Chapter 9

Chemical Characteristics and Nutritional Properties of Hybrid Palm Oils

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Additional information is available at the end of the chapter

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Abstract

Nutritional guidelines and environmental issues are adversely affecting palm oil's image among consumers. However, hybrid palm oils are currently receiving increasing attention because of their interesting chemical characteristics and nutritional properties. Interspecific hybridization *Elaeis oleifera* × *E. guineensis* (O×G) has been originally exploited with the main aim of developing disease-resistant varieties. However, available literature data contribute to reinforcing the idea that interspecific hybrid O×G palm oil could be a potential substitute for other vegetable oils rich in monounsaturated fatty acids (i.e., high oleic sunflower and safflower oils). The chapter aims to review current knowledge on various aspects of hybrid palm oil chemical composition (fatty acids, triacylglycerols, partial glycerides, unsaponifiable matter components) and their changes during fruit ripening. The nutritional attributes of hybrid palm oils are compared with the ones of conventional African palm oils.

Keywords: interspecific hybrid palm, palm oil, ripening, *Elaeis oleifera*, tocotrienols, positional analysis, fatty acids, triacylglycerols

1. Introduction

Fruits of palms (drupes) belonging to the genus *Elaeis* have been exploiting to produce edible oils for 5000 years. "Palm oil" is obtained from the reddish pulp (mesocarp) of the fruits, mainly those of the African palm (*Elaeis guineensis* Jacq.) (EG) and, to a considerably small amount, those of the palm native in central and northern South America (*Elaeis oleifera* [H.B.K.] Cortés) (EO), also known as "caiaué." "Palm kernel oil" derives from the kernel inside the shell (endocarp) [1]. The

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African palm grows spontaneously or in cultivated fields in tropical regions of Africa, Southeast Asia, and South and Central America, whereas the American oil palm only occurs in spontaneous populations from the south of Mexico to Amazon areas in Brazil and Colombia. High productivity, perennial nature of the plant, and low cost of oil production make the palm oil obtained from *E. guineensis* (henceforth referred to as "palm oil") the most produced and marketed vegetable oil worldwide. A total of 66.9×10^6 t of palm oil and 7.8×10^6 t of palm kernel oil were produced in 2017; Malaysia and Indonesia are the most important producers, with 57×10^6 t in all, corresponding to 85% of the world production [2].

Palm oil is a typical multipurpose vegetable oil; it is used in food products (cooking oils, margarine and other spreads, crisps, baked food, food additives, confectionary, dairy and dairy replacements, prepared foods, snacks), in food for livestock and household pets (as fat supplement), and in several non-food productions (biodiesel, oleochemicals, cosmetics and textiles). The wide range of applications for mesocarp oil is due to its fatty acid (FA) composition. Palm oil has approximately equal amounts of saturated (SFA) and unsaturated fatty acids (UFA), while the mesocarp oil from EO is much more unsaturated [3–6].

Despite its technological characteristics, public perception of palm oil is getting worse and worse; new evidence concerning the presence of process contaminants [7] and environmental issues [8] have been added to the well-known health impact of high dietary intake of SFA. Palm oil is considered "the worst" edible oil in France, in French Belgium and in Italy, as regard to both people's health and environmental impact, whereas in the extra-European countries (USA, UK, Canada, Australia, China, Saudi Arabia) the negative opinion on palm oil is really low [9]. Campaigning against palm oil has been quite tenacious in Italy; in the last 3 years, several petitions have been promoted by online magazines (Il FattoAlimentare), consumer associations (AltroConsumo), and farmer associations (Coldiretti); even a parliamentary motion to ban palm oil from canteens has been proposed. This induced some important brands (Misura, Mulino Bianco) and retailers (Coop, Esselunga) to meet the consumer demand by introducing foodstuffs without palm oil.

In such a climate, interspecific hybrid between the cultivated oil palm EG and its wild relative EO (O×G) is receiving increasing attention by researchers and stakeholders. The O×G hybrid provides a crude oil that contains significantly higher amount of oleic acid (O) and lower percentages of palmitic (P) and stearic (S) acid than conventional African palm oil. Hardon [10, 11] first provided data on crossability, cytogenetics, fertility, growth, yield, and FA composition of F1 hybrids O×G, with the objective of developing varieties resistant to diseases [12]; in fact, hybrid expresses less severe symptoms and a slower progression of "bud rot" disease than EG. Besides, hybrid is significantly less preferred by *Rhynchophorus palmarum* than African oil palm [13]. O×G hybrids inherit from the American parent other characters of interest, such as slower vertical stem growth [14], which could result in reduced harvesting costs.

Only in recent years, a wide range of characteristics of O×G interspecific hybrids has been thoroughly studied and described: yield and morphology [15–19]; phenological stages [20]; genome size [21, 22]; sensitivity to water stress [23, 24]; physiological and biochemical response to aluminum toxicity [25]; nutritional status [26]; seed germination [27]; fruit abscission process [28]; and mycorrhization process [29]. Even a comparative characterization of the physiological and

biochemical performance of seedlings of O×G hybrids grown in hydroponics was carried out [30]. Nevertheless, very few studies have been conducted on the composition of the mesocarp oil. The chapter aims to review current knowledge about the various aspects of hybrid palm oil chemical composition: FAs, triacylglycerols (TAGs), partial glycerides, and unsaponifiable matter components. Available data on the composition of the hybrid palm oil during ripening are also summarized. Eventually, the nutritional attributes of hybrid palm oils are discussed in view of recently published papers about the consumption of crude oils from O×G hybrids.

