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Characterization of the lipid profile from coconut (*Cocos nucifera* L.) oil of different varieties by electrospray ionization mass spectrometry associated with principal component analysis and independent component analysis

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ABSTRACT

Coconut oil (CO) from fifteen different varieties of coconuts (*Cocos nucifera* L.) and one CO processed on an industrial scale were analyzed by electrospray ionization mass spectrometry (ESI-MS) and the data processed using the chemometric tools principal component analysis and independent component analysis. ESI-MS fingerprinting of lipid compounds showed predominance of diacylglycerols and triacylglycerols, as confirmed by high-resolution MS measurements. Chemometric processing of the ESI-MS data differentiated the coconut oil samples, showing that different coconut varieties/cultivars produce oils with distinguishable abundances of lipidic compounds. Thus ESI-MS analysis followed by data treatment using chemometric tools offers a tool able to classify the industrial coconut oils in a fast, simple and effective way, as well as serving as a potential method to identify the coconut varieties by the CO origin, and the occurrence of any adulteration. The procedure may also be applied for quality control of the industrial processes.

1. Introduction

Coconut (*Cocos nucifera* L.) is one of the most important oil crops in tropical regions (Tan & Che Man, 2002). The fruit of coconut palm is typically made up of three distinct layers: 1) epicarp or exocarp, the outermost layer; 2) mesocarp, the middle layer known as husk; and, 3) the endocarp, the hard outer layer. The coconut seed is inside of the fruit and is formed by the tegument and by the solid and liquid endosperm. The tegument is the thin brown color layer that involves the solid endosperm that is represented by the white, fleshy and oily pulp of the seed. Internally, surrounded by this white pulp, the seed has a large cavity full of an opalescent water that is the liquid endosperm. Coconut oil is extracted from the tegument, the solid endosperm and the desiccated coconuts, also known as copra. The demand for coconut oil (CO) has increased considerably due to it is increasing use in several applications such as: replacement of other vegetable oils (Ibrahim et al., 2016; Ng, Lai, Abas, Lim, & Tan, 2014), biodiesel production (Kalam, Rashed, Imdadul, & Masjuki, 2016; Qiu et al., 2016; Woo, Kook, Hawkes, Rogers, & Marquis, 2016), as a renewable alternative fuel source through the presence of mono alkyl esters of long chain fatty acids (Hossain, Chowdhury, Rekhu, Faraz, & Islam, 2012), production of transesterification products such as polymers (Beneš, Paruzel, Trhlíková, & Paruzel, 2016; Costa et al., 2016) and surfactants/polymers for cosmetic preparations (Ivić et al., 2017). The neutral character of its molecules also makes coconut oil products very mild and appropriate secondary surfactants, such as coconut oil polyglycerol-6 esters from transesterification reaction, used for the manufacturing of sensitive skin cosmetic formulations. (Cortese, Ricciutelli, Censi, & Di Martino, 2015).

The size and weight of the coconut and the copra yields are variety-dependent. Accordingly to Ohler (1999), the dwarf variety is represented by green, red and yellow fruit; is self-pollinated; its fruits are suitable for consumption of coconut water; the first inflorescence appears 2 years after planting; and, has a production lifetime between 30 and 40 years. The tall variety, also called typical, has coloration that varies from green to brownish; is cross-pollinated, and the fruits are

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mainly destined for use by industry; the first inflorescence appears between 6 and 10 years after planting; and, this variety has a production lifetime of 60-70 years. Hybrids are cultivars that result from natural or artificial crossing between tall and dwarf coconut varieties with intermediate characteristics.

Coconut oil contains compounds with 6-12 carbon atoms in their chains and is, therefore, considered rich in sources of medium chain fatty acids, making up about 60% of its composition. Other long chain fatty acid oils have 14-24 carbon atoms. Major compounds are saturated medium-chain fatty acid triacylglycerols (TAG), approximately 85%, with a high level of low molar mass saturated fatty acids such as lauric (La), myristic (M), capric (C), and palmitic (P) acids corresponding to about 25% of LaLaLa, 19-21% of CLaLa, 14-16% of CCLa, 13-15% of LaLaM, 7-9% of LaMM, being the lauric acid the most common. Other components are also present such as diacylglycerols (DAG) (7%), monoglycerideos (3%), free fatty acids (FFA) (0.13%), and phospholipids (0.2%) such as phosphatidylcholine, phosphatidytethanolamine and phosphatidylinositol (Laureles et al., 2002; Maruyama, Wagh, Gioielli, da Silva, & Martini, 2016; Rahman, 2000).

Different methods have been applied to extract CO, such as: i) wet extraction directly from coconut milk, without the use of solvent (Onsaard, Vittayanont, Srigam, & McClements, 2005); (ii) cold extraction using chilling, freezing and thawing techniques (Seow & Gwee, 1997); (iii) hot extraction using high temperature which may or not use solvent (Seneviratne, Hapuarachchl, & Ekanayake, 2009); (iv) fermentation: use of non-pathogenic bacteria cultures, such as *Lactobacillus plantarum* (Che Man, Abdul Karim, & Teng, 1997); and, (v) enzymatic in an aqueous extraction process, with enzyme mixtures for cellulase, a-amylase, polygalacturonase, and protease (Che Man, Suhardiyono, Asbi, Azudin, & Wei, 1996). Simpler methods have also been used, such as sun drying or under low heat, smoke drying, the cold press technique or direct solvent extraction, from coconut milk under controlled temperature, using water or isopropanol (Amarasiri & Dissanayake, 2006; Marina, Man, Nazimah, & Amin, 2009).

The characterization of major TAG compounds in each coconut oil variety is important for their various industrial and food applications. Different analytical tools have been used to evaluate its chemical composition and properties. For example, TAGs and FFA profiles of different Philippine coconut hybrids and their parents were analyzed by high-performance liquid chromatography (HPLC) coupled with refractive index detection (RI), and by gas chromatography (GC) coupled with flame ionization detection (FID) (Laureles et al., 2002.). This study showed that the TAG composition varied significantly between CO from hybrids and their dwarf or tall parents, highlighting the different contents of lauric acid and other FFA among the evaluated cultivars. There are also reports on the characterization of waste coconut oil to determine FFA composition by GC-MS (Oliveira et al., 2010) and detection of adulteration in virgin coconut oil by Fourier transform mid infrared (FT-MIR) spectroscopy (Rohman & Man, 2011).

Since coconut oil has attracted great interest from the cosmetics and pharmaceutical industries, the effective characterization of its lipid profile in terms of TAG composition of different cultivars becomes important for its typification, quality control and to screen for adulteration and contamination. This characterization may allow selecting cultivars that directly interest each industrial field (food, health, pharma etc.) based on fatty acid contents (Laureles et al., 2002).

