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ARTICLE

Amazonian Vegetable Oils and Fats: Fast Typification and Quality Control via Triacylglycerol (TAG) Profiles from Dry Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI−TOF) Mass Spectrometry Fingerprinting

Sérgio A. Saraiva,[†] Elaine C. Cabral,[‡] Marcos N. Eberlin,[†] and Rodrigo R. Catharino*[,§]

[†]ThoMSon Mass Spectrometry Laboratory, Institute of Chemistry, State University of Campinas, UNICAMP, Campinas, SP, Brazil, [‡]Institute of Chemistry, São Paulo University, São Paulo, SP, Brazil and [§]Department of Clinical Pathology, School of Medical Sciences, State University of Campinas, P.O. Box 6111, 13083-887 Campinas, SP, Brazil

Amazonian oils and fats display unique triacylglycerol (TAG) profiles and, because of their economic importance as renewable raw materials and use by the cosmetic and food industries, are often subject to adulteration and forgery. Representative samples of these oils (andiroba, Brazil nut, buriti, and passion fruit) and fats (cupuaçu, murumuru, and ucuba) were characterized without preseparation or derivatization via dry (solvent-free) matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF MS). Characteristic profiles of TAG were obtained for each oil and fat. Dry MALDI−TOF MS provides typification and direct and detailed information, via TAG profiles, of their variable combinations of fatty acids. A database from spectra could be developed and may be used for their fast and reliable typification, application screening, and quality control.

KEYWORDS: Amazonian oil; Amazonian fat; triacylglycerol; MALDI−TOF−MS fingerprinting

INTRODUCTION

The search for alternatives to promote renewable exploration and preservation (*1*) of the Amazonian forest and its great biodiversity is an endeavor of worldwide interest. The commercial exploration of the Amazonian oil seed species seems to be one of the most attractive alternatives. Brazil nut (*Bertholletia excelsa*), andiroba (*Carapa guianensis*), babaçu (*Orbignya* spp.), cupuaçu (*Theobroma grandflorum*), murumuru (*Astrocaryium murumuru*), buriti (*Mauritia flexuosa*), passion fruit (*Passiflora* spp.), and ucuúba (*Virola sebifera*) are representative examples of the many Amazonian vegetal species of economic importance because their oils and fats have found various applications as nutritional, pharmaceutical, soap, cosmetic, painting, and additive products (*2*, *3*).

Amazonian oils and fats display unique composition and beneficial properties and are currently used in many cosmetic formulations (*4*). Comprehensive knowledge of their chemical compositions and geographical and seasonal variations is therefore essential to develop new commercial products based on Amazonian vegetable oils and fats (natural raw materials) (*5*).

Oils and fats are mainly constituted (about 95%) of complex mixture of triacylglycerols (TAGs) acting also as a solvent for several minority components, such as vitamins (tocopherols/tocotrienes), pigments including chlorophyll and carotens, phenolic compounds, phospholipids, free fatty acids, and mono- and diacylglicyerols (*6*). The task of determining the exact composition of TAG in oils and fats is complex, because of the variety of natural fatty acids (varying in length chain and unsaturation) and their location on the glycerol backbone.

Gas chromatography (GC) (*7*, *8*) or GC coupled to mass spectrometry (GC−MS) (*9*) are among the most common techniques used to characterize oils and fats via the determination of the fatty acid composition after TAG hydrolysis and derivatization of the free fatty acids. Fatty acid composition of oils and fats has been also determined by high-performance liquid chromatography (HPLC) without derivatization (*10*−*12*). Infrared (*13*) and nuclear magnetic resonance (*14*) are also used as important techniques for characterization of oil and fat composition.