2. Quality parameters

A set of quality parameters (free acidity, unsaponifiable content, water content, and insoluble matter content) gives an overall assessment of the whole amount of non-glyceridic constituents, which is relevant in determining the commercial value of raw fatty substances. In crude oils obtained by pressing pulp of hybrids palm drupes, unsaponifiable matter accounts for about 1 g/100 g oil, without any significant difference due to harvest time [31, 32]; water content ranges from 0.20 to 0.73 g/100 g oil; and insoluble matter content lies in the range 0.09–0.20 g/100 g oil [31]. The free fatty acid (FFA) content ranges between 0.35 (as g/100 g oil, determined by GC areas) and 2.91 (as palmitic acid %, determined by titration) [31–33]. Higher FFA contents (9.7–36.7%, as palmitic acid) were ascribed to improper handling of raw material [34]. In fact, mesocarp lipase (triacylglycerol acyl hydrolase, EC 3.1.1.3) has been associated with the membranes of oleosomes (lipid bodies) and is activated when any kind of damage occurs to fruits, during harvest, transportation, and storage. Due to lipase activity lower than EG, interspecific O×G hybrids are considered as promising crosses with better stability of the drupes after harvest, if they have been properly handled before oil extraction [35].

As regard to the oxidative state, hydroperoxides have not been detected by conventional titrimetry (determination of peroxide number) in samples of freshly pressed oils [3], thus confirming the stability toward oxidation of crude palm oils [36]. Nevertheless, induction times measured at 100°C are spread over a wide range (5.7–17.2 hours) [3]: these inconsistencies could be related to differences in the qualitative and quantitative composition of components with antioxidant properties (tocols, polyphenols).

3. Acylglycerols

Edible vegetable oils mainly consist of TAGs; however, partial glycerides, namely diacylglycerols (DAGs) and monoacylglycerols (MAGs), are always present and their origin could be traced to both biosynthetic and lipolytic processes, the latter being of enzymatic or chemical nature.

Hardon [10] first quantified the amounts of MAG (0.88%) and DAG (5.55%) in F1 hybrids. Recently, a more detailed data have become available; 1(3)-P, 1(3)-O, and 1(3)-L were detected in the range 70–300 mg/100 g oil, with no significant differences related to ripening stage; small quantities of the corresponding 2-MAGs have also been identified. DAG types identified

are the α,β- (1,2- + 2,3- racemic mixture) and 1,3-isomers of PP, PS, PO, PL, SO, OO, OL, and LL. The most represented are PO and OO isomers, which globally account for 58–66% of total DAGs, 43–78% of α,β-DAGs, and 62–80% of 1,3-DAGs, in agreement with the of different TAG species [3, 31]. The presence of 1,3-DAGs is not "natural", as they are neither biosynthetic nor lipolytic intermediates; yet their presence may be due to both non-specific (chemical) lipolysis of TAGs and rearrangement of natural α,β-DAGs to the thermodynamically stable 1,3-isomers [3]. Hence, the presence of 1,3-DAGs is associated with mediocre quality of raw materials and unsuitable conditions during extraction and storage of oil. The biosynthesis of DAGs in fruit mesocarps accelerates during the period of maximum oil accumulation (18–22 weeks after anthesis, WAA). A decrease of relative abundance of PP and a corresponding increase of PO and OO were also observed [31]; this finding was consistent with results about changes in TAG composition during ripening described by the same authors.

3.1. Fatty acid composition

Two main FAs, O and P, account for about 80% of total FAs in hybrid palm oil and their ratio typically lies in the range 1.5–1.9 (**Table 1**), while in African palm oil O/P ratio is close to one and in EO oleic acid is the main FA (36.4–61.7%) and P is the second most represented one (21.0–37.0%) [3, 4]. Several authors have pointed out the wide range of oil composition from EO, reflecting the wider genetic diversity of EO than EG [4, 37]. Oleic acid comes with *cis*-vaccenic acid (C18:1Δ11) in an amount equal to about 0.7–1% of total FAs [3, 4]. Besides FAs listed in **Table 1**, other saturated (C8:0, C10:0, C24:0) and ω9 unsaturated (C22:1Δ13, C24:1Δ15) FAs were identified, which globally account for 0.2% of total FAs [3].

Despite the importance of determining the optimal harvest time for fruit bunches, only a very limited number of studies have been focused on the FA changes during fruit ripening. In cold pressed oils from fruits harvested between 18 and 24 WAA, a significant decrease of P (from 40.3 ± 0.3% to 32.2 ± 0.3%) and S (from 3.8 ± 0.1% to 2.7 ± 0.1%) and a corresponding increase in the relative percentage of O (from 49.7 ± 0.4% to 57.0 ± 0.4%) and L (from 4.1 ± 0.1% to 5.6 ± 0.0%) were observed [31]. Other researchers [33] detected an opposite behavior (an increase of P from 28.1 ± 2.3% to 31.3 ± 1.9% and a decrease of O from 56.4 ± 2.4% to 51.8 ± 2.1%), but in a different ripening period (phenological stages from 806 to 809, which roughly corresponds to 24–27 WAA).