The objective of this study was therefore to characterize the lipid profile from coconut oils of different coconut cultivars by using an easy, simple and fast method based on ESI-MS and chemometric tools of PCA and ICA in order to differentiate the lipid profile from each cultivar. The analyses were performed using the “fingerprinting” method (Catharino et al., 2005) that applies direct infusion, with no previous separation, of the sample solution into the ESI-MS system.

Table 1
Corresponding code numbers of samples.

Code number of samples	Varieties/cultivars
1-3	PB141
4-6	PYT
7-9	PB132
10-12	PB113
13-15	PB121
16-18	BYDG
19-21	BRDG
22-24	MYD
25-27	PB111
28-30	WAT
31-33	RIT
34-36	BGDJ
37-39	CRD
40-42	MRD
43-45	BRTPF
46-48	Industrial oil

2. Materials and methods

2.1. Samples and coconut oil extractions

Fifteen cultivars of coconuts (*Cocos nucifera* L.) were obtained from the SOCOCO S/A Food Industry and identified as: (a) dwarf: BYDG (Brazilian Yellow Dwarf - Gramame), MYD (Malayan Yellow Dwarf), BRDG (Brazilian Red Dwarf - Gramame), CRD (Cameroon Red Dwarf), BGDJ (Brazilian Green Dwarf - Jiqui), MRD (Malayan Red Dwarf); (b) tall: WAT (West African Tall), RIT (Rennell Islands Tall), PYT (Polynesian Tall), BRTPF (Brazilian Tall - Praia do Forte); (c) hybrid: PB 111 (CRD x WAT), PB 113 (CRD x RIT), PB 121 (MYD x WAT), PB 132 (MRD x PYT), PB141 (BGD x WAT). A commercial sample of coconut oil processed at the SOCOCO S/A Food Industry was also evaluated. Table 1 lists the code number of samples of all cultivars studied.

The solid endosperm of three seednuts of the same plant from each cultivar were crushed, grounded and then homogenized using an industrial blender. The resulting coconut milk was extracted with distilled hot water, collected in glass flasks and placed in an oven for 20 h at 70 °C (Beneš et al., 2016). After this time, the oil remaining on the glass surface was collected with pipettes and transferred to vials. The oil processed in the SOCOCO S/A Food Industry was extracted from the thin brown coat that covers the solid endosperm of the seeds.

2.2. ESI-MS analysis

The samples were prepared from a solution of 1 μL of the coconut oil in 1 mL of methanol:chloroform (1:1, *v/v*), HPLC-grade, obtained from Merck (Rio de Janeiro, Brazil). These coconut oil solutions were analyzed using a high capacity ion trap mass spectrometer (HCT) from Bruker Daltonik (Bremen, Germany) equipped with an ESI source operating in the positive ion mode, ESI(+). Direct infusion of the sample solutions was performed with an auxiliary syringe pump from Harvard Apparatus (Holliston, CA, USA). The ESI(+)-MS conditions were as follows: flow rate of 300 $\mu L\,h^{-1}$, capillary voltage of 3000 V, skimmer voltage of 40 V and source temperature of 300 °C. The ESI(+)-MS data were acquired in the ultra scan mode within a *m/z* 100–1000 range. Each sample was analyzed in triplicate. The mass spectra were processed using the software ESI Compass 1.3 for HCT/esquire from Bruker Daltonik (Bremen, Germany).

High-resolution MS coupled with ESI (HR-ESI-MS) was also applied to the analysis of the coconut oils. A representative CO sample of PYT (Polynesian Tall) was selected to be analyzed by HR-ESI(+)-MS. The measurement was performed on a 7.2 T LTQ FT Ultra mass spectrometer from Thermo Fisher Scientific (Bremen, Germany) with a ESI(+) source. The following parameters were used: flow rate of 5 $\mu L\,min^{-1}$, source voltage of 3.5 V, capillary temperature of 280 °C and tube lens

voltage of 85 V. The HR-ESI-MS data were acquired within a *m/z* 100–1000 range from LTQ FT Ultra 2.0 software using a mass resolving power of $m/\Delta m_{50\%}$ = 400,000 at *m/z* 400.

2.3. Chemometric treatment of data

The data set was composed of 48 lines (samples, including the different varieties of coconut and the replicates) and 17 columns (the *m/z* values of interest 327, 355, 383, 411, 467, 495, 523, 549, 577, 605, 633, 661, 689, 717, 745, 771, and 799). This makes extracting the desired information from the data complicated. For this reason, multivariate methods of PCA and ICA were used.

PCA analysis were carried out using PLS Toolbox version 8.5.2 from Eigenvector Research (Manson, WA, USA) and Matlab version 8.2 (R2013b) from MathWorks (Natick, MA, USA).

ICA analysis was performed with JADE algorithm run in Matlab from MathWorks (Natick, MA, USA). The number of ICs was selected based on the ICA by blocks procedure (Rutledge & Bouveresse, 2013). Due to intensity differences in *m/z* values, data was auto-scaled prior to both PCA and ICA analysis.

3. Results and discussion

3.1. Coconut oil lipid profiles obtained with electrospray ionization mass spectrometry

Fig. 1 shows representative ESI(+)-MS for four samples, which are coconut oil from samples of Polynesian Tall, hybrid PB121, Brazilian Green Dwarf – Jiqui (BGDJ) and industrial oil (see Fig. S1 for the ESI-MS of all oil samples). Note that the ion distributions of the samples are similar while the ion abundances are quite distinct in two different regions of the ESI(+)-MS. A representative sample of PYT was selected to be analyzed by HR-ESI(+)-MS, aiming to assign the molecular formulas for the different lipid ions detected in the sample. Table 2 summarizes the HR-ESI(+)-MS data obtained for this PYT sample (Fig. S2). The first region, within the *m/z* 300-530 range, is known to display ions related to the methoxy fatty acids, dicarboxylic acids, fatty alcohols, dicarboxylic acids, hydroperoxy fatty acids and diacylglycerols (DAG), whereas the second region, within the *m/z* 530-800 range, is dominated by TAG signals. (Santos et al., 2016; Zanqui et al., 2015b). The HR-ESI (+)-MS analysis (Table 2) made it possible to assign all molecular formulas with an error less than 1 ppm, where the assigned major ions correspond to $[M + H]^+$ and $[M + Na]^+$.

