miraliakbari and Shahidi (2008) who reported PS as the highest component with 2700 mg/kg oil, followed by PC with very close concentration (2400 mg/kg) and PI (1300 mg/kg).

Sphingolipids were quantified in walnut oils (Miraliakbari and Shahidi 2008; Table 5.1), accounting a total of 2900 mg/kg. Alasalvar and Pelvan (2011) identified 12 ceramides and 8 cerebrosides in this nut oil. Fang et al. (2005) stated a concentration of 25 mg/kg nut ceramides in walnuts. However, effort is needed to establish reliable data for these compound, due to the importance of sphingolipids in metabolic pathways in the human body.

As reported in Table 5.3, VWO showed a sterol content ranging from 1498 to 2187 mg/kg (Gong et al. 2017), which is very close to virgin olive oil (1100–2100 mg/kg; Aparicio and Luna 2002) and several other vegetable oils (Codex Stan 210 1999), whereas, a higher maximum level was apparently observed in solvent-extracted oils (1144–3070 mg/kg (Table 5.3). As expected, β -sitosterol was found as

Table 5.3 Sterol composition (mg/kg) in virgin walnut oil

Chol	Camp	Stigma	β -sito	Total (g/kg)	References
Virgin oil					
–	4.7–5.1	–	87.8–90.0	–	Martínez et al. (2006) ^a
–	63–104	15–26	1034–1515	1498–2187	Gong et al. (2017)
–	5.4	0.3	93.6	1009	Rabadán et al. (2018)
Solvent-extracted oil					
0.8–3.8	61–108	0.0–8.0	1093–1757	1207–2026	Amaral et al. (2003)
0.1–0.1	180–190	330–350	2160–2250	–	Miraliakbari and Shahidi (2007)
–	190	350	2250	3070	Alasalvar and Pelvan (2011)
–	101	0	1118	–	Derewiaka et al. (2014)
4.0–6.3	5.0–88.0	1.0–5.8	974–1494	1144–1679	Abdallah et al. (2015)

Chol cholesterol, Camp campesterol, Stigma stigmasterol, β -sito β -sitosterol

^aIndividual sterols expressed as %

the predominant phytosterol with a content of 1034–1515 mg/kg in VWO and 974–2250 mg/kg in solvent-extracted oils; followed by campesterol with 61–190 mg/kg, corresponding to approximately 4–5% (Table 5.3). The walnut variety is a relevant factor both on sterols total content and on their profile. Amaral et al. (2003) performed a study on six different walnut cultivars, showing a range of β -sitosterol from 1093 mg/kg oil (Parisienne variety) up to 1757 mg/kg (Marbot variety), reporting a total sterol concentration of 1207–2026 mg/kg. According to Martínez et al. (2006), little differences were observed between Franquette and Chandler varieties: 90.0% and 87.8% for β -sitosterol and 4.7–5.1% of campesterol, respectively.

Triterpenic and aliphatic alcohols from walnut oils have also been studied accounting a range between 242 mg/kg (Parisienne) and 620 mg/kg (Local). Cycloartenol was the compound with the highest concentration (226–532 mg/kg; Abdallah et al. 2015). For aliphatic alcohols, local variety showed the lowest amount (24.3 mg/kg) and Franquette the highest (51.0 mg/kg), wherein hexacosanol (9.7–28.2 mg/kg) and tetracosanol (4.2–12.7 mg/kg) were the major compounds.

4 Minor Bioactive Components

Tocopherols are a fat-soluble vitamin found in vegetable oils and act as a potent antioxidant reducing the peroxidation of unsaturated lipids via chain-breaking mechanism (Shin et al. 2009). As depicted in Table 5.4, VWO exhibited a high tocopherols content accounting for 223–646 mg/kg (Martínez et al. 2010; Górnas et al. 2014; Gong et al. 2017; Ojeda-Amador et al. 2018b), mainly in the form of its γ -tocopherol isomer, wherein the Hartely variety was the richest (554 mg/kg; quantified as α -tocopherol; Ojeda-Amdor et al. 2018b). This form of vitamin E represents about 85% of the total tocopherols in the VWO; whereas the other main isomers, α - and δ -tocopherols, account for 10–62 mg/kg and 11–38 mg/kg,