Direct analysis (without pre-separation) by mass spectrometry has also been used for characterization of oils and fats. For instance, direct infusion of vegetable oils or its polar fraction using electrospray ionization mass spectrometry has been shown to provide fast and effective oil characterization (*15*, *16*). Matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) MS has also been added recently to the arsenal of efficient analytical techniques for oil and fat analysis. Its main advantage is simplicity, speed, and the

*To whom correspondence should be addressed. Telephone: (+55)-19-35213049. Fax: (+55) 19-35217370. E-mail: rrc@fcm.unicamp.br.

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possibility of determining TAG profiles directly without preseparation or derivatization (*17*−*23*). Different approaches to TAG analysis by MALDI−TOF MS have been developed (*18*, *19*, *22*, *23*), and a dry (solvent-free) MALDI−TOF MS protocol for analysis has been recently described (*24*).

Little data are available about the composition of Amazonian oils and fats. Mlayah et al. (*7*) analyzed the composition and physical properties of different palm oils (saponifiable and unsaponifiable fractions), whereas Artz et al. (*25*) identified the main TAG in pequi oil via HPLC−atmospheric pressure chemical ionization (APCI)−MS, and Jandera et al. (*11*) used the same technique to analyze the Brazil nut oil. There is however no comparative work for the fatty acid/TAG composition of the principal oils of the Amazonian rain forest. Herein, we present the first comparative analysis of the TAG composition of major Amazonian oils and fats via dry MALDI−TOF MS and show that this technique provides a fast fingerprinting method for their typification and quality control.

MATERIALS AND METHODS

Chemicals and Samples. All chemicals were of at least analytical grade. 2,5-Dihydroxybenzoic acid (DHB) was used as a matrix in dry MALDI. Certified samples were acquired from Naturais da Amazônia (Belém, Brazil), Crodramazon (Campinas, Brazil), and Beraca Sabara (São Paulo, Brazil). Brazil nut, andiroba, buriti, and passion fruit oils and cupuaçu, murumuru, and ucuúba fats were analyzed (four samples of each oil and fat).

Sample Preparation. For the TAG analysis, a dry MALDI (solvent-free protocol, mini-ball approach) was used (*22*).The sample and the matrix powder (in a ratio of 1:10) were mixed using a mini-bead beater with two metal beads in glass tubes. The matrix was added to the sample followed by the beads. The capped tube was placed in a two-dimensional shaker arm and shaken for 1 min. A minimum amount of the powder was applied to the MALDI target, spread carefully on the appropriate spot, and affixed by pressing with a spatula.

Instrumental Conditions. Mass spectra were acquired in the positive-ion mode using a MALDI−TOF instrument (Micromass, Manchester, U.K.) in the m/z 500−1200 range in the reflecton mode. The following main operational conditions were used: pulse voltage, 2500 V; reflectron, 2000 V; source, 15 000 V; and MCP, 1800 V. Desorption/ionization was accomplished using a UV laser (337 nm). Data were collected and analyzed by means of the MassLynx software (Waters, Manchester, U.K.). Isotopologue ions were ignored for simplicity. When appropriate, ion intensities were always corrected for the M + 2 contribution.

To classify oil samples after dry MALDI−TOF MS fingerprint, principal component analysis (PCA) was performed on the data using the Piroutte version 4.0 program (Infometrix, Seattle, WA).

RESULTS AND DISCUSSION

As exemplified by the spectrum of the Brazil nut oil (**Figure 1**), dry MALDI−TOF mass spectra of Amazonian vegetable oils were reproducible, displayed typical profiles, and detected characteristic packages of ions in two separate regions. One advantage of the dry MALDI protocol is the much enhanced homogeneity of sample deposition on the MALDI plate (as compared to solvent MALDI protocols), which assures improved reproducibility. The ions in the m/z 800−1000 range corresponded to TAG detected mainly as their sodium adducts, that is, $[TAG + Na]^+$. Minor ions because of $[TAG + K]^+$ adducts were also detected but in much lower intensities (*20*, *21*). The ions detected in the m/z 550−650 range corresponded mostly to fragments from the $[TAG + Na]^+$ ions because of the loss of a fatty acid moiety, as observed before (*21*, *27*).