As a rule, the FA composition of oils from F1 O×G interspecific hybrids is intermediate between those of their parents [3, 4, 38], while FAs in the F1 × F1 (i.e. the F2 generation) exhibit the composition of F1 [38]. This behavior has been attributed to a codominant and additive heredity in hybrid palms. The differences in FA composition between oils from African and hybrid palms should be related to the expression of genes encoding β-ketoacyl-ACP synthase (KAS) II, which is specifically used for chain lengthening of C16:0 to C18:0, and stearoyl/palmitoyl-ACP Δ^9-desaturase. Hereditariness and expression of genes linked to FAs and TAGs biosynthesis were explored by several authors [1, 6, 39–41]. Different quantitative trait loci (QTLs) for iodine value (index of total unsaturation) and FAs (C14:0, C16:0, C16:1, C18:0, C18:1, C18:2) have been identified, and a few structural genes encoding the enzymes involved in the *de novo* synthesis of FAs and in the TAG assembly (e.g., acyl-ACP thioesterases, acyl-CoA synthetase, diacylglycerol acyltransferase) have been localized in those genomic intervals. It is interesting to notice

Reference	[10]	[34]	[42]	[38][a]	[5]	[44]	[3]	[33]	[31]	[6]	[6]	[4]
Samples origin	Congo, Malaysia, Colombia	Nigeria, Colombia	Nigeria	Malaysia	Malaysia	Malaysia	Colombia	Colombia	Colombia	Malaysia	Malaysia	Costa Rica
Hybrid	F1	F1	BC1 (with EG)	F1; BC1 (with EG and EO); F2	F1	F1; BC1 (with EG)	F1	F1	F1	F1	BC2 (with EG)	BC3 (with EG); BC3 × EO
Oil extraction system		pressure	pressure				pressure	pressure	pressure			solvent
N. of samples	3	7	14		126		3	21[b]	12[c]	85	111	2
Fatty acid												
C12:0 (La)	0.01–0.1	tr		tr			0.5–1.7		0.4–0.5			
C14:0 (M)	0.47–0.9	0.4–0.9	0.3–0.9	0.4–0.8	0.1–0.5	0.5–1.6	0.5–0.9		0.4–0.4	0.14–0.55	0.14–0.75	0.9–0.9
C15:0							tr		0.1–0.1			
C16:0 (P)	27.3–32.5	29.3–35.5	28.9–38.6	36.2–41.4	22.4–44.7	32.2–43.1	27.7–29.5	28.1–31.3	32.2–40.3	22.25–34.33	24.73–41.69	37.0–43.5
C16:1Δ9				tr		0.1–0.3	0.3–0.4		0.3–0.5	0.20–0.83	0.07–0.34	0.2–0.2
C17:0							0.1–0.2		0.1–0.4			
C17:1							tr		0.1–0.1			
C18:0 (S)	3.4–6.1	3.0–4.6	3.3–5.9	0.4–1.5	1.4–4.9	3.2–4.1	2.6–3.1	2.3–2.7	2.7–3.8	1.50–3.10	2.11–9.43	4.0–4.3
C18:1 (O)	48.0–52.5	50.2–53.4	44.9–56.0		36.9–60.1	34.4–51.8	53.5–55.2	51.8–56.4	49.7–57.0	48.20–61.45	37.58–54.48	38.7–43.4
C18:2Δ9,12 (L)	11.3–11.8	10.3–13.9	9.3–11.5	6.5–9.3	8.2–16.8	10.8–16.5	10.7–11.5	9.4–10.4	4.1–5.6	10.45–15.15	8.15–17.65	10.7–12.7
C20:0 (A)	0.0–0.11			tr – 0.1			0.2–0.3		0.3–0.4			
C18:3 Δ9,12,15 (Ln)	0.4–1.3			0.1–0.7		0.5–0.5	0.4–0.4		0.1–0.2	0.40–0.65	0..00–0.53	0.3–0.4
C20:1 Δ11							0.2–0.2		0.1–0.2			

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Reference	[10]	[34]	[42]	[38][a]	[5]	[44]	[3]	[33]	[31]	[6]	[6]	[4]
C22:0									0.1–0.1			
ΣSFA							33.2–34.1	31.5–34.7	36.6–46.1			42.4–49.1
ΣMUFA							53.8–55.8		50.6–57.6			39.8–44.5
ΣPUFA							11.1–11.9		4.2–5.8			11.1–13.1
ΣSFA/ ΣUFA							0.50–0.52		0.58–0.84			0.7–1

[a]mol %.

[b]Samples collected between the phenological stages 806 and 809.

[c]Samples collected between 18 and 24 weeks after anthesis (WAA).

BCn = back-cross. Cm:nΔx: m = number of carbon atoms, n = number of double bonds, x = position of double bonds. tr. = trace. C18:1 = sum of oleic and *cis*-vaccenic acids. SFA = saturated fatty acids. MUFA = monounsaturated fatty acids. PUFA = polyunsaturated fatty acids.

Table 1. FA composition (% w/w) of O×G interspecific hybrid palm oil.

that, while most of the FAs and total unsaturation indicate additive or co-dominance effects, L seems to be an exception; in fact, the percentage of this essential FA does not undergo significant changes between African palm and O×G hybrids [3, 4, 38, 42]. In this case, EG seems to be dominant and dictates the level of L in the hybrid.

While great emphasis in breeding has been given to the mesocarp oil, less attention has been focused on the composition of kernel oils from EG, EO and their hybrids. Medium chain FAs characterize the composition of *Elaeis* kernel oils. Lauric acid (La) represents the most abundant FA, followed by myristic acid (M) and O; these three FAs account for 75–80% of total FAs. Besides, *cis*-vaccenic acid was only present at trace levels in kernel oil (~0.1%) [4]. Unlike the mesocarp oils, the kernel oils of the hybrids do not display an intermediate composition between their American and West African parents (**Table 2**); hybrids and back-crosses show a composition close to the one of EG kernel oil [5, 34, 43].