Table 5.4 Tocopherols (mg/kg) and pigments (mg/kg) in walnut oil

α -tocoph	γ -tocoph	T tocoph	β -carotene	T carot	T chloro	References
Virgin oil						
63	323	582	2.2	–	4.0	Górnas et al. (2014)
51–68	250–337	337–448	–	–	–	Martínez et al. (2006)
9.6–26	201–235	223–287	–	–	–	Gong et al. (2017)
24–26	517–554	596–647	–	4.2–7.3	3.3–9.9	Ojeda-Amador et al. (2018b)
Solvent-extracted oil						
10–17	208–262	242–297	–	–	–	Amaral et al. (2005)
38	376	402	–	–	–	Miraliakbari and Shahidi (2007)
		249				Arranz et al. (2008)
38	376	437	–	–	–	Alasalvar and Pelvan (2011)
1.9–13	163–359	187–436	0.2–0.6	0.3–0.8	0.2–0.5	Abdallah et al. (2015)

α -tocoph α tocopherol, γ -tocoph γ tocopherol, T tocoph Total tocopherols, T carot Total carotenoids, T chloro Total chlorophylls

respectively (Table 5.4). Other virgin nut oils such as those obtained from pistachio, almond and hazelnut exhibited similar tocopherols levels, although almond and hazelnut oils show a different isomers distribution, being α -tocopherol the most abundant (Gong et al. 2017). In the solvent-extracted oils, Amaral et al. (2005) found that Lara cultivar had the lowest total tocopherols content (242 mg/kg) and Franquette had the highest (297 mg/kg), as well as the presence of a low quantity of β -tocopherol (0.9–1.8 mg/kg). Other authors reported a total content close to 400 mg/kg for solvent-extracted oils (Table 5.4). Walnut oil is therefore a good source of vitamin E with recognized antioxidant activity, both in vivo and in food stuff (Burton 1994). In this respect, it is worth to remark that γ -tocopherol is recognized as a more efficient food lipid antioxidant than α -tocopherol (Wagner et al. 2004).

Pigments in solvent-extracted walnut oils, have been described in different cultivars (Abdallah et al. 2015). Table 5.4 presents the content of chlorophyll ‘a’ which is from 0.12 mg/kg in Franquette cultivar to 0.31 mg/kg in Lauzeronne, and a lower content of chlorophyll ‘b’ was found (0.06–0.16 mg/kg). The carotenoids family (0.33–0.75 mg/kg) in solvent-extracted oils is constituted mainly of β -carotene in a range from 0.22 mg/kg (Local) to 0.62 mg/kg (Hartley), and of lutein (0.01–0.06 mg/kg) and violaxanthin (0.01–0.04 mg/kg). In VWO, a content of 2.16 mg/kg of β -carotene and a total chlorophyll content of 3.97 mg/kg was reported (Górnas et al. 2014). Similar contents were reported by Ojeda-Amador et al. (2018b) in three different VWO varieties: total chlorophylls was 3.3 mg/kg in Hartley and 9.9 mg/kg in Chandler, and for carotenoids 4.2 mg/kg in Hartley and 7.3 mg/kg in Chandler.

Walnut is the nut with a high content in phenolic compounds (Kornsteiner et al. 2006; Yang et al. 2009). Indeed, the total concentration of these compounds measured by Folin-Ciocalteu, ranged from 10,045 to 12,474 mg/kg (Figuerola et al. 2016; Ojeda-Amador et al. 2018b; Table 5.1). The main phenolic families found in walnuts kernel are hydrolyzable tannins, about 70% of total (Slatnar et al. 2015), wherein the most abundant compound was Di-HHDP glucose (Di-hexahydroxydiphenoyl-glucose) with an observed concentration range from 918 mg/kg (Lara) and up to 2226 mg/kg (Hartley; Ojeda-Amador et al. 2018b). Flavanols were the second family in importance, ranging from 26% (796 mg/kg Chandler) to 35% of the total content (2433 mg/kg Hartley; Ojeda-Amador et al. 2018b), wherein procyanidin dimer was the most relevant compound (from 753 to 2366 mg/kg in Chandler and Hartley varieties respectively). Slatnar et al. (2015) found up to 996 mg/kg of flavanols in the Franquette walnut variety.

