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Revisão

AMAZON RAINFOREST COSMETICS: CHEMICAL APPROACH FOR QUALITY CONTROL

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The market for natural cosmetics featuring ingredients derived from Amazon natural resources is growing worldwide. However, there is neither enough scientific basis nor quality control of these ingredients. This paper is an account of the chemical constituents and their biological activities of fourteen Amazonian species used in cosmetic industry, including açaí (*Euterpe oleracea*), andiroba (*Carapa guianensis*), bacuri (*Platonia insignis*), Brazil nut (*Bertholletia excelsa*), buriti (*Mauritia vinifera* or *M. flexuosa*), cumaru (*Dipteryx odorata*), cupuaçu (*Theobroma grandiflorum*), guarana (*Paullinia cupana*), mulateiro (*Calycophyllum spruceanum*), murumuru (*Astrocaryum murumuru*), patawa (*Oenocarpus bataua* or *Jessenia bataua*), pracaxi (*Pentaclethra macroloba*), rosewood (*Aniba rosaeodora*), and ucuuba (*Virola sebifera*). Based on the reviewed articles, we selected chemical markers for the quality control purpose and evaluated analytical methods. Even though chromatographic and spectroscopic methods are major analytical techniques in the studies of these species, molecular approaches will also be important as used in food and medicine traceability. Only a little phytochemical study is available about most of the Amazonian species and some species such as açaí and andiroba have many reports on chemical constituents, but studies on biological activities of isolated compounds and sampling with geographical variation are limited.

Keywords: Amazonian species; quality control; chemical markers; biological activities.

INTRODUCTION

The market for natural cosmetics featuring ingredients derived from Amazon rainforest is growing worldwide. We have been attracted to exotic fragrance perfume, high potency moisturizing skin cream, etc. In Brazil, most of the cosmetics company have a series of products focused on Amazon ingredients, such as "andiroba", "copaíba", "murumuru", etc.[1] Traditionally, the extracts of these plants have been used by indigenous people as sun protection, dry hair treatment, ointment for wound healing, etc. They are based on the beliefs, experiences, and the knowledge handed down from generation to generation. On the other hand, when we purchase natural cosmetics, there is no doubt that we would like to know if the cosmetics really have efficacy or if they contain genuine ingredients. Among more than 40 thousands species of Amazonian plants,[2] only a few tens of species are used in cosmetic industries and, about most of them, the efficacy and its responsible chemical constituents have not been proven.

To guarantee product quality, a lot of aspects can be considered: minimum threshold for natural ingredients; geographical indication, manufacturing process including extraction, preservation and transportation; extent of contamination; safety under the conditions of use; efficacy with clinical data; safety issues associated with genetic modification.[3]

In the herbal medicines, chemical markers are generally employed for quality control purposes.[4] They are used for both identification and quantification and when they have therapeutic activity, they can serve for control of efficacy. In the same way, chemical markers can be applied to the control of cosmetic products.

In this work, we reviewed chemical studies on fourteen species from Amazon rainforest used in the industry of personal hygiene, perfumery, and cosmetics, with the brief descriptions about traditional and cosmetic use of these species. Our object is to provide the information useful for quality control, principally, to pick out chemical markers which stand out chemically and may have biological activities.

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AMAZONIAN SPECIES

The Table 1 summarizes the plant source, compound class, compound's name, biological activity and reference. The chemical structures of the compounds mentioned throughout this review are shown in Figures 1 to 12 with numbering **1–112**.

Chemical composition and biological activities of *Euterpe oleracea* ("açaí")

Fruits of *E. oleracea* have been consumed as energy drink by indigenous and rural people, and are recently employed to prepare a variety of healthy foods, in both tropical and non-tropical countries.[61] The oil yielded from the fruit pulp can be used in after-sun products, creams, lotions, shampoo, face masks, and other cosmetics. It is considered to have regenerative and anti-aging properties on the skin due to its constituents like essential fatty acids, phytosterol, and vitamins.[61]

Phenolic constituents are associated with the anti-oxidant activities in various plant-derived foods. The fruit of *E. oleracea* contains phenolics as major secondary metabolites remarkably anthocyanins (**1**–**5**), which is water-soluble pigments responsible for the dark purple color, and other flavonoids (**6**–**21**).[5-14] Cyanidin-3-rutinoside (**2**) is most abundant anthocyanin followed by cyaniding-3-glucoside (**1**).[5,7-11] Non-anthocyanin fractions include a diversity of flavonoids (**6**–**21**) and phenolic acids (**22**–**25**). Among them, flavone-C-glycosides of luteolin (orientin **8**, homoorientin **9**) and apigenin (isovitexin **10**, vitexin **11**) are dominant.[5,7,8,10,11,13,14]