3.2. Composition and structure of triacylglycerols

A TAG type is defined by its three constitutive FAs. Data on the FA composition of individual TAG molecular species can be achieved through the combination of the separation properties

Reference	**[5, 43]**	**[5, 43]**	**[34]**	**[4]**
Samples origin	Malaysia	Malaysia	Nigeria, Colombia	Costa Rica
Hybrid	F1	BC1 (with EO)	F1	BC3 (with EG); BC3 × EO
Oil extraction system	Solvent	Solvent	Solvent	Solvent
N. of samples	12	5	6	2
C6:0	0.2–0.2	0.2	tr	
C8:0	3.2–3.4	4.0	1.3–3.2	1.2–2.3
C10:0	2.7–2.9	3.5	1.8–3.2	1.1–2.2
C12:0 (La)	44.4–46.8	50.0	40.6–49.0	35.0–42.3
C14:0 (M)	18.1–18.6	16.5	17.4–22.1	19.6–24.7
C16:0 (P)	7.9–8.8	7.8	8.0–9.5	9.1–10.2
C18:0 (S)	2.1–2.2	2.2	1.5–2.5	2.4–3.5
C18:1 (O)	14.8–16.3	13.1	14.1–18.5	17.2–19.1
C18:2Δ9,12 (L)	3.2–3.4	2.4	1.0–4.5	4.4. – 4.7
ΣSFA				75.9–78.2
ΣMUFA				17.5–19.3
ΣPUFA				4.4–4.7
ΣSFA/ ΣUFA				3.2–3.7

BCn = back-cross. Cm:nΔx: m = number of carbon atoms, n = number of double bonds, x = position of double bonds. tr. = trace. C18:1 = sum of oleic and *cis*-vaccenic acids. SFA = saturated fatty acids. MUFA = monounsaturated fatty acids. PUFA = polyunsaturated fatty acids.

Table 2. FA composition (% w/w) of O×G interspecific hybrid palm kernel oil.

of instrumental chromatographic techniques, both in liquid [45, 46] and gas [3] phase, and the powerful of mass spectrometers, as detection system.

Mozzon et al. [3, 31] identified 23 TAG molecular species (**Table 3**), by direct GC-MS analysis of oils. Other 14 TAG molecular species characterized by the presence of medium chain SFAs (8:0, 10:0, 12:0, and 14:0), which globally accounted for about 0.7% of oil samples, have been identified after TLC fractionation of oil. These are the TSTAGs 32:0 (LaLa8:0), 34:0 (LaLa10:0), 36:0 (LaLaLa), 38:0 (LaLaM), 40:0 (LaMM+LaLaP), 42:0 (LaMP), 44:0 (LaPP+MMP), and the DSTAGs 42:1 (LaLaO), 44:1 (LaMO). TAG structures with three (LaLaLa) and two (LaLaM, LaLaP, LaLaO) lauryl groups constitute 69.4–72.0% of medium chain TAGs.

No qualitative differences between TAG species of O×G hybrid palm oil and its African parent have been detected. From a quantitative viewpoint, most (about 80%) of total TAGs are made up of both saturated (16:0, 18:0) and unsaturated (18:1, 18:2) FAs (DSTAG + MSTAG). Lower percentages of MPP, PPP, MOP, PPS, PPO, PPL, POS, and higher contents of OOO (2.5 times), OOL (three times), POO, PLO, SOA (from 0.1–0.2% to 0.9–1.2%) than African parent were observed in oil samples from O×G hybrid. Grouped data reflect the discoveries summarized above: oil samples from the hybrid are characterized by higher contents of MSTAGs (47.5–51.0% vs 36.7–37.1%) and TUTAGs (15.5–15.6% vs 5.2–5.4%) than EG [3]. Despite similar FA compositions, other authors [33, 35] observed different TAG profiles, namely lower percentages of POO and PPO, and higher percentages of PPL, PLO, OOL, PLL + POLn.

The pattern of TAGs of mesocarp oils, according to the number of acyl carbon atoms (CN), follows a typical unimodal distribution with an apex at CN 52 for the hybrid palm oil, at CN 50–52 in African palm oil, and at CN 52–54 in EO oils [3, 5]. In kernel oils of EG and its interspecific hybrids (F1 hybrids, back-crosses), the major TAG groups range from CN 36–38 (the most represented) to CN 44 (**Table 3**), whereas in EO kernel oils they range from C36 to C54. A bimodal distribution with maxima at CN 38 and C 48 characterizes the TAG profile of EO kernel lipids [5, 43].

Pancreatic lipase degradation of TAGs was extensively applied in the TAGs structure studies [47–49]. Experimental data reveal an asymmetric structure of the hybrid palm oil TAGs, thus suggesting that the length of carbon chain and the number of double bonds could constitute discriminating factors in the acylation steps. SFAs (C16:0, C18:0) are acylated mainly in positions sn-1,3, while unsaturated fatty acids (C18:1Δ9, C18:2Δ9,12) are preferably acylated in position sn-2 [3, 38]. The conservation of FAs regiodistribution in TAGs of O×G hybrid with respect to its African parent could indicate that hybridization cannot affect the general pattern of stereospecific acylation of glycerol [3].