Nevertheless, VWO contained a low level (Table 5.5) of these compounds, 10–26 mg/kg (Górnas et al. 2014; Ojeda-Amador et al. 2018b), due to their polarity, but similar to other virgin seed oils (e.g. 10–30 mg/kg soybean, sunflower, rapeseed, corn and pumpkin; Siger et al. 2008). Only a few phenolic compounds have been identified in VWO (di-HHDP glucose, glansreginin A, glansreginin B and HHDP galloyl glucose 1; Table 5.5). All identified compounds belonging to the hydrolyzable tannins family, ranging between 0.91 and 2.91 mg/kg accounting Hartley and Chandler with the lowest and highest concentration, respectively. Glansreginin A is

Table 5.5 Polar phenolic compounds (mg/kg) identified in walnut oils

di-HHDP glucose	Glansreginin A	Glansreginin B	HHDP galloyl glucose 1	Total phenolics	References
Virgin oil					
–	–	–	–	9.5	Górnas et al. (2014)
–	0.01–0.24	0.01–0.05	–	19–80	Slatnar et al. (2015)
–	–	–	–	17	Rabadán et al. (2018)
0.11–0.84	0.37–0.85	0.01–0.17	0.21–1.05	14–26	Ojeda-Amador et al. (2018b)

apparently the main compound with a concentration up to 0.85 mg/kg (Slatnar et al. 2015; Ojeda-Amador et al. 2018b).

Hydrocarbons have been studied by Martínez et al. (2006) in three VVO varieties. They identified 15 compounds and the profile of all samples was characterized by the predominance of even n-alkanes from C14 to C20. The composition of the alkane fraction is unique and has been considered as a fingerprint of each crop in virgin olive oil (Osorio-Bueno et al. 2005). These differences were attributed to genotypical and environmental influences in walnut (Martínez et al. 2006). Squalene is a hydrocarbon (30 carbon atoms) that acts as a biosynthetic precursor to all steroids in plants. Moreover, it has been related to protective effect attributed to its possible antioxidant functions decreasing the risk of developing certain cancers and reducing serum cholesterol levels (Smith 2000). Squalene has been detected in a concentration of 9.7 mg/kg in walnut oil (Maguire et al. 2004).

5 Antioxidant and Health-Promoting Effects

A great interest in acquiring more knowledge regarding the health-promoting effects ascribed to nuts exists among the scientific community, since there are increasing evidence from prospective observational studies that nut intake lowers the risk of cardiovascular disease (Souza et al. 2017). Moreover, nuts have a beneficial impact on hypertension, diabetes, inflammation and cancer (Salas-Salvadó et al. 2008; Grosso et al. 2015; Amarowicz et al. 2017), as reported in the PREDIMED study (Prevention with Mediterranean Diet) and in other epidemiological and clinical trials. These benefits are probably due to the content in healthy unsaturated fatty acids and phytochemicals like phenolics, sterols, tocopherols and other biologically active compounds (Kamal-Eldin and Moreau 2010).

Among nuts, walnuts are known to be a good source of essential linoleic acid, which decreases LDL-cholesterol and increases HDL-cholesterol (Davis et al. 2007). Moreover, walnut oil possesses a 4:1 ratio between *n*-6 and *n*-3 PUFA, which helps to prevent diseases, although makes it more susceptible to oxidation, which is balanced by the high content in natural antioxidants that contributes to health (Gharibzadeh et al. 2014). Furthermore, walnuts also possess phytosterols,

dietary fibre, phenolics and tocopherols that may be beneficial for health (Anderson et al. 2001; Amaral et al. 2005). The consumption of nuts and their oils suppresses appetite, enhances satiety and reduces food intake (Hughes et al. 2008). Phenolic compounds are potentially relevant for human health due to their good antioxidant, antiatherogenic, anti-inflammatory and antimutagenic properties (Anderson et al. 2001; Carvalho et al. 2010). However, in walnut oils its content is low due to their low-fat solubility, and therefore the corresponding antioxidant activity is also low (e.g. 0.10 mg/kg DPPH and 1.0 mg/kg ORAC; Ojeda-Amador et al. 2018b), although similar to other virgin nut oils (Miraliakbari and Shahidi 2008).