Figure 2 compares the TAG region of the MALDI−TOF MS of the four Amazonian oils investigated, whereas **Table 1** summarizes the TAG composition profiles as determined from these spectra. The data showed that each oil displayed characteristic and quite unique dry MALDI−TOF MS fingerprints in the TAG region that allowed their rapid and clear typification.

Brazil nut oil and buriti oil possess mainly TAG derived from oleic and linoleic acids (parts **a** and **b** of **Figure 2**). The use of the dry MALDI protocol seemed to provide very reproducible TAG profiles, which were found to vary by less than 5%. The most abundant $[TAG + Na]^+$ ions were those of m/z 881 (OOP) and 907 (OOO). The fingerprint spectrum of the Brazil nut oil displayed, however, a much richer and characteristic series of ions, mainly those of m/z 905 (OOL or LLS), 903 (LLO or OOLn), 901 (LLL), 879 (PLO), and 877 (PLL). These ions corresponded to $[TAG + Na]^+$ adducts that had linoleic acid in their structures. Brazil nut oil is known to contain ca. 30−47% of linoleic acid, whereas buriti oil contains only ca. 2−5% of this multi-unsaturated fatty acid (*3*).

Linoleic acid is known to be the main fatty acid present in passion fruit oil (∼70%) (*4*), hence its dry MALDI−TOF MS (**Figure 2d**) was characterized mainly by having TAG species containing linoleic acid, which were the $[TAG + Na]^+$ ions of m/z 901 (LLL), 903 (LLO), and 877 (LLP). The dry MALDI−TOF MS for andiroba oil (**Figure 2c**) displayed mainly $[TAG + Na]^+$ ions of the oleic and palmitic acids of m/z 855 (PPO), 881 (OOP), and 907 (OOO). Andiroba and buriti oils displayed the most similar dry MALDI−TOF MS fingerprints, but Buriti oil was richer in oleic acid (71−76%) (*3*), hence its ion of m/z 907 was about twice as intense. Andiroba oil had a relatively higher percentage of palmitic acid, as shown by the abundance of the ions of m/z 855 and 829 (PPP).

Figure 3 displays the dry MALDI−TOF MS for the Amazonian fats, which are also very characteristic, permitting their rapid and clear typification. In comparison to oils, fats are known to be formed by TAG with shorter and saturated fatty acid chains. Accordingly, the dry MALDI−TOF MS of the Amazonian fats detected $[TAG + Na]^+$ ions at a lower m/z 600−900 range. The most intense ions in their fingerprints were the TAG species consisting of saturated fatty acids. A unique exception was provided by the cupuaçu fat (**Figure 3c**), whose spectrum was to some extent similar to those of the oils (**Figure 2**).

These spectra show that murumuru (**Figure 3a**) and ucuúba fats (**Figure 3b**) contained the TAG species consisting of lauric and myristic acids. The most abundant $[TAG + Na]^+$ ions in the murumuru fat were those of m/z 681 (LaLaLa) and 689 (LaLaM), whereas for the ucuúba oil, the main ions were those of m/z 717 (MMLa) and 745 (MMM). These profiles are in agreement with the reported fatty acid composition (*2*, *3*, *26*), which have shown that the ucuúba fat has high percentages of myristic acid (64−73%) and lauric acid (13−15%). Murumuru fat had the opposite distribution, which was 43−51% of lauric acid and 26−37% of myristic acid. The ucuúba fat fingerprint was also unique because of the detection of quite abundant $[TAG + K]^+$ adducts, which were those of m/z 705 $[C_{41}H_{78}O_6 + K]^+$, 733 $[C_{43}H_{82}O_6 + K]^+$, 761 $[C_{45}H_{84}O_6 + K]^+$, and 789 $[C_{45}H_{86}O_6 + K]^+$.