Trends in FAs availability during ripening (18–24 WAA) mainly affect TSTAGs and TUTAGs: total TSTAG relative percentage halves from 3.6 ± 0.1 to 1.8 ± 0.1, whereas ΣTUTAG increased from 16.9 ± 0.1% to 18.9 ± 0.3%, mainly because of the increase of OOO and decrease in PPP. As saturated and unsaturated FAs have opposite trends during ripening, ΣDSTAG and ΣMSTAG overall changes are very inconspicuous, although they are statistically significant. No significant differences have been observed for medium chain TAGs [31].

Reference		[5]	[33]	[35]	[3]	[31]	[5, 43]	[5, 43]
		Mesocarp oil					**Kernel oil**	
Samples origin		Malaysia	Colombia	Colombia	Colombia	Colombia	Malaysia	Malaysia
Hybrid		F1	F1	F1	F1	F1	F1	BC1 (with EO)
Oil extraction system			Pressure	Pressure	Pressure	Pressure		
N. of samples		38	21[a]	3[b]	3[c]	12[d]	12	5
TAG m:n	TAG ABC							
ΣC28							0.1–0.2	0.1
ΣC30							0.4–0.7	0.7
ΣC32							2.9–3.9	4.7
ΣC34							4.8–6.0	7.1
ΣC36							17.9–19.6	24.5
ΣC38							17.2–18.0	18.9
ΣC40							10.9–11.3	10.3
ΣC42							9.9–10.6	9.1
ΣC44							8.0–8.8	6.7
46:0	MPP				0.1 ± 0.0	0.1–0.5		
46:1	MMO + LaPO				0.3 ± 0.2	tr – 0.3		
ΣC46		0.0–1.1					6.3–7.2	5.1
48:0	PPP		0.0–0.6		1.3 ± 1.3	1.5–2.8		
48:1	MOP				0.8 ± 0.0	0.4–0.6		
48:2	MLP		0.0–0.7	0.4 ± 0.0	0.2 ± 0.1	tr - 0.1		
ΣC48		0.9–8.9					7.1–8.0	6.0
50:0	PPS		0.0–0.2	n.d.	0.4 ± 0.3	0.2–0.6		

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Reference		[5]	[33]	[35]	[3]	[31]	[5, 43]	[5, 43]
		Mesocarp oil					Kernel oil	
50:1	PPO		10.4–15.3	17.0 ± 2.4	20.4 ± 0.2	20.3–21.1		
50:2	PPL		5.6–9.4	9.4 ± 0.9	5.5 ± 0.2	2.5–3.2		
50:2	MOO				0.5 ± 0.1	0.3–0.5		
ΣC50		11.1–25.5					3.3–3.9	2.3
52:0	PSS				tr	tr		
52:1	POS		1.5–1.8	2.8 ± 0.5	3.3 ± 0.2	2.8–3.8		
52:2	PLS				1.6 ± 0.3	1.7–2.0		
52:2	POO		21.9–24.8	23.4 ± 0.7	32.6 ± 2.4	33.1–35.8		
52:3	PLO		17.8–20.2	17.7 ± 0.8	11.2 ± 0.2	7.4–8.9		
52:4	PLL + POLn		7.4–9.4	6.7 ± 0.6	2.0 ± 0.0	1.1–1.9		
ΣC52		43.5–50.5					2.9–3.3	1.9
54:1	SSO		0.2–0.4	n.d.	0.3 ± 0.0	0.3–0.4		
54:2	SOO		1.1–2.5	1.8 ± 0.3	2.6 ± 0.1	2.3–3.5		
54:3	SLO				0.7 ± 0.7	1.4–1.5		
54:3	OOO		8.5–12.8	7.6 ± 1.0	10.7 ± 0.2	12.2–14.2		
54:4	OOL		8.5–11.3	7.6 ± 0.6	4.7 ± 0.1	4.6–5.2		
54:5	OLL		3.9–5.0	3.2 ± 0.3	0.2 ± 0.1	tr - 0.3		
ΣC54		21.8–44.7					3.0–3.5	2.6
56:1	SOA				1.1 ± 0.1	0.9–1.1		
56:2	AOO				0.1 ± 0.0	0.1–0.1		
ΣC56		0.0–0.6						
	ΣTSTAG				1.6 ± 1.6	1.8–3.6		

Reference		[5]	[33]	[35]	[3]	[31]	[5, 43]	[5, 43]
		Mesocarp oil					Kernel oil	
	ΣDSTAG				33.3 ± 0.3	29.8–31.5		
	ΣMSTAG				49.6 ± 1.8	47.7–49.5		
	ΣTUTAG				15.5 ± 0.1	16.9–18.9		

[a]Samples collected between the phenological stages 806 and 809.

[b]Phenological stage 807.

[c]24 weeks after anthesis (WAA).

[d]Samples collected between 18 and 24 WAA. BCn = back-cross. m:n = acyl carbon number:double bonds number. In TAG species composition (TAG ABC), the order of the abbreviations, e.g. PLO, does not mean the binding position of each FA. FAs like in **Table 1**. tr = trace values (< 0.1%). n.d. = not detected. TAG types listed in **Table 3** have been grouped according to the type of FA bonded to the glycerol moiety as TSTAG, trisaturated TAGs (MPP, PPP, PPS, PSS); DSTAG, disaturated TAGs (MMO + LaPO, MOP, MLP, PPO, PPL, POS, PLS, SSO, SOA); MSTAG, monosaturated TAGs (MOO, POO, PLO, PLL + POLn, SOO, SLO, AOO); TUTAG, triunsaturated TAGs (OOO, OOL, OLL).