Table 1. Compounds obtained from Amazonian species and biological activities

Species / Compound class		Compounds	Biological activities	References
Euterpe oleracea				
Anthocyanin	**1**	Cyanidin 3-glucoside		5-11
	2	Cyanidin 3-rutinoside		5,7-11
	3	Pelargonidin 3-glucoside		6,9,10
	4	Cyanidin 3-sambubioside		7,10,11
	5	Peonidin 3-rutinoside		7,8,10,11
Flavonoid	**6**	(+)-Catechin		6,8,12
	7	(-)-Epicatechin		6,8
	8	Orientin		5,7,8,10,11,13
	9	Homorientin (isoorientin)	ROS PMN[13]	5,7,8,10,11,13
	10	Isovitexin	ORAC[14]	5,7,8,10,11,14
	11	Vitexin	ORAC, ROS PMN[13]	10,11,13
	12	Scoparin		7,8,11
	13	Luteolin	ORAC, CAP-e[13]	10,13
	14	Chrysoeriol		10,11,13
	15	Quercetin	ORAC, CAP-e, ROS PMN[13]	11,13
	16	Velutin	ORAC, SEAP	14
	17	5,4´-Dihydroxy-7,3´,5´-trimethoxyflavone		14
	18	Taxifolin deoxyhexose		5,7,8
	19	Dihydrokaempferol	ORAC, CAP-e, ROS PMN	13
	20	(2*S*,3*S*)-Dihyrokaempferol 3-*O*-β-D-glucoside	ORAC	14
	21	(2*R*,3*R*)-Dihyrokaempferol 3-*O*-β-D-glucoside	ORAC	14
Phenolic acid	**22**	Protocatechuic acid		6,10-12
	23	*p*-Hydroxybenzoic acid		6,10,12
	24	Vanillic acid		8,10-12
	25	Syringic acid		8,10,12
Carboxylic acid	**26**	Fatty acid (FA)		7,11
Sterol	**27**	β-Sitosterol		7
Methylated phenol	**28**	Tocopherol (-α, -β, -γ, -δ)		15
Acylglycerol	**29**	Triacylglycerol (TAG)		16
Carapa guianensis				
Limonoid	**30**	17β-Hydroxyazadiradione		17
	31	Gedunin		17-19
	32	6α-Acetoxygedunin		17-20
	33	7-Desacetoxy-7-oxogedunin		17-20
	34	7-Deacetylgedunin		19,20
	35	6α-Acetoxy-7-deacetilgedunin		20
	36	1,2-Dihydro-3β-hydroxy-7-deacetoxy-7-oxogedunin		17
	37	Methyl angolensate		17-20
	38	6-Hydroxy-methyl angolensate		20
	39	Xyloccensin k		17
	40	Andirobin		19
	41	Carapanolide A	Anticancer	21
Acylglycerol	**29**	TAG		16,22,23
Carboxylic acid	**26**	FA		23
Platonia insignis				
Terpene alcohol	**42**	Linalool		24
	43	(*E*)-Linalool oxide (furanoid)		24
	44	(*Z*)-Linalool oxide (furanoid)		24
	45	(*E*)-Linalool oxide (pyranoid)		24
	46	(*Z*)-Linalool oxide (pyranoid)		24
	47	Hotrienol		24
	48	2,6-Dimethyl-octa-3,7-dien-2,6-diol		24
	49	(*Z*)-2,6-Dimethyl-octa-2,7-dien-1,6-diol		24
	50	(*E*)-2,6-Dimethyl-octa-2,7-dien-1,6-diol		24
	51	2,6-Dimethyl-octa-1,7-dien-3,6-diol		24
Xanthone	**52**	1,3,6-Trihydroxy-7-methoxy-2,8-bis(3-methylbut-2-enyl) xanthen-9-one (α-mangostin)		25

Table 1. Compounds obtained from Amazonian species and biological activities (cont.)