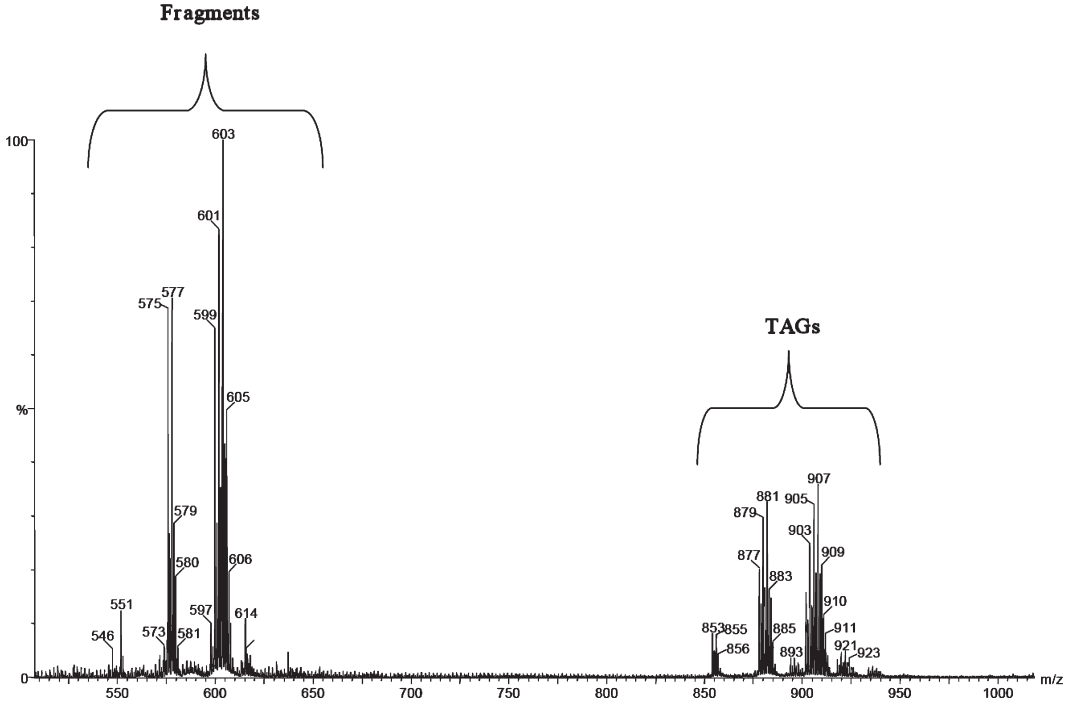

Figure 1. Dry MALDI−TOF MS fingerprint of Brazil nut oil.