Table 3. Triacylglycerol (TAG) composition (% w/w) of O×G interspecific hybrid mesocarp oil and kernel oil.

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4. Unsaponifiable matter

A full characterization of the unsaponifiable matter (UM) of the hybrid palm oil is required to assess its potential as a source of health-promoting bioactive compounds. However, only few specific studies have been conducted about the composition of UM of the O×G hybrid oil (**Table 4**).

Reference	**[10]**	**[44]**	**[33]**	**[32]**	**[31]**
Samples origin	Congo, Malaysia, Colombia	Malaysia	Colombia	Colombia	Colombia
Hybrid	F1	F1; BC1 (with EG)	F1	F1	F1
Oil extraction system			pressure	cold pressed	cold pressed
N. of samples	3		21[a]	3[b]	12[c]
Squalene				247.4 ± 3.3	20.3–83.1
4-desmethylsterols					
Cholesterol		3–5%		10.0 ± 2.6/1.8 ± 0.4%	7,8–10.2/3.5–5.4%
Campesterol		20–22%		93.1 ± 23.4/19.3 ± 1.2%	18,8–47.6/11.8–16.3%
Ergosterol				11.0 ± 3.4/1.9 ± 0.3%	
Stigmasterol		13–19%		62.8 ± 10.8/13.1 ± 0.6%	25,8–45.2/15.3–16.3%
Δ^7-campesterol				1.7 ± 0.7/0.5 ± 0.3%	2,3–3.6/0.8–1.9%
β-sitosterol		58–61%		275.6 ± 57.4/59.3 ± 1.0%	98,2–180.9/61.5–62.4%
Δ^5-avenasterol				8.8 ± 1.3/1.9 ± 0.2%	1,6–3.9/0.9–1.4%
$\Delta^{5,24}$-stigmastadienol				2.1 ± 1.4/0.5 ± 0.2%	2,3–3.6/1.1–1.9%
Fucosterol				5.6 ± 2.9/1.1 ± 0.6%	
Other unidentified sterols				2.1 ± 1.4/0.5 ± 0.2%	
Total 4-desmethylsterols		700–1400	469–1417	472.7 ± 102.8	158.7–293.8
Isoprenoid alcohols					
Phytol				120.7 ± 26.1	127.5–175.0
3,7,11,15-tetramethyl-2,6-hexadien-1-ol				11.3 ± 2.1	
3,7,11,15-tetramethyl-2,6,10-hexatrien-1-ol				7.7 ± 1.5	
Geranylgeraniol				129.0 ± 31.7	31.3–76.3
Isoprenoid alcohol (X_1)				tr	

Reference	[10]	[44]	[33]	[32]	[31]
Isoprenoid alcohol (X_2)				tr	
Total Isoprenoid alcohols				269.3 ± 60.0	160.7–251.3
***n*-Alkanols (Ak)**					
n-octadecanol				5.3 ± 2.1	
n-docosanol				1.8 ± 1.3	0.5–1.4
n-tetracosanol				1.2 ± 0.5	0.4–1.2
n-hexacosanol				2.7 ± 0.2	0.4–2.5
n-octacosanol				7.3 ± 0.8	3.0–5.2
n-nonacosanol				tr	
n-triacontanol				15.6 ± 1.6	7.2–12.9
n-hentriacontanol				0.7 ± 1.2	
n-dotriacontanol				18.1 ± 6.5	6.9–13.1
n-tritriacontanol				0.7 ± 1.2	
n-tetratriacontanol				8.2 ± 7.6	2.2–37.4
Total *n*-Alkanols				61.7 ± 17.0	24.9–37.4
4-methylsterols					
gramisterol					
obtusifoliol					2.7–5.2
citrostadienol					4.2–9.8
Total 4-methylsterols				12.7 ± 1.5	6.9–14.9
4,4-dimethylsterols					
Cycloartenol					14.6–24.9
24-methylene-cycloartanol					2.0–3.4
Isoarborinol					2.0–3.9
Unknown					
9,19-cyclopropanesterol					0.8–1.6
Total 4,4-dimethylsterols				74.0 ± 12.3	20.0–33.7
Tocols					
α-tocopherol		11–24%		27.1 ± 7.4/10.0 ± 0.2%	1.5–7.4
β- tocopherol				tr/0.3 ± 0.3%	
γ- tocopherol				tr/0.3 ± 0.4%	
α-tocotrienol		22–31%		44.7 ± 13.7/15.0 ± 1.9%	
β-tocotrienol				3.7 ± 1.2/1.4 ± 0.4%	
γ-tocotrienol		42–51%		148.1 ± 23.3/59.7 ± 1.1%	9.4–18.9

Reference	[10]	[44]	[33]	[32]	[31]
δ-tocotrienol		5–9%		31.8 ± 4.2/11.7 ± 0.8%	
α-tocomonoenol				4.0 ± 1.7/1.6 ± 0.3%	
Total Tocols		600–1000	452–2189	259.3 ± 48.4	10.9–26.2
Other (Hc + carotenoids)	1070–1800	800–2400	514–1375	10389.3 ± 1004.9	

Hc = hydrocarbons.

[a]Samples collected at phenological stages 806–809.

[b]Ripe fruit (24 WAA).

[c]Samples collected between 18 and 24 WAA.

Table 4. Literature data on composition of the unsaponifiable fraction of O×G interspecific hybrid palm oil. Data are provided as mg/Kg oil unless % is indicated. Percentages refer to within class of unsaponifiable components.