Species / Compound class		Compounds	Biological activities	References
	53	1,3,5,6-Tetrahydroxy-2-(2-methylbut-3-en-2-yl)-7-(3-methyl-but-2-enyl)xanthen-9-one (γ-mangostin)		25
Polyisoprenylated benzophenones	**54**	Garcinielliptone FC	Vasorelaxant effect	26
Bertholletia excelsa				
Triterpene hydrocarbon	**55**	Squalene		27
Methylated phenol	**28**	Tocopherol		27,28
	22	Protocatechuic acid		29
	56	Gallic acid		29
	57	Ellagic acid		29
Acylglycerol	**29**	TAG		16,22
Mauritia flexuosa				
Carotenoid	**58**	*all-trans*-β-Carotene		30
	59	13-*cis*-β-Carotene		30
Methylated phenol	**28**	Tocopherol		31,32
Hydroxycinnamic acid derivate	**60**	Caffeic acid hexoside		33
Flavonoid	**11**	Vitexin		33
	12	Scoparin		33
	61	Myricetin		33
	62	Rutin		33
Anthocyanin	**1**	Cyanidin-3-glucoside		33
	2	Cyanidin-3-rutinoside		33
Acylglycerol	**29**	TAG		16,22
Dipteryx odorata				
Benzopyrone	**63**	Coumarin		34
	64	Umbelliferone		34
Benzopyran	**65**	7-Hydroxychromone		35
Diterpene	**66**	Vouacapenic acid		36
	67	Dipteryxic acid		35
Chalcone	**68**	Isoliquiritigenin	QR, MMOC	35
Aurone	**69**	6,4´-Dihydroxy-3´-methoxyaurone	QR	35
	70	Sulfuretin	QR	35
Lignan	**71**	(±)-Balanophonin	QR	35
	72	(-)-Lariciresinol		35
Flavonoid	**73**	Butin		35
	74	Eriodictyol		35
	75	7,3´-Dihydroxy-8,4´-dimethoxyisoflavone		35
Isoflavonolignan	**76**	5-Methoxyxanthocercin A		35
Theobroma grandiflorum				
Xanthine	**77**	1,3,7,9-Tetramethyl uric acid		37
	78	Caffeine		38
	79	Theobromine		38
	80	Theophylline		38
Flavonoid	**6**	(+)-Catechin		39
	7	(-)-Epicatechin		39
	15	Quercetin	Antioxidant	39
	81	Kaempferol		39
	82	Quercetin 3-*O*-β-D-glucuronide	Antioxidant	39
	83	Quercetin 3-*O*-β-D-glucuronide 6″-methyl ester	Antioxidant	39
	84	Isoscutellarein 8-*O*-β-D-glucuronopyranoside 3″-*O*-sulfate (theograndin I)		39,40
	85	Hypolaetin 8-*O*-β-D-glucuronopyranoside 3″-*O*-sulfate (theo-grandin II)		39,40
	86	Isoscutellarein 8-*O*-β-D-glucuronide		39,40
	87	Hypolaetin 8-*O*-β-D-glucuronide		39,40
	88	Isoscutellarein 8-*O*-β-D-glucuronide 6″-methyl ester		39
	89	Hypolaetin 3´-methyl ether 8-*O*-β-D-glucuronide		40
	90	Hypolaetin 3´-methyl ether 8-*O*-β-D-glucuronide 3″-*O*-sulfate		40
Carboxylic acid	**26**	FA		41
Acylglycerol	**29**	TAG		22,41

Table 1. Compounds obtained from Amazonian species and biological activities (cont.)

Species / Compound class		Compounds	Biological activities	References
Paullinia cupana				
	79	Theobromine		43
	80	Theophylline		43
Flavonoid	**6**	(+)-Catechin		43-45
	7	(-)-Epicatechin		44,45
Calycophyllum spruceanum				
seco-Iridoid	**91**	7-Methoxydiderroside	Antitrypanosomal	46
	92	6´-Acetyl-β-D-glucopyranosyldiderroside	Antitrypanosomal	46
	93	8-*O*-Tigloyldiderroside		46
	94	Secoxyloganin	Antitrypanosomal	46
	95	Kingiside		46
	96	Diderroside	Antitrypanosomal	46
Iridoid	**97**	Loganetin		46
	98	Loganin		46
Astrocaryum murumuru				
Carboxylic acid	**26**	FA (lauric acid)		47
Acylglycerol	**29**	TAG		22
Oenocarpus bataua				
Carboxylic acid	**26**	FA (oleic acid)		32,47,48
Sterol	**99**	Δ^5-Avenasterol		49
	100	Campesterol		49
Stilbene dihexoside	**101**	Tetrahydroxystilbene dihexoside		50
	102	Trihydroxymethoxystilbene dihexoside		50
Hydroxycinamic acid	**103**	5-*O*-Caffeoylquinic acid (chlorogenic acid)		50
Pentaclethra macroloba				
Carboxylic acid	**26**	FA (behenic acid)		51
Saponin	**104**	Saponin derivative of hederagenin	Larvicidal	52
Aniba rosaeodora				
Monoterpene	**42**	Linalool		53-55
	43	(*E*)-Linalool oxide (furanoid)		53-55
	44	(*Z*)-Linalool oxide (furanoid)		53-55
Sesquiterpene	**105**	α-Selinene		53-55
	106	β-Selinene		53-55
	107	α-Copaene		53-55
Virola sebifera				
Carboxylic acid	**26**	FA (myristic acid, lauric acid)		56
Acylclycerol	**29**	TAG		22
Polyketide	**108**	1-(2´,6´-dihydroxyphenyl)-11-phenylundecan-1-one		57
Neolignan	**109**	(2*S*,3*S*,4*R*)-4-Hydroxy-2,3-dimethyl-5,6-methylenedioxy-4-piperonyl-1-tetralone		57
	110	(2*R*,3*R*)-3-(3,4-Dimethoxybenzyl)-2-(3,4-methylenedioxybenzyl)-butyrolactone		58
	111	*rel*-(2*R*,3*S*)-2-Acetyl-3-hydroxy-2-methyl-5,6-methylenedioxy-3-veratrylindan-l-one		59
	112	Epieudesmin		60