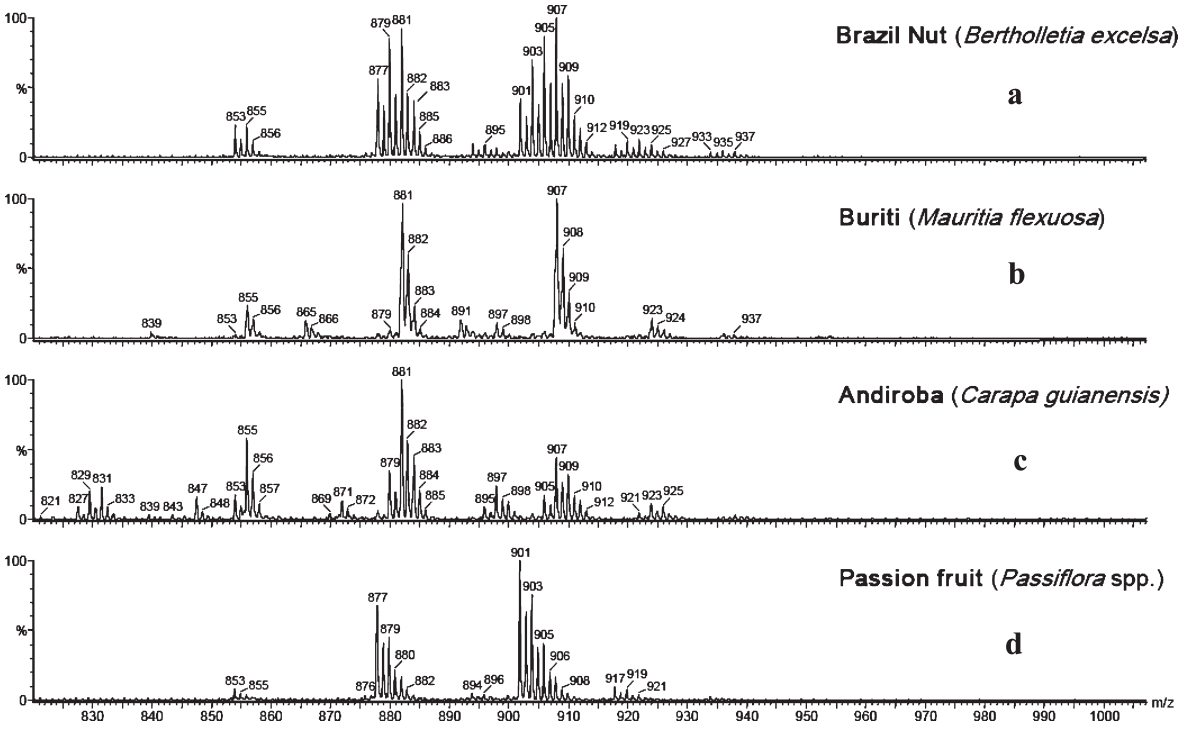

Figure 2. MALDI−TOF MS fingerprints of the Amazonian vegetable oils.

The cupuaçu fat fingerprint was also very unique (**Figure 3c**), displaying TAG ions mainly in the *m*/*z* 850−1000 range (**Figure 3c**). The main $[TAG + Na]^+$ ions were those containing stearic and oleic acids, such as SSO (*m*/*z* 911), OOS and/or SSL (*m*/*z* 909), OOO and/or SOL (*m*/*z* 907), SSS (*m*/*z* 913), and those containing one palmitic acid, which were OOP (*m*/*z* 881), POS (*m*/*z* 883), and SSP (*m*/*z* 885). TAG ions with one arachidic acid, which were OOA and/or ASL (*m*/*z* 937), ASO (*m*/*z* 939), and AAS (*m*/*z* 941), or two arachidic acids, which were AAL (*m*/*z* 965), AAO (*m*/*z* 967), and AAS (*m*/*z* 969), were also detected. It was noted that the ions of *m*/*z* 633 and 635 corresponded to fragment ions (**Figure 1**).

To test statistically the performance of dry MALDI−TOF MS fingerprints to typify the Amazonian oils and fats, PCA treatment was performed. **Figure 4** shows a scatter plot of PC1 versus PC2 for the MS data of the oils and cupuaçu fat (whose fingerprinting ions appear in the same *m*/*z* region as for the oils). Each of the four types of oils was clearly grouped and separated. Cupuaçu fat was also quite distant from the oils. Although not shown in **Figure 4** for clarity, PCA also placed the murumuru and ucuúba fats far away from the oils and all three fats fell within well-defined groups.

In conclusion, dry MALDI−TOF MS provided characteristic TAG fingerprints of Amazonian vegetable oils and fats.

Table 1. Assignment and Relative Percentage of the Main Ions Observed in the Dry MALDI−TOF MS Fingerprints of the Amazonian Oils and Fats