For all coconut oil, the TAG profiles are found to be composed mainly of capric and lauric acids, since the ions of *m/z* of 577, 605, 633, 661, 689, 717 and 745 have been attributed to $[M + H]^+$ or $[M + Na]^+$ forms in which M = CaCaCa, CaCaLa, LaLaCa, LaLaLa/MLCa, LaLaM, LaLaP/MMLa or MMM/LaLaS/LaMP (the acronyms are shown in Table 2). Kumar and Krishna (2015) analyzed different Indian coconut oils using liquid chromatography with a refractometric detector (LC-RID) and the major TAGs were found to be: CaCaLa, CaLaLa, LaLaLa, LaLaM, and LaMM. Laureles et al. (2002) evaluated the TAG profiles from different Philippine coconut hybrids and their parentals using the HPLC-RID technique and the results showed that the carbon number varied significantly between the different oils studied. The TAG that was constituted of lauric acid was significantly higher in two hybrids and in one of the dwarfs, whereas none of the hybrids had higher FFA content than their parentals.

If TAG compositions found by ESI-MS in our study are compared to those of other common vegetable oils, it is seen that the TAG composition of coconut oil is considerably lower in terms of molar mass (MM), as revealed by the predominance of ions of relatively low *m/z values*. For example, andiroba oil is dominated by the following TAG: PPL (*m/z* 853), PPO (*m/z* 855), PLO (*m/z* 879), POO (*m/z* 881), POS (*m/z* 883), OOL or LLS (*m/z* 905), OOO or SOL (*m/z* 907), and OOS or SSL (*m/z* 909) while castor oil has RRO (*m/z* 939) and RRR (*m/z* 955) (Bataglion et al., 2014). The main FFAs composing the TAGs of chia oil are palmitic, linoleic and linolenic, that its ESI-MS is dominated by PPLn (*m/z* 851), PPL (*m/z* 853), LnLnP (*m/z* 873), PLLn (*m/z* 875), LnOP (*m/z* 877) (Zanqui et al., 2015). Soybean oil is also known to provide a TAG profile dominated by $[TAG + Na]^+$ ions with the following composition: PLL (*m/z* 887), LLL (*m/z* 901) and LLO (*m/z* 903) (Funasaki et al., 2012). These vegetable oils present characteristic TAG profiles but with ions in an *m/z* 800-1000 range. Therefore CO is unusual in terms of TAG profile as are seed oils from *Virola bicuhyba* and *Syagrus coronata* collected in Brazil, which display TAG ions in the *m/z* 650–850 and *m/z* 600–1000 ranges. Oils from both *V. bicuhyba* and *S. coronata* seeds, which are composed of principally of medium-chain TAG, were proposed to serve as feedstock to produce lighter biofuels such as biogasolines and aviation fuels (Dos Santos et al., 2016). This same application could be extended to the coconut oils studied herein.

3.2. Chemometric analysis to differentiate the coconut oils from the MS lipid profile

3.2.1. Principal component analysis (PCA)

Among the multivariate analysis techniques, principal component analysis (PCA) is probably the most frequently used to decrease the dimensionality of the data. PCA is based on the decomposition of the X matrix containing a set of *n* objects (placed in rows) and *p* variables (placed in columns) (Beebe, Pell, & Seasholtz, 1998; Bro & Smilde, 2014), and is based on the decomposition of the original data matrix X into a product of two smaller matrices (Eq. (1)), T and P, the scores and the loadings respectively, plus the error matrix E that accounts for the residual information of the X matrix:

$$X = TP^T + E \quad (1)$$

where P^T indicates a transposed matrix.

The scores matrix contains information about the sample characteristics whereas the loadings matrix contains information about the influence of the variables on these characteristics. For this reason, a joint observation of loadings and scores graphs should allow the understanding of the variables that contribute to the more important similarities or differences.

The CO ions obtained by the ESI(+)-MS analysis corresponding to those of *m/z* 327, 355, 383, 411, 467, 495, 523, 549, 577, 605, 633, 661,689, 717, 745, 771 and 799 were used for data treatment. Fig. 2A shows the scores of the two first PCs (PC1 x PC2), the sample score plot on PC1 (Fig. 2B) and the loadings graph on PC1 (Fig. 2C). The first two PCs accounts for 83.86% of the total variance and therefore are the most important for the separation of the varieties.

According to Fig. 2A, samples 4-6 (PYT), 28-30 (WAT) and 43-45 (BRTPF) present the highest dissimilarities in PC1, as also can be visualized in the sample score plot of Fig. 2B. The loading graphs of PC1 in Fig. 2C had higher abundances of the ions of *m/z* 327, 355, 383, 411 (variables 1, 2, 3 and 4, respectively), 549, 577, 605 (variables 8, 9 and 10, respectively) and lower abundances in those of *m/z* 467, 495 and 523 (variables 5, 6 and 7 respectively).

Fig. 2A shows that for PC2, samples 13-15 (PB121) show the most difference, as seen in the graph of scores in Fig. 3A. The loading graph in Fig. 3B shows that this separation is due to variables 10-16, which correspond to the ions of *m/z* 605, 633, 661, 689, 717, 745 and 771, which are the TAG ions.

3.2.2. Independent component analysis (ICA)

Independent component analysis (ICA) is a relatively recent method (Jutten & Herault, 1991) that assumes that each row of the data matrix is a weighted sum of pure source signals, the weights being proportional to the contribution of the corresponding pure signals to that particular mixture. The original source signals and their proportions in the analyzed mixtures are unknown. ICA aims therefore to extract these pure sources that underlie the observed signals, as well as their