Carotenoids are responsible for the color of the oils obtained from mesocarp of palm fruits. A wide range (500–10,000 mg/Kg oil) of their level in hybrid palm oils was reported in literature [3, 10, 33, 44]. Eleven types of carotenes have been identified (α-, β-, ζ-, γ-, and δ-carotene, phytoene, phytofluene, neurosporene, α- and β-zeacarotene, and lycopene), with no qualitative variations among EO, EG and their hybrids. β-carotene is the most represented (52–60% of total carotenes), followed by α-carotene (33–36% of total carotenes). Major quantitative differences are related to lycopene, whose levels account for 1–8% of total carotenes in EG whereas in EO and O×G hybrids lycopene percentages are less than 0.1% [44]. Squalene ranges from 20 to 250 mg/Kg oil [31, 32]. African palm oil was characterized by higher contents of carotenes [44] and squalene [32] than O×G interspecific hybrid oil.

More than 40 alcoholic compounds, belonging to six classes (4-desmethylsterols, 4,4-dimethylsterols, isoprenoid alcohols, n-alkanols and tocols) have been identified in screw pressed crude palm oil obtained from interspecific hybrids. Desmethylsterols and isoprenoid alcohols are the most represented classes, accounting for 79–85% of total alcohols, followed by *n*-alkanols (4–8% of total alcohols), 4,4-dimethylsterols (5–6%), tocols (3–4%), and 4-methylsterols (1–3%) [32].

Quantitative data expressed in mg/kg oil show a trend of progressive accumulation of squalene, desmethylsterols, isoprenoid alcohols, tocols, and 4,4-dimethylsterols in crude hybrid palm oil during ripening, whereas *n*-alkanols and 4-methylsterols show apparently stable levels in total lipids, which can be attributed to the increase in their amounts at the same time TAGs were synthesized [32, 33].

4.1. 4-desmethylsterols

The content of phytosterols in hybrid palm oil ranges from 160 to 1400 mg/kg oil [31–33, 44]. Δ^5-sterols represent 97% of total sterols in hybrid palm oil. The identified molecules are "campesterol" (campesterol +22,23-dihydrobrassicasterol), stigmasterol, β-sitosterol, Δ^5-avenasterol, $\Delta^{5,24}$-stigmastadienol, fucosterol, and clerosterol; ergosterol (ergosta-5,7,22-trien-3β-ol) was tentatively identified, whereas Δ^7-campesterol (ergosta-7-en-3β-ol) is the only Δ^7-sterol clearly identified in hybrid palm oil. β-sitosterol is the most represented phytosterol (58–62% of total sterols), followed by campesterol (12–22%) and stigmasterol (13–19%). Cholesterol is a significant component of sterol fraction, accounting for 2–5% of total sterols

[31, 32, 45]. As described above, an increase in total sterols content of oil samples occurs during ripening, whereas no significant variations in the composition of the desmethylsterol fraction were observed [31].

4.2. 4,4-dimethylsterols

Very little information is available on the occurrence of 4,4-dimethylsterols (or triterpenic alcohols, or triterpenols) in hybrid palm oil. Three 9,19-cyclopropanesterol have been identified: cycloartenol, 24-methylenecycloartanol, and a third triterpenol characterized by a mass spectrum very similar to 24-methylenecycloartanol, compatible with cyclobranol or cycloaudenol. The structure of isoarborinol was tentatively attributed by Mozzon et al. [32] to a fourth triterpenol. The content of 4,4-dimethylsterols ranges between 20 and 85 mg/Kg g oil (corresponding to 0.6% of total unsaponifiable matter), with no significant differences between African and hybrid palm oils. The composition of the triterpenol fraction does not show significant variations between the African and hybrid palm oils, as well; cycloartenol (70–75% of total triterpenols), and 24-methylenecycloartanol (14–20%) are the two most represented components [31, 32]. Oil levels of 4,4-dimethylsterols increase from 200 mg/Kg at 18 WAA (beginning of inolition) to 340 mg/Kg at 24 WAA (maximum of inolition) [31].

4.3. 4-methylsterols

Citrostadienol was the main 4-methylsterol in hybrid palm oil, followed by obtusifoliol (4,14-dimethylergosta-8,24(28)-dien-3-ol). Gramisterol (24-methylenelophenol) was also identified. The content of 4-methylsterols ranges 7–15 mg/Kg g oil (corresponding to 0.1–0.2% of total unsaponifiable matter), with no significant differences between African and hybrid oils. The composition of the 4-methylsterols fraction does not show significant variations between the African and hybrid palm oils too; cytrostadienol ranged from 44.5 to 50.3% of total 4-methylsterols, obtusifoliol from 14.3 to 31.5%, and gramisterol from 24.0 to 35.4%. Total content of 4-methylsterols does not significantly change during ripening [31, 32].

4.4. Aliphatic alcohols

A complete series of aliphatic alcohols of even number of carbon atoms from 18 to 34 was identified in mesocarp oil from hybrid palm fruits. Odd carbon number alkanols C29, C31, and C33 were also identified [31, 32]. *n*-alkanols level ranges 25–80 mg/Kg oil, without significant differences between African and hybrid palm oil. The pattern of *n*-alkanols, according to the number of carbon atoms, follows a typical unimodal distribution with a maximum abundance of alcohol C32, in both EG and hybrid oil types [32]. Ripening stage affects aliphatic alcohol fraction neither from a qualitative nor from quantitative viewpoint [31].