m/z [M + Na]$^+$	elementary composition	TAG [a]	CN/DB[b]	Brazil nut [c]	buriti [c]	andiroba [c]	passion fruit [c]	murumuru [c]	ucuba [c]	cupuaçu [c]
633	$C_{37}H_{70}O_6$	LaLaCa	34:0					6.7		
661	$C_{39}H_{74}O_6$	LaLaLa, MLCa	36:0					26.7	1.2	
689	$C_{41}H_{78}O_6$	LaLaM, MMCa	38:0					27.0	5.3	
717	$C_{43}H_{82}O_6$	LaLaP, MMLa	40:0					15.9	38.5	
743	$C_{45}H_{84}O_6$	LaLaO	42:1					1.3		
745	$C_{45}H_{86}O_6$	LaLaS, MMM	42:0					7.3	40.5	
771	$C_{47}H_{88}O_6$	MMPo	44:1					1.9	0.8	
773	$C_{47}H_{90}O_6$	MMP	44:0					2.4	5.7	
799	$C_{49}H_{92}O_6$	MMO	46:1					1.6	0.8	
801	$C_{49}H_{94}O_6$	MMS	46:0							
825	$C_{51}H_{94}O_6$	PPoPo	48:2					1.3		
827	$C_{51}H_{96}O_6$	PPPo	48:1			2.1		1.1		
829	$C_{51}H_{98}O_6$	PPP	48:0			5.0				
851	$C_{53}H_{96}O_6$	PPLn	50:3							
853	$C_{53}H_{98}O_6$	PPL	50:2	3.2	1.1	4.3	2.1	0.8	1.2	
855	$C_{53}H_{100}O_6$	PPO	50:1	3.2	8.5	13.7	1.1	0.5		1.4
857	$C_{53}H_{102}O_6$	PPS	50:0	0.7	1.8	2.1				
877	$C_{55}H_{98}O_6$	PLL	52:4	7.9			18.2	0.8		
879	$C_{55}H_{100}O_6$	PLO	52:3	11.8		8.3	12.0	0.8		
881	$C_{55}H_{102}O_6$	POO	52:2	12.7	34.5	23.6	4.5	0.5		5.2
883	$C_{55}H_{104}O_6$	POS	52:1	5.7	7.8	10.6				11.2
885	$C_{55}H_{106}O_6$	PSS	52:0			5.0				2.3
899	$C_{57}H_{96}O_6$	LLLn	54:7							
901	$C_{57}H_{98}O_6$	LLL	54:6	5.8			26.7	1.3	2.8	
903	$C_{57}H_{100}O_6$	LLO, OOLn	54:5	9.7			19.8	1.1	2.0	
905	$C_{57}H_{102}O_6$	OOL, LLS	54:4	12.0		4.0	11.0	0.8	1.2	
907	$C_{57}H_{104}O_6$	OOO, SOL0	54:3	13.9	35.6	10.4	4.5			4.9
909	$C_{57}H_{106}O_6$	OOS, SSL	54:2	8.3	10.7	7.6				18.6
911	$C_{57}H_{108}O_6$	SSO	54:1	2.9		3.3				28.7
913	$C_{57}H_{110}O_6$	SSS	54:0	0.7						7.2
933	$C_{59}H_{106}O_6$	ALL	56:4	0.8						
935	$C_{59}H_{108}O_6$	AOL	56:3	0.7						
937	$C_{59}H_{110}O_6$	ASL, OOA	56:2							7.7
939	$C_{59}H_{112}O_6$	ASO	56:1							12.9

[a] 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; Ln, linolenic acid; A, arachid acid. [b] Carbon number/number of double bounds of the three fatty acid moieties. [c] Relative porcentage.