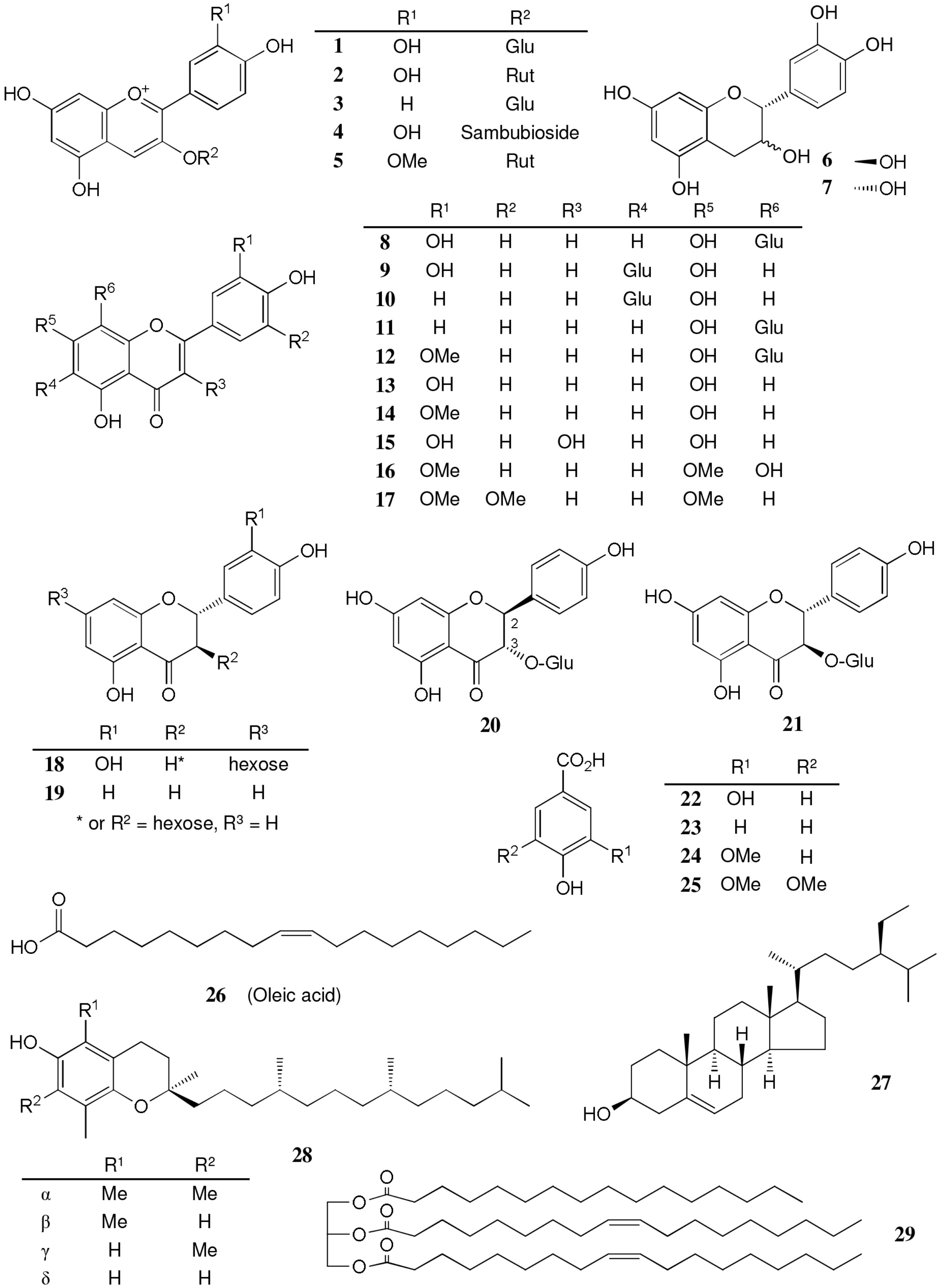
The liquid chromatography with mass spectrometry (LC/MS) based fingerprinting analysis and mass profiling led to the identification of chemical constituents in the three different processed açaí raw materials. In the case of dichloromethane extracts containing mainly fatty acids (FA) (**26**), there were no significant difference in chemical profile among the three raw materials, whereas the variations and similarities were obtained in methanol extracts, which showed the presence of anthocyanin (**1**, **2**, **4**, **5**), non-anthocyanin (**8**–**12**, **14**, **15**) polyphenols and phenolic acids (**22**, **24**).[11]

Anti-oxidant capacities of flavonoids isolated from the pulp of *E. oleracea* were evaluated using a chemical-based assay and two cell-based assays: oxygen radical absorbance capacity (ORAC) assay, cell-based anti-oxidant protection (CAP-e) assay and reactive oxygen species formation in polymorphonuclear cells (ROS PMN) assay.[13] By combining these assays, quercetin (**15**) and dihydrokaempferol (**19**) were found to be a good anti-oxidant with cell penetration ability.