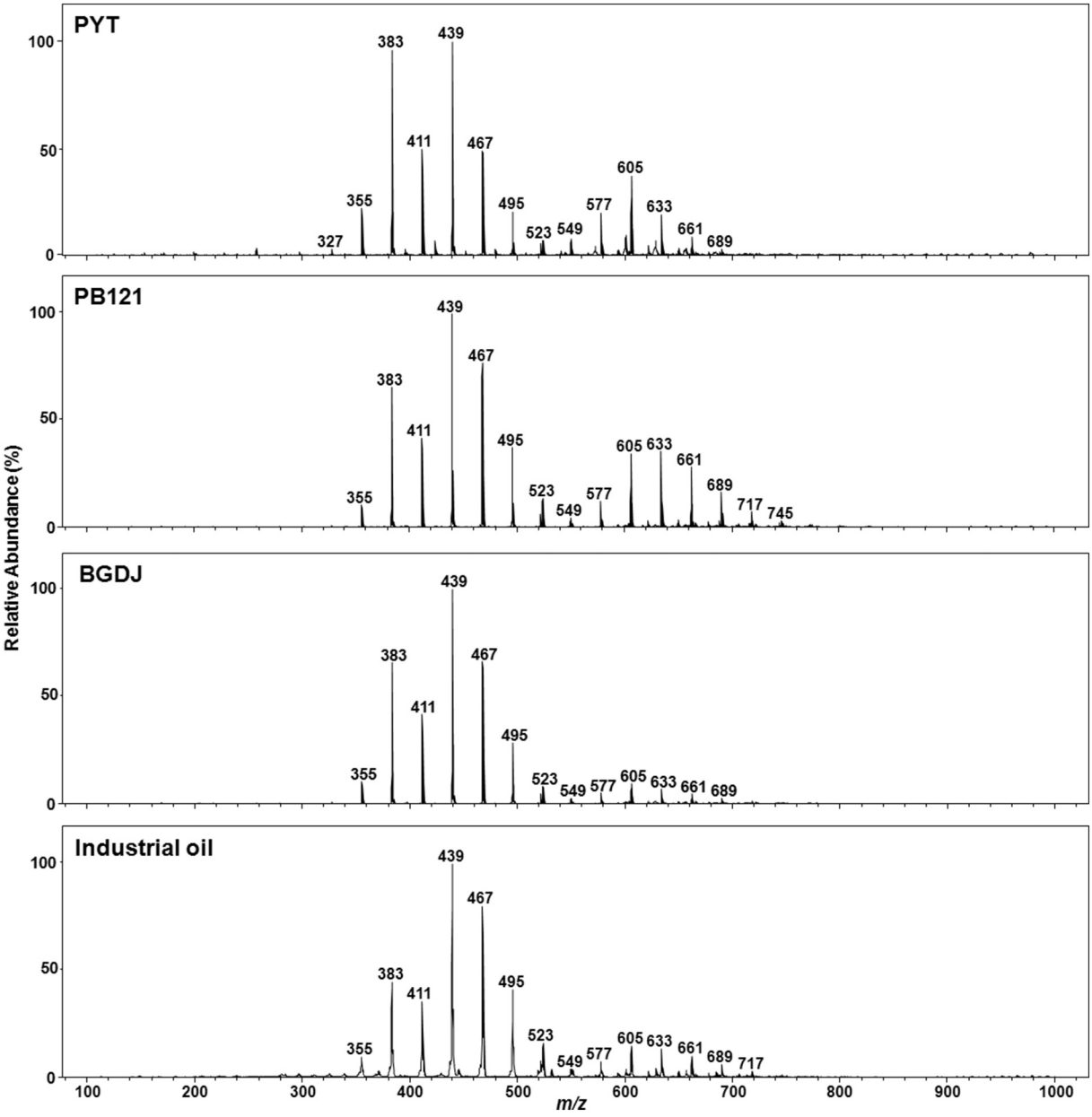

Fig. 1. ESI(+)-MS for the coconut oil solutions of PYT, PB121, BGDJ and industrial samples.

concentration in each mixture. Considering X as the matrix that contains the mixed signals, S the matrix of pure signals and A the matrix of pure signal *proportions* (the mixing matrix), ICA can be described by Eq. (2):

$$\mathbf{X = AS} \quad (2)$$

The signals in the rows of X are linear mixtures of pure source signals (the rows of S), the weights being given in the corresponding columns of A. The objective of ICA is to find physically meaningful vectors, called the independent components (ICs), which represent the rows of S and are as independent as possible (Rutledge & Bouveresse, 2013; Rutledge & Bouveresse, 2015).

Two independent components were selected based on ICA-by-blocks procedure. Fig. 4 shows the graphs of proportions on IC1 (A) and IC2 (B) and the extracted signals of IC1 (C) and IC2 (D).

The joint observation of IC1 proportions (Figs. 4A) and signals (Fig. 4C) indicate that samples 4-6 (PYT), 28-30 (WAT) and 43-45 (BRTPF) present higher amounts of the ions corresponding to variables 1, 2, 3 and 4 (ions of *m/z* 327, 355, 383 and 411, respectively) and 8,9,10 (ions of *m/z* 549, 577 and 605, respectively), and lower amounts of the ions 5, 6, 7 (ions of *m/z* 467, 495 and 523, respectively). Similarly, the joint observation of IC2 proportions (Figs. 4B) and signals (Fig. 4D) indicates that samples 13-15 (PB121) are the most dissimilar and that variables 10-16 are the ones that contribute the most to this separation, which correspond to the ions of *m/z* of 605, 633, 661, 689, 717, 745 and 771. Therefore, PCA and ICA provided very similar and consistent results about the differences between the samples and the variables that are responsible for such differentiations. Note that ICA allowed a simpler interpretation of the results, since there was no change to another variable system (Principal Components), as in PCA.

This study shows therefore that a simple and rapid analysis by ESI-MS followed by data treatment by proper chemometric tools can quickly classify coconut oil varieties/cultivars according to their distinctive lipid profiles. This task is clearly shown (Fig. 2A) when the analysis of the industrial oil (46-48) was included in the data and classified with a lipid profile similar to MYD (22-24) and to CRD (37-39) oils. This classification suggests that the fruits used in the extraction

Table 2
Experimental and theoretical *m/z*, molecular formula, error, compounds and class of ions obtained from the HR-ESI(+)-MS analysis of the PYT coconut oil.