6 Contribution to Organoleptic Properties

Volatile compounds in vegetable oils are mainly formed by the oxidative pathways of linoleic acid, due to the activity of the linoleate oxygen oxidoreductase (LOX) which catalyzes the oxidation of PUFA (Robinson et al. 1995; Martínez and Maestri 2008). As depicted in Table 5.6, the profile of the VWO is characterized by aldehydes (22–81%), acids (14–30%) and alcohols (20–25%) with different proportions depending on the variety (Ojeda-Amador et al. 2018b).

The major aldehyde component present in the head-space of virgin walnut oils (mainly hexanal, 2-heptenal, octanal, nonanal, 2-decenal and 2-undecenal) are theoretically related with hydroperoxide precursors (Torres et al. 2005; Choe and Min 2006). Regarding VWO produced from different varieties, Chandler showed the highest aldehydes concentration (3.16 mg/Kg) followed by Lara (2.19 mg/Kg) and Hartley (1.37 mg/Kg), showing significant statistical differences between them (Ojeda-Amador et al. 2018b). Hexanal, related to green descriptor (Morales et al. 2005), is the major contributor within the aldehyde's family accounted for 1.79 mg/kg in Chandler VWO and 0.60 mg/kg in Lara variety (56% and 27%, respectively). On the contrary nonanal, associated with citrus odour (Kochhar 1993), was the main compound of this family in Hartley variety (0.38 mg/kg, 28%), but also high in Chandler (17%) and Lara VWOs (27%); similarly to what reported by Martínez and Maestri (2008), who measured a range of 16.2–34.7% n-pentano and 15.7–34.1% 2,4-decadienal in VWO.

Table 5.6 Volatile compounds (%) found in virgin walnut oils

Hexanal	2-Decenal	Aldehydes ^a	Alcohols	Acids	Ketones	References
4.9–6.7	3.6–6.3	37–46	0.0–4.3	–	0.0–0.7	Torres et al. (2005)
8.1–21	3.0–6.8	55–81	0.0–1.9	–	–	Martínez et al. (2008)
6.6–32	–	22–42	2.6–12	21–43	1.0–4.8	Bail et al. (2009)
4.7–28	1.6–3.2	22–51	20–25	14–30	1.8–3.6	Ojeda-Amador et al. (2018b)

^aTotal aldehydes

Volatile acids and alcohols showed closed proportions in the headspace composition of VWO (Table 5.6), with a concentration range of 0.87–3.19 mg/kg for acids and 1.25–1.55 mg/kg for alcohols (Ojeda-Amador et al. 2018b). Within the acids family, acetic acid accounted from 5% to 26% of the total (0.25–2.53 mg/kg, depending on the variety), according to studies reported by Bail et al. (2009) and Uriarte et al. (2011), who found acetic acid and hexanal as the main headspace components of the VWO. Although the concentration of acetic acid (expressed as the internal standard 4-methyl-2-pentanol) is apparently high, it is closed to its odor detection threshold, and therefore, it could be not perceived. Regarding alcohols, 1-dodecanol and 1-nonen-3-ol were the most important compounds found at levels of 0.56–0.88 mg/kg and 0.15–0.29 mg/kg, respectively. 1-pentanol (about 5% of this family and 1% of the total volatiles, according to Martínez and Maestri 2008)-related to fruity notes (Morales and Aparicio 1999)- was also present due to the transformation of linoleic acid (Choe and Min 2006).

Other families of volatiles, such as terpenes and ketones were present in much less concentrations, only accounting for 7–13% and 2–3% each one, respectively of the total volatile compounds in VWO (Bail et al. 2009; Ojeda-Amador et al. 2018b). Some commercial VWO have shown to contain pyrazines (up to 13% of totals) and furans (up to 10%), which are formed when a high temperature is used during the extraction or when roasting nuts are used for oil extraction (Bail et al. 2009; Zhou et al. 2016; Ojeda-Amador et al. 2018b).

Regarding the CIE L*a*b* color space in VWO, the 'b*' parameter (yellow-blue component) ranged from 25.5 to 30.9 and from -2.9 to -3.8 for the 'a*' parameter (red-green component) depending on the variety used for oil extraction, resulting in a clear yellow tonality (Ojeda-Amador et al. 2018b), which was in agreement with what observed by Górnas et al. (2014).

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