Anti-inflammatory assay showed that velutin (**16**), an uncommon flavone, inhibited secreted embryonic alkaline phosphatase (SEAP) secretion in RAW-Blue™ cells induced by LPS or oxLDL at low micromole level.[14]

E. oleracea fruit is rich in lipids with a high amount of unsaturated FA (**26**) (74%), of which oleic acid (omega-9) and linoleic acid (omega-6) are predominant with 56% and 13%, respectively.[7] In addition, it has a high phytosterol level, mainly β-sitosterol (**27**)[7] and these compounds are known to have beneficial effects on skin protection.[62]

Vitamin E, a general term for tocopherols and tocotrienols (α-, β-, γ-, and δ-), which are effective lipid-soluble antioxidants and α-tocopherol has been reported to play an important role in skin photoprotection.[63] Darnet *et al.*[15] reported that tocopherol (**28**) profiles (α, β+γ, δ) in *E. oleracea* fruit pulp from three different locations of Amazon estuary were found to be similar, but the mean total tocopherol value (404.5 μg g^{-1}) was high with a concentration equivalent to many nuts.[12]



	R¹	R²
1	OH	Glu
2	OH	Rut
3	H	Glu
4	OH	Sambubioside
5	OMe	Rut

	R¹	R²	R³	R⁴	R⁵	R⁶
8	OH	H	H	H	OH	Glu
9	OH	H	H	Glu	OH	H
10	H	H	H	Glu	OH	H
11	H	H	H	H	OH	Glu
12	OMe	H	H	H	OH	Glu
13	OH	H	H	H	OH	H
14	OMe	H	H	H	OH	H
15	OH	H	OH	H	OH	H
16	OMe	H	H	H	OMe	OH
17	OMe	OMe	H	H	OMe	H

	R¹	R²	R³
18	OH	H*	hexose
19	H	H	H

* or R² = hexose, R³ = H

	R¹	R²
22	OH	H
23	H	H
24	OMe	H
25	OMe	OMe

	R¹	R²
α	Me	Me
β	Me	H
γ	H	Me
δ	H	H

Figure 1. *Structures of compounds 1-29 from* Euterpe oleracea

Chemical composition and biological activities of *Carapa guianensis* (“andiroba”)

Seed oil of *C. guianensis* has traditionally been used as a household liniment for treatment of sprains, rashes, sore, and inflammation, as well as insect repellent by indigenous people.[64] In the cosmetic industry, the seed oil is used as soap, cream, massage oil, etc.

The bitter taste, origin of name “andiroba” in the Tupi-Guarani language, is due to limonoids, highly oxygenated and modified terpenoids. Limonoids (**30**–**41**) are known to have a variety of biological activities like insecticidal, antifeedant, antibacterial, antimalarial, and antiviral.[65] Recently, a number of limonoids have been isolated from the seed oil.[17-21] Among them, carapanolide A (**41**) exhibited moderate cancer cell growth inhibition using murine L1210 leukemia cells with IC_{50} 8.7 μM.[21]

High performance liquid chromatography (HPLC) method, optimized by central composite design, determined the amount of four limonoids, gedunin (**31**), 6α-acetoxygedunin (**32**), 7-desacetoxy-7-oxogedunin (**33**), and methyl angolensate (**37**), being **33** most abundant.[18]

Cabral *et al.*,[23] characteryzed the triacylglycerols (TAG) (**29**), FA (**26**) and limonoid profiles of the seed oil via mass spectrometry fingerprinting using direct electrospray ionization mass spectrometry (ESI-MS). The technique, requiring no pre-separation of sample, could detect adulteration of the andiroba oil with soybean oil at levels as low as 10%.