Experimental *m/z*	Theoretical *m/z*	Molecular Formula	Error (ppm)	Compound*	Class
		$[M + H]^+$ or $[M + Na]^+$			
327.25286	327.25298	$C_{19}H_{35}O_4$	−0.37616	8-methoxy-13-hydroxy-9,11-octadecadienoic acid, 11-methoxy-12,13-epoxy-9-octadecenoic acid, 1-heptadecene-2,3R-dicarboxylic acid, 2-hydroxy-4-oxoheptadec-16-en-1-yl acetate or 2,4-dihydroxyheptadec-16-yn-1-yl acetate, 1,2-dihydroxyheptadec-16-yn-4-yl acetate,	Methoxy fatty acids, dicarboxylic acids or fatty alcohols
355.28421	355.28428	$C_{21}H_{39}O_4$	−0.20407	1-(9Z,12Z-octadecadienoyl)-rac-glycerol, 1-methoxy-9S,11R,15S-trihydroxy-5Z,13E-prostadiene or 1-nonadecene-2,3R-dicarboxylic acid	Dicarboxylic acids, prostaglandin or monoacylglycerols
383.31552	383.31558	$C_{23}H_{43}O_4$	−0.16091	methyl 9-butylperoxy-10,12-octadecadienoate or methyl 13-butylperoxy-9,11-octadecadienoate	Hydroperoxy fatty acids
411.34683	411.34688	$C_{25}H_{47}O_4$	−0.13636	NI	–
439.37814	439.37818	$C_{27}H_{51}O_4$	−0.10020	NI	–
467.40946	467.40948	$C_{29}H_{55}O_4$	−0.06694	NI	–
495.44075	495.44078	$C_{31}H_{59}O_4$	−0.06960	NI	–
523.47205	523.47208	$C_{33}H_{63}O_4$	−0.00573	NI	–
549.41259	549.41256	$C_{31}H_{58}O_6Na$	0.05460	NI	–
577.44394	577.44386	$C_{33}H_{62}O_6Na$	0.13449	1,2,3-tridecanoyl-sn-sn-glycerol (CaCaCa)	Triacylglycerols
605.47524	605.47516	$C_{35}H_{66}O_6Na$	0.13210	1,2-didecanoyl-3-dodecanoyl-sn-glycerol (CaCaLa)	
633.50658	633.50646	$C_{37}H_{70}O_6Na$	0.18942	1,2-didodecanoyl-3-decanoyl-sn-glycerol (LaLaCa)	
661.53797	661.53776	$C_{39}H_{74}O_6Na$	0.31744	1,2,3-tridodecanoyl-sn-sn-glycerol (LaLaLa)	
689.56926	689.56906	$C_{41}H_{78}O_6Na$	0.29003	1,2-didodecanoyl-3-tetradecanoyl-sn-glycerol (LaLaM)	
717.60064	717.60036	$C_{43}H_{82}O_6Na$	0.39019	1,2-didodecanoyl-3-hexadecanoyl-sn-glycerol (LaLaP)or1-dodecanoyl-2,3-ditetradecanoyl-sn-glycerol (MMLa)	
745.63200	745.63166	$C_{45}H_{86}O_6Na$	0.45599	1,2,3-tritetradecanoyl-sn-glycerol (MMM), 1,2-didodecanoyl-3-octadecanoyl-sn-glycerol (LaLaS) or 1-dodecanoyl-2-tetradecanoyl-3-hexadecanoyl-sn-glycerol (LaMP)	
771.64755	771.64731	$C_{47}H_{88}O_6Na$	0.31102	1,2-ditetradecanoyl-3-(9Z-hexadecenoyl)-sn-glycerol (MMPo)	
799.67892	799.67861	$C_{49}H_{92}O_6Na$	0.38766	1,2-ditetradecanoyl-3-(9Z-octadecenoyl)-sn-glycerol (MMO)	

NI: Not identified.

* Fatty acid abbreviations: Ca, capric acid; La, lauric acid; M, myristic acid; Po, palmitoleic acid; P, palmitic acid; O, oleic acid; S, stearic acid; L, linoleic acid.

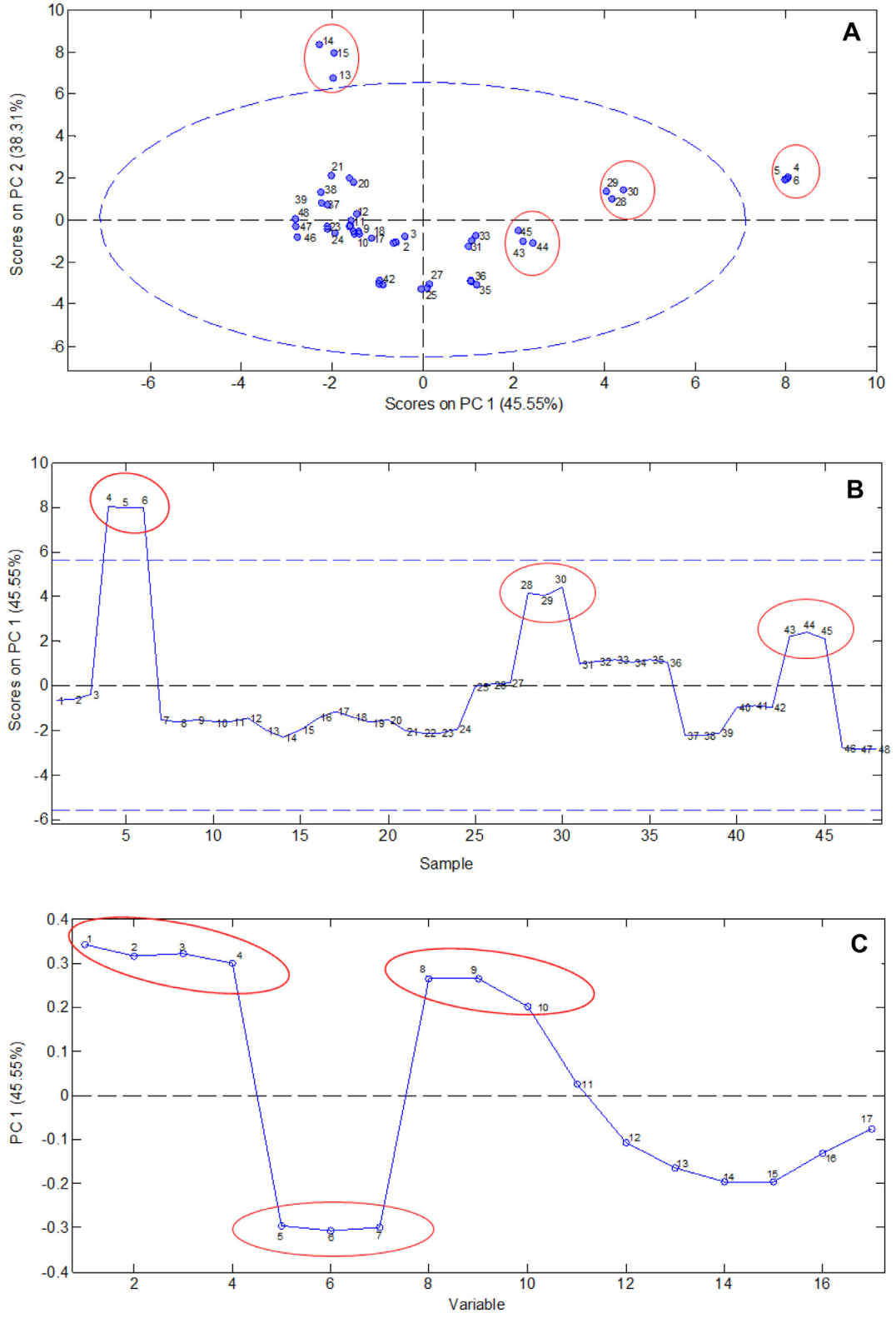

Fig. 2. Scores PC1 x PC2 (A), sample score plot on PC1(B) and loadings graph on PC1 (C). The analysis was performed with N = 3 for each sample. The identification of samples is presented in Table 1.

of the industrial oil were probably collected from the areas corresponding to these specific varieties, although the industrial extraction process was different.