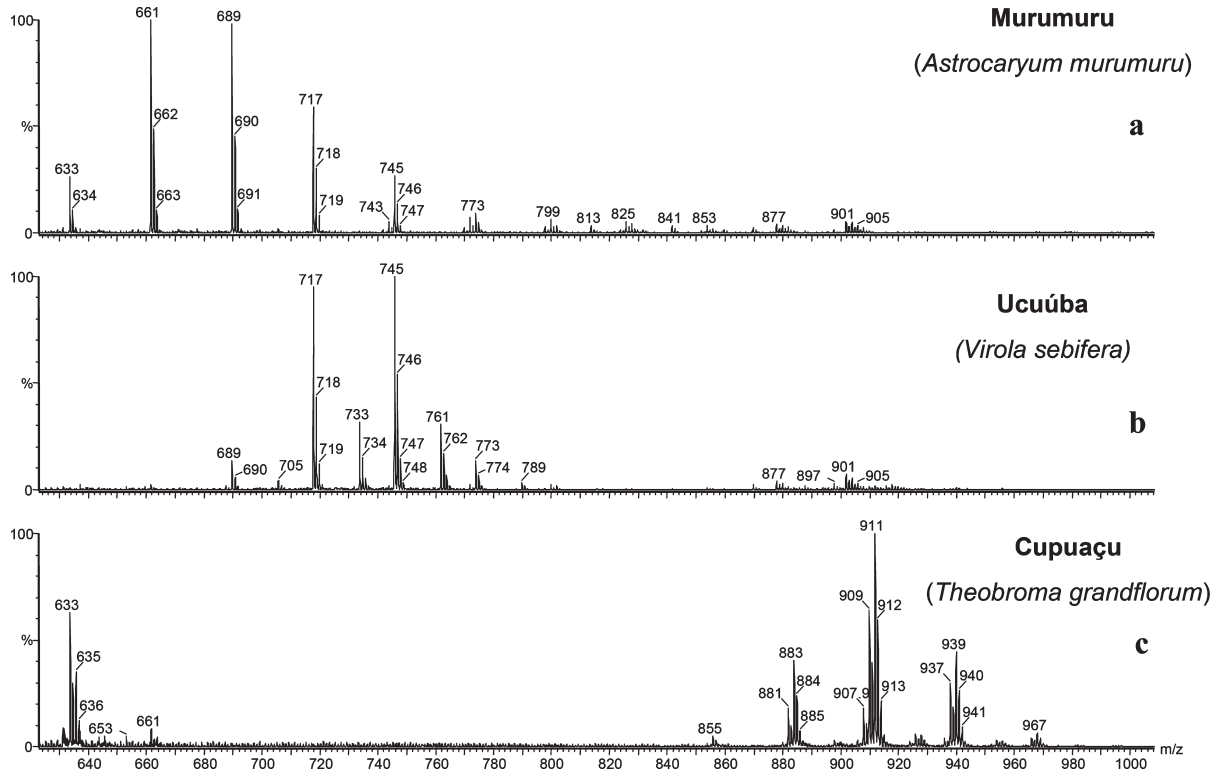

Figure 3. Dry MALDI−TOF MS fingerprints of the Amazonian vegetable fats.

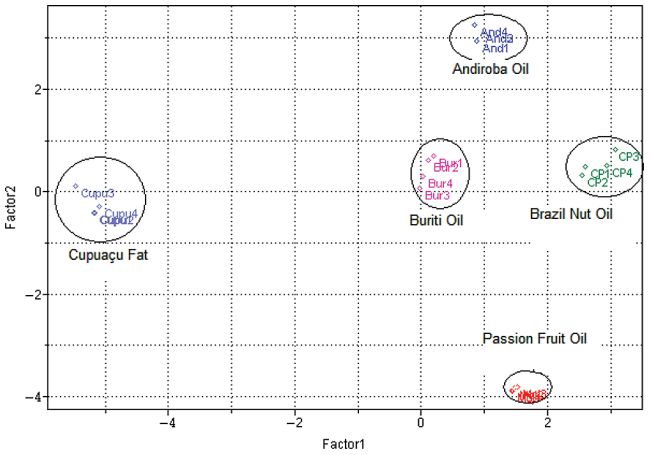

Figure 4. PCA of the dry MALDI−TOF MS data of the oils (andiroba, Brazil nut, buriti, and passion fruit) and a representative fat sample (cupuaçu).

The procedure was rapid and reproducible and required minimal sample preparation and no pre-separation or derivatization. Dry MALDI−TOF MS fingerprints are therefore a suitable technique to qualitatively typify these important Amazonian fats and oils.

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