After 4-desmethylsterols, isoprenoid alcohols (terpenols) are the most represented class of alcoholic components of unsaponifiable matter of hybrid pal oil. A series of terpenols with 20 carbon atoms and 1 (phytol), 2, 3, and 4 (geranylgeraniol) double bonds has been identified. Hybrid palm oil is characterized by higher (160–330 mg/Kg), although not statistically significant, contents of isoprenoid alcohols, and by a higher phytol/geranylgeraniol ratio than EG mesocarp oil [32].

4.5. Tocols

At least seven different tocols were identified in mesocarp oil from hybrid palm fruits [31, 32, 44]: 5,7,8-trimethyl (α isomer) tocol and tocotrienol, 5,8-dimethyl (β isomer) tocol and tocotrienol, 7,8-dimethyl (γ isomer) tocol and tocotrienol, and 8-monomethyl (δ isomer) tocotrienol. The whole amount of tocols in hybrid palm oils greatly varies between 10 and 2200 mg/Kg [31–33, 44]. Experimental data about tocols composition of hybrid palm oils [32, 44] report a range of 10–24% for α-tocopherol, 42–60% for γ-tocotrienol, 15–31% for α-tocotrienol, and 5–12% for δ-tocotrienol. A trend of increase in total tocols content was observed during fruit ripening [31, 33].

5. Hybrid palm oil and health

Several drawbacks contribute to negatively affect the reputation of conventional palm oil among consumers. Involvement of dietary SFAs, mainly P, in the serum lipids profile and in the development of obesity, metabolic syndrome, type 2 diabetes and cancer were thoroughly discussed and confirmed [50]. Besides, it is estimated that only a quarter of palm oil worldwide is used as a crude oil. In EU and USA fatty substances from palm drupes are mostly used in their odorless and pale-yellow forms resulting from refining processes. Refining aims to remove volatile (off-odors, water) and non-volatile (FFA, phospholipids, pigments) oil components other than TAGs. The process causes not only a strong reduction of nutritionally valuable components (antioxidants, such as tocols and polyphenols) but also generates new toxicant. Since late 2000s, non-volatile chloropropanols (3-monochloropropane-1,2-diol, 3-MCPD; 2-monochloropropane-1,3-diol, 2-MCPD), glycidol, and their esters with FAs have been receiving increasing attention. Due to the elevated temperatures reached, the deodorization step is the most important contributor to the generation of those toxicants. Among the most consumed edible fatty substances, palm oil has the highest levels of MCPD and glycidol esters (**Table 5**). On the basis of available data, the European Food Safety Authority (EFSA) have concluded that estimated exposure of the younger aged groups of population to 3-MCPD could substantially exceed the tolerable daily intake (TDI) [7].

	3-MCPD	2-MCPD	Glycidol
Palm oil	2912	1565	3955
Sunflower oil	503	233	650
Rapeseed oil	232	109	166
Olive oil	48	86	15
Soybean	394	167	171
Palm kernel oil	624	270	421

Table 5. Occurrence (mean values, μg/Kg) of 3-MCPD, 2-MCPD and glycidol (from esters) in edible fats and oils during the period 2012–2015. Data referred to five edible oils most consumed in EU (globally 90% of total edible oil consumption); palm kernel oil as comparison (data from [11]).

Hence, the use of unrefined vegetable oils can both avoid the exposure to toxicants originating during processing and provide significant levels of substances (antioxidants) that are able to protect from negative effects of free radicals and reactive oxygen species. Indeed, EVOO is the most famous (among edible fats/oils) source of nutritionally valuable bioactive compounds (polyphenols) and, for the latest decades, a great amount of literature has been producing on the role of EVOO antioxidants in the prevention of chronic and degenerative diseases (cardiovascular diseases, obesity, type 2 diabetes, inflammatory processes, cancer, aging). Recently, tocotrienols have gained attention for their higher biological effectiveness than tocopherols, as antioxidant and anticancer agents. Crude palm oil obtained from O×G interspecific hybrid contains high amount of tocotrienols and carotenoids, together with a more favorable SFA/UFA ratio than the traditional African palm oil. Recently, phenolics of crude hybrid palm oil and their evolution during ripening were studied [51]: total amount of phenolic substances ranges between 190 and 260 mg GAE/kg oil and a decreasing trend during ripening has been observed. Those levels are comparable to phenolic amounts in EVOO and several molecules that already have been identified in EVOO have been found in hybrid palm oil as well (protocatechuic acid, protocatechualdehyde, *p*-salicylic acid, vanillic acid, syringic acid, syringaldehyde, ferulic acid).

Lucci and co-workers [52] found that consumption of crude palm oil from interspecific hybrids has a favorable effect on plasma lipids pattern (total cholesterol, low-density lipoprotein cholesterol, and high-density lipoprotein cholesterol) and that this effect is not statistically different from dietary EVOO. Recently, Ojeda et al. [53] explored the impact of daily crude oil consumption (25 mL/day for 3 months) on plasma/serum antioxidant capacity (trolox equivalent antioxidant capacity, TEAC, and oxygen radical absorbance capacity, ORAC, assays) and total phenolic content in adults aged 50–77; they also compared the effect of hybrid palm oil and EVOO supplementations. Palm oil significantly increases the total phenolic content and the antioxidant capacity of human plasma (measured by both ORAC and TEAC methods); furthermore, no significant differences have been found between crude palm oil and EVOO groups for the measured parameters. Due to those interesting discoveries, it has been suggested to consider crude palm oil from interspecific hybrid as the "tropical equivalent of olive oil".

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