Chemical composition and biological activities of *Platonia insignis* (“bacuri”)

The sticky and white fruit of *P. insignis* is consumed row by local people, and is often made into various condiments and beverages due to its distinctive taste with pleasant odor and subacid flavor.[66] The seeds contain high amount of oil, being used for treatment of eczemas and herpes.[67] In cosmetics, the oil is used as soap, skin care product, and moisturizer,[68] but the cultivation is very limited and most of the fruit production is extractive.[69]

Analysis of the volatile fractions of the fruits demonstrated that terpene alcohols (**42**–**51**) are the most abundant, and among them, linalool (**42**) and related compounds (**43**–**51**) may indicate the biosynthetic origin.[24]

The antioxidant and toxicity activities of the dichloromethane and ethyl acetate fractions of ethanolic extract of the seeds were evaluated.[25] Both fractions demonstrated *in vitro* antioxidant effects, by 1,1-diphenyl-2-picryl-hydrazyl (DPPH) and

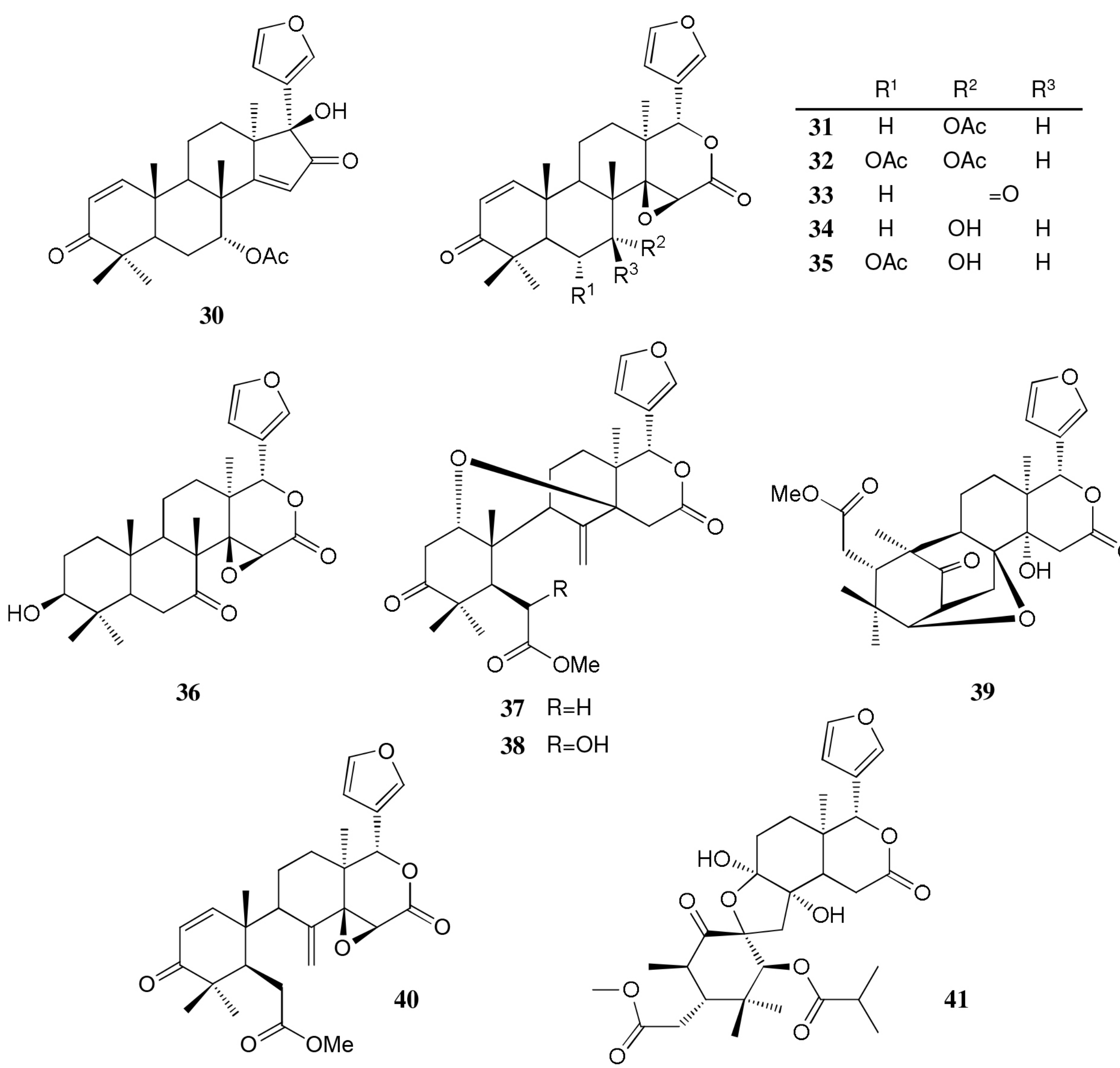


Figure 2. *Structures of compounds 30-41 from* Carapa guianensis

2,2´-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS) assays, as well as *in vivo* effects in antioxidant-defective *Saccharomyces cerevisiae* strains. These activities could be attributed to xanthones (**52**, **53**), present in these fractions as major compounds. The xanthones isolated from other species have been reported to demonstrate anti-cancer and anti-inflammatory activities.[70]