Samples from PYT, WAT and BRTPF presented the ions of *m/z* 327, 355, 383, 411, 549, 577 and 605 as the most abundant. The ions of *m/z* 577 and 605 are due to TAG composed by two medium-chain fatty acids, capric and lauric acids. According to Jeyarani, Khan, and Khatoon (2009) and Ibrahim et al. (2016) the medium-chain TAG are digested more easily and absorbed more rapidly by both animal and human bodies, because they require no bile salts or enzymes, unlike the

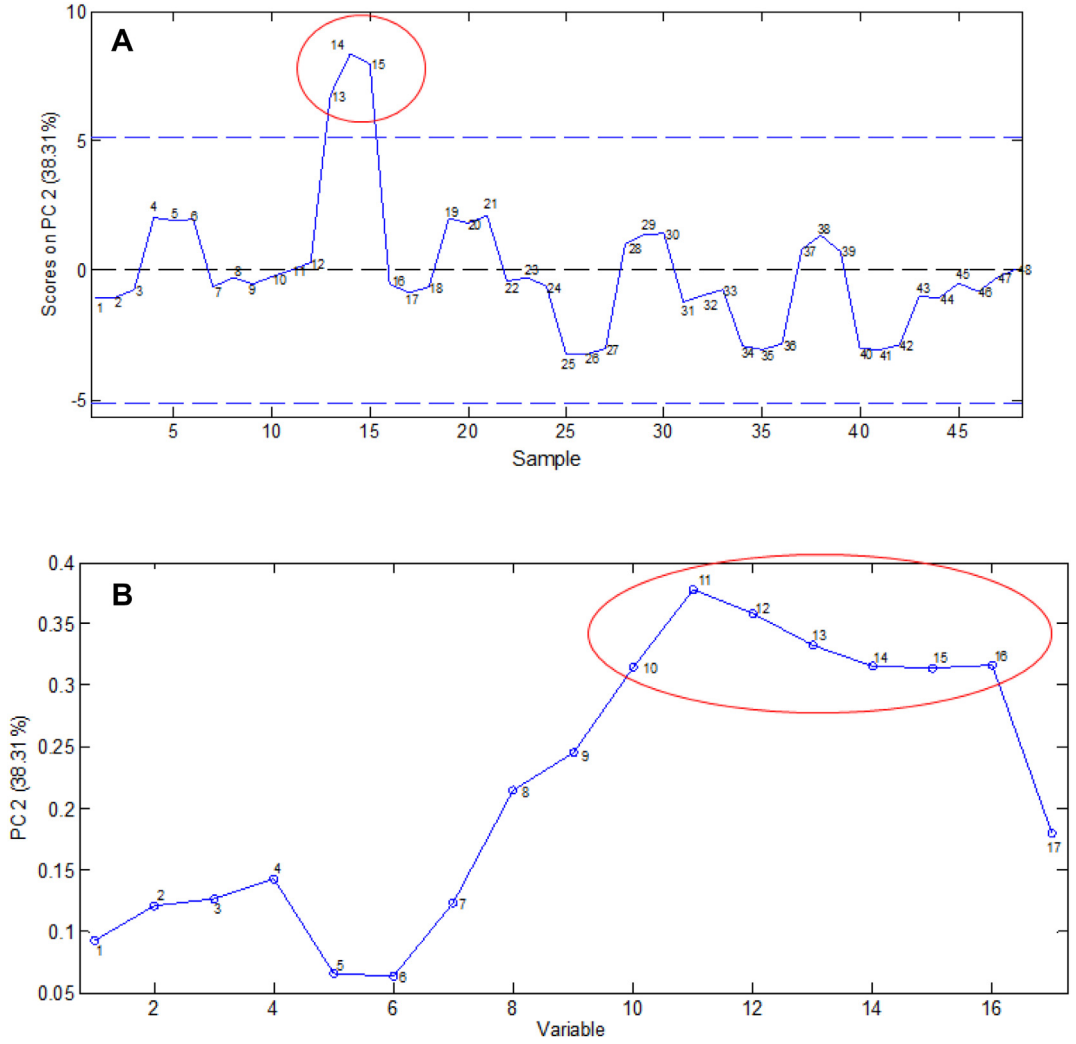

Fig. 3. Sample score plots for PC2 (A) and loadings graphs of PC2 (B). The analysis was performed with $N = 3$ for each sample. The identification of samples is presented in Table 1.

long-chain triglycerides.

Hybrid PB121, the most cultivated coconut hybrid in Brazil, presented the ions of *m/z* of 605, 633, 661, 689, 717, 745 and 771 as the most abundant. These ions are due to TAGs composed by lauric, capric, myristic and palmitic saturated fatty acids, which account for the stability of the coconut oil against oxidative rancidity. This stability permits the use of these oils in confectionery products, due to the increased shelf life of a product without trans fatty acids (Jeyarani et al., 2009).

The replicates of each cultivar/variety from CO of hybrids and their respective parents were plotted to compare their lipid profile (Fig. S3). Note that there were no significant differences between the triplicates, as expected, but different lipid profiles were observed between the parents and hybrids, except for PB 113 that is similar to CRD (yellow group). The hybrids PB 141 (purple group), PB 121 (black group) and PB 111 (green group) have also been found to have WAT (the male parental) in common and their major lipid differences are between compounds detected as the ions of *m/z* 600-800. For the hybrid PB132 (blue group), its ESI-MS lipid profile is more similar to MRD when compared to PYT, which is quite different. The main differences are related to the TAG ions of *m/z* 605 (CaCaLa) and 633 (LaLaLa). Our results agree with the results obtained by Laureles et al. (2002) in which the TAG composition varied significantly between parentals, dwarfs and talls and between hybrids and parentals. Azeez (2007) evaluated the fatty acid profile of coconut oil in relation to season and nut maturity in different cultivars and the results showed that the long chain fatty acids decreased, while the small to medium chain fatty acids increased with nut maturity, as also did the unsaturated fatty acid concentrations.

4. Conclusion

This study made it possible to differentiate the coconut varieties/cultivars regarding the lipid profile obtained by ESI-MS analysis, showing that they may produce oils with a different abundance of TAGs. This may further direct new coconut plantings for specific purposes, such as pharmaceuticals, foodstuff and cosmetics. The method was able to classify the industrial coconut oil in terms of the variety of coconut in a fast, simple and effective way, which suggests a useful tool for quality control of industrial coconut oils.