Garcinielliptone FC (**54**), a polyisoprenylated benzophenones, present in the seed of *P. insignis*, promoted an endothelium-independent vasorelaxation on phenylephrine-induced vasoconstriction.[26]

Chemical composition and biological activities of *Bertholletia excelsa* (Brazil nut)

B. excelsa is internationally traded seed crop and is collected exclusively from natural forests because the tree is unsuitable for cultivation. The reasons for that are the very slow growth, taking 10 to 30 years to fructify, and their unique reproductive system, which requires specific bees for pollination.[71] The nut, which consists of 60-70% fat and 17% protein, has long been a valuable source of nutrient for indigenous and local people residing in the Amazon region.[71] The oil extracted from the nut is high in mono- and polyunsaturated fatty acid and selenium,[72] and has recently been used in cosmetic industries such as emollient or moisturizing creams.[73]

Squalene (**55**) is a triterpene hydrocarbon, a precursor in the synthesis of steroids. In human skin surface, it prevents lipid peroxidation.[74] According to the studies by Maguire *et al.*[75] and Ryan *et al.*,[27] the Brazil nut contained the highest squalene (1377.8 $\mu g\ g^{-1}$) among ten edible nuts.

Tocopherols (**6**) are also remarkable compounds found in this nut (total tocopherol contents in oil 199.1 $\mu g\ g^{-1}$)[27] like as other species of nuts. The decreasing order of total tocopherol level was almond > hazelnut > walnut > pistachio > pine nut > Brazil nut > pecan > peanut > macadamia > cashew.[27,75] We determined tocopherol contents of Brazil nut oils from different Amazon regions as well as some commercial oils. The rates of γ-tocopherol/α-tocopherol of authentic oils didn´t show distinct variation when compared to that of other species. This fact indicates that the tocopherol profile can be useful to distinguish Brazil nut oil from other vegetable oil.[28]