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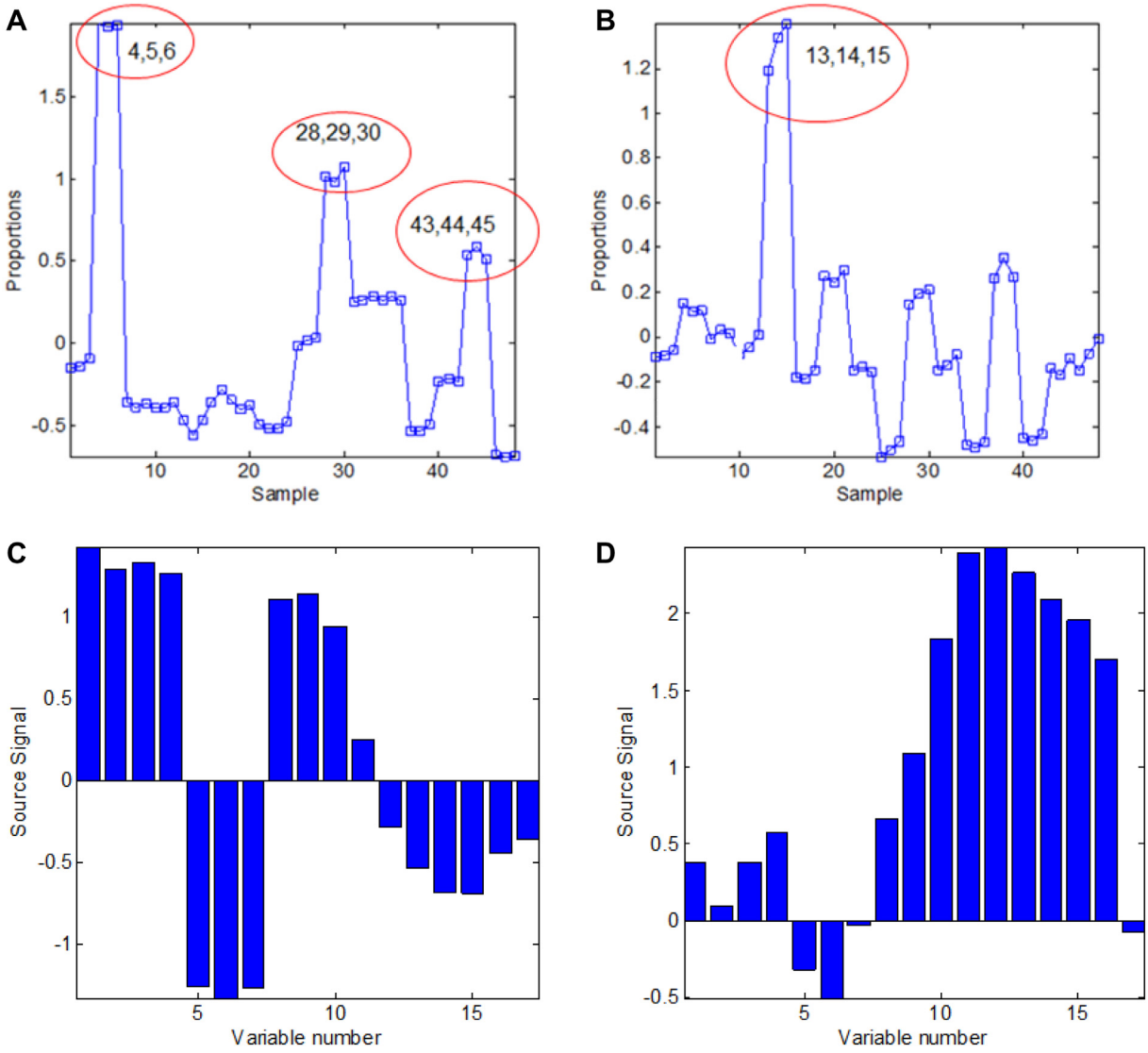

Fig. 4. Graphs of the proportions of IC1 (A) and IC2 (B) and graphs of the signals of IC1 (C) and IC2 (D). The identification of samples is presented in Table 1.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodres.2019.04.052.

References

Amarasiri, W. A., & Dissanayake, A. S. (2006). Coconut fats. *Ceylon Medical Journal, 51*, 47–51.

Azeez, S. (2007). Fatty acid profile of coconut oil in relation to nut maturity and season in selected cultivars/hybrids. *British Food Journal, 109*, 272–279.

Bataglion, G. A., Da Silva, F. M. A., Santos, J. M., Dos Santos, F. N., Barcia, M. T., de Lourenço, C. C., ... Koolen, H. H. F. (2014). Comprehensive characterization of lipids from Amazonian vegetable oils by mass spectrometry techniques. *Food Research International, 64*, 472–481.

Beebe, K. R., Pell, R. J., & Seasholtz, M. B. (1998). *Chemometrics: a practical guide.* New York: Wiley.

Beneš, H., Paruzel, A., Trhlíková, O., & Paruzel, B. (2016). Medium chain glycerides of coconut oil for microwave-enhanced conversion of polycarbonate into polyols. *European Polymer Journal, 86*, 173–187.

Bro, R., & Smilde, A. K. (2014). Principal component analysis. *Analytical Methods, 6*, 2812–2831.

Catharino, R. R., Haddad, R., Cabrini, L. G., Cunha, I. B. S., Sawaya, A. C. H. F., & Eberlin, M. N. (2005). Characterization of vegetable oils by electrospray ionization mass spectrometry fingerprinting: classification, quality, adulteration, and aging. *Analytical Chemistry, 77*, 7429–7433.

Che Man, Y. B., Abdul Karim, M. I. B., & Teng, C. T. (1997). Extraction of coconut oil with Lactobacillus plantarum 1041 IAM. *Journal of the American Oil Chemists Society, 74*, 1115–1119.

Che Man, Y. B, Suhardiyono, Asbi, A. B., Azudin, M. N., & Wei, L. S. (1996). Aqueous enzymatic extraction of coconut oil. *Journal of the American Oil Chemists Society, 73*, 683–686.

Cortese, M., Ricciutelli, M., Censi, R., & Di Martino, P. (2015). Qualitative characterization of a transesterification product of coconut oil by FIA-APCI-MS. *International Journal of Cosmetic Science, 37*, 379–385.

Costa, C. S. M. F., Fonseca, A. C., Moniz, J., Godinho, M., Serra, A. C., & Coelho, J. F. J. (2016). Soybean and coconut oil based unsaturated polyester resins: Thermomechanical characterization. *Industrial Crops and Products, 85*, 403–411.

Dos Santos, F. N., Santos, J. M., Mesquita, P. R. R., Oliveira, K. B., Rodrigues, F. M., Lopes, W. A., & Eberlin, M. N. (2016). Immediate differentiation of unusual seed oils by easy ambient sonic-spray ionization mass spectrometry and chemometric analysis. *Analytical Methods, 8*, 3681–3690.

Funasaki, M., Oliveira, R. S., Zanotto, S. P., Carioca, C. R. F., Simas, R. C., Eberlin, M. N., & Alberici, R. M. (2012). Quality control via triacylglyceride profiles provided by easy ambient sonic-apray ionization mass spectrometry. *Journal of Agricultural and Food Chemistry, 60*, 11263–11267.

Hossain, M. A., Chowdhury, S. M., Rekhu, Y., Faraz, K. S., & Islam, M. U. (2012). Biodiesel from coconut oil a renewable alternative fuel for diesel engine. *International Journal of Chemical and Molecular Engineering, 6*, 524–528.

Ibrahim, A. H., Khan, M. S. S., Al-Rawi, S. S., Ahamed, M. B. K., Majid, A. S. B. A., Al-Suede, F. S. R., ... Majid, A. M. S. A. (2016). Safety assessment of widely used fermented virgin coconut oil (*Cocos nucifera*) in Malaysia: Chronic toxicity studies and SAR analysis of the active components. *Regulatory Toxicology and Pharmacology, 81*, 457–467.

Ivić, J. T., Milosavić, N., Dimitrijević, A., Jankulović, M. G., Bezbradica, D., Kolarski, D., & Veličković, D. (2017). Synthesis of medium-chain length capsinoids from coconut oil catalyzed by *Candida rugosa* lipases. *Food Chemistry, 218*, 505–508.

Jeyarani, T., Khan, M. I., & Khatoon, S. (2009). Trans-free plastic shortenings from

coconut stearin and palm stearin blends. *Food Chemistry, 114*, 270–275.
Jutten, C., & Herault, J. (1991). Blind separation of sources, part I: An adaptive algorithm based on neuromimetic architecture. *Signal Processing, 24*, 1–10.
Kalam, M. A., Rashed, M. M., Imdadul, H. K., & Masjuki, H. H. (2016). Property development of fatty acid methyl ester from waste coconut oil as engine fuel. *Industrial Crops and Products, 87*, 333–339.
Kumar, P. K. P., & Krishna, A. G. G. (2015). Physicochemical characteristics of commercial coconut oils produced in India. *Grasas y Aceites, 66*, e062.
Laureles, L. R., Rodriguez, F. M., Rean, C. E., Santos, G. A., Laurena, A. C., & Mendoza, E. M. T. (2002). Variability in fatty acid and triacylglycerol composition of the oil of coconut (*Cocos nucifera* L.) hybrids and their parentals. *Journal of Agricultural and Food Chemistry, 50*, 1581–1586.
Marina, A. M., Man, Y. B. C., Nazimah, S. A. H., & Amin, I. (2009). Chemical properties of virgin coconut oil. *Journal of the American Oil Chemists' Society, 86*, 301–307.
Maruyama, J. M., Wagh, A., Gioielli, L. A., da Silva, R. C., & Martini, S. (2016). Effects of high intensity ultrasound and emulsifiers on crystallization behaviour of coconut oil and palm olein. *Food Research International, 86*, 54–63.
Ng, S. P., Lai, O. M., Abas, F., Lim, H. K., & Tan, C. P. (2014). Stability of a concentrated oil-in-water emulsion model prepared using palm olein-based diacylglycerol/virgin coconut oil blends: Effects of the rheological properties, droplet size distribution and microstructure. *Food Research International, 64*, 919–930.
Ohler, J. G. (1999). *Modern coconut management: Palm cultivation and products.* London: Intermediate Technology Publications.
Oliveira, J. F. G., Lucena, I. L., Saboya, R. M. A., Rodrigues, M. L., Torres, A. E. B., Fernandes, F. A. N., ... Parente, E. J. S., Jr. (2010). Biodiesel production from waste coconut oil by esterification with ethanol: The effect of water removal by adsorption. *Renewable Energy, 35*, 2581–2584.
Onsaard, E., Vittayanont, M., Srigam, S., & McClements, D. J. (2005). Properties and stability of oil-in-water emulsions stabilized by coconut skim milk proteins. *Journal of Agricultural and Food Chemistry, 53*, 5747–5753.
Qiu, T., Guo, X., Yang, J., Zhou, L., Li, L., Wang, H., & Niu, Y. (2016). The synthesis of biodiesel from *coconut* oil using novel Bronsted acidic ionic liquid as green catalyst. *Chemical Engineering Journal, 296*, 71–78.
Rahman, H. I. H. (2000). The chemistry of coconut oil. Accessed 4 December 2012 http://fos.ubd.edu.bn/sites/default/files/2000-Paper2.pdf.
Rohman, A., & Man, Y. B. C. (2011). The use of Fourier transform mid infrared (FT-MIR) spectroscopy for detection and quantification of adulteration in virgin coconut oil. *Food Chemistry, 129*, 583–588.
Rutledge, D. N., & Bouveresse, J. R. D. (2013). Independent components analysis with the JADE algorithm. *Trends in Analytical Chemistry, 50*, 22–32.
Rutledge, D. N., & Bouveresse, J. R. D. (2015). Corrigendum to 'independent components analysis with the JADE algorithm'. *Trends in Analytical Chemistry, 67*, 220.
Santos, F. N., Santos, J. M., Mesquita, P. R. R., Oliveira, K. B., Rodrigues, F. M., Lopes, W. A., & Eberlin, M. N. (2016). Immediate differentiation of unusual seed oils by easy ambient sonic-spray ionization mass spectrometry and chemometric analysis. *Analytical Methods, 8*, 3681–3690.
Seneviratne, K. N., Hapuarachchl, C. D., & Ekanayake, S. (2009). Comparison of the phenolic-dependent antioxidant properties of coconut oil extracted under cold and hot conditions. *Food Chemistry, 114*, 1444–1449.
Seow, C. C., & Gwee, C. N. (1997). Coconut milk: chemistry and technology. *International Journal of Food Science and Technology, 32*, 189–201.
Tan, C. P., & Che Man, Y. B. (2002). Differential scanning calorimetric analysis of palm oil, palm oil based products and coconut oil: effects of scanning rate variation. *Food Chemistry, 76*, 89–102.
Woo, C., Kook, S., Hawkes, E. R., Rogers, P. L., & Marquis, C. (2016). Dependency of engine combustion on blending ratio variations of lipase-catalysed coconut oil biodiesel and petroleum diesel. *Fuel, 169*, 146–157.
Zanqui, A. B., de Morais, D. R., da Silva, C. M., Santos, J. M., Chiavelli, L. U. R., Bittencourt, P. R. S., ... Matsushita, M. (2015). Subcritical extraction of *Salvia hispanica L.* oil with n-propane: composition, purity and oxidation stability as compared to the oils obtained by conventional solvent extraction methods. *Journal of the Brazilian Chemical Society, 26*, 282–289.
Zanqui, A. B., de Morais, D. R., da Silva, C. M., Santos, J. M., da Silva, C. M., Visentainer, J. V., ... Matsushita, M. (2015b). Subcritical extraction of flaxseed oil with n-propane: Composition and purity. *Food Chemistry, 188*, 452–458.