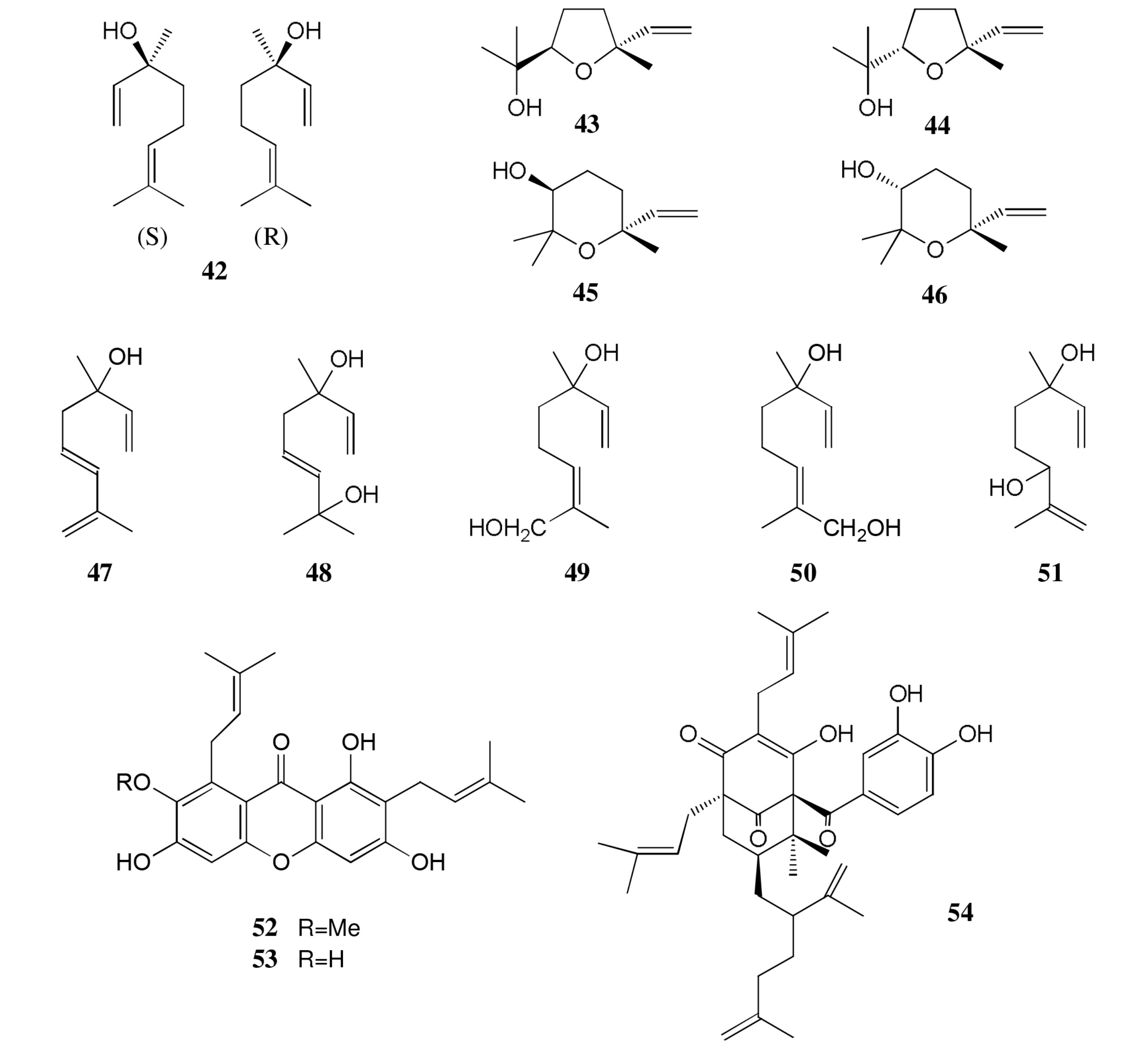


Figure 3. *Structures of compounds 42-54 from* Platonia insignis

John and Shahidi[29] identified and quantified free- and bound phenolics in kernel, brown skin and whole nuts. Phenolic acids and flavonoids, including (+)-catechin (**6**), protocatechuic acid (**22**), vanillic acid (**24**), gallic acid (**56**), and ellagic acid (**57**), were found and the concentration of phenolics was the highest in the brown skin. Similarly, Trolox Equivalent Antioxidant Capacity (TEAC), DPPH, and ORAC assays showed that the brown skin had the highest antioxidant activities.[29]

Chemical composition and biological activities of *Mauritia flexuosa* ("buriti")

M. flexuosa (syn. *M. vinifera*) is a beautiful palm tree and the common name "buriti" means "that contains water" in Tupi-Guarani language because it develops in water logged areas throughout the tropical region of South.[76] The oil extracted from the fruits is traditionally used to cure respiratory problem, pneumonia, asthma, cough, influenza, fever, snake bite and heart problems as well as to treat dry hair[77] and can be used as adjuvant in sun protection formulation.[78]

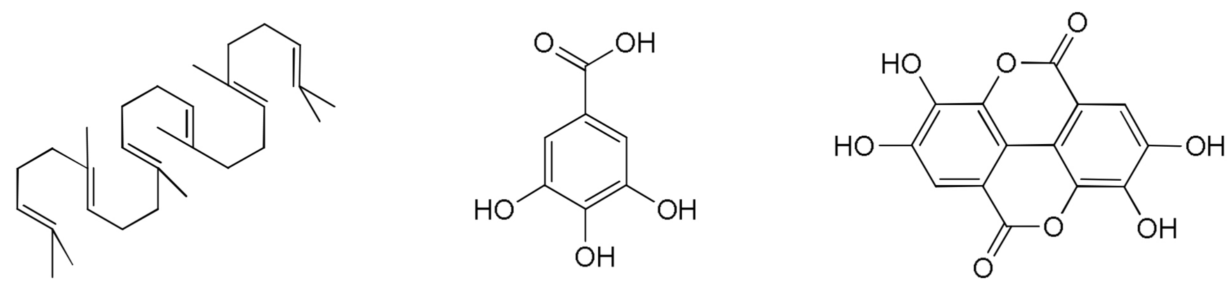
Carotenoids (**58**, **59**) are a class of yellow to red pigment, belong to the tetraterpenoids built from four terpene units. They act as antioxidant and some of them can be converted to vitamin A in the human body. Further, when present in the skin, they have an important role in photoprotection against UV radiation.[79] Among the numerous food already analyzed, the fruit of *M. flexuosa* has the highest β-carotene amount, as well as other provitamin A.[80] Unique profile of carotenoids was obtained by HPLC- MS/MS analysis, with total carotenoid content of 513 $\mu g\ g^{-1}$.[30]

Tocopherol (**26**) content of the fruit pulp of *M. flexuosa* is very high (1169 $\mu g\ g^{-1}$ of dry matter)[32] and the profile with a predominant β+γ tocopherol fraction is similar to that of other seed and nut oil, as Brazil nut, cashew nut, pecan nut, and walnut.[27,75]

Further, Koolen *et al*.[33] reported that the fruits contained a considerable amount of phenolic compounds (**1**, **2**, **11**, **12**, **60–62**), being glycosylated flavonoids: vitexin (**11**), scoparin (**12**), and rutin (**62**), and anthocyanins: cyanidin-3-glucoside (**1**) and cyanidin-3-rutinoside (**2**), as the main constituents, and it may justify the observed antioxidant activities. Further studies are needed to clarify the relationship between phenolic compounds and activities as well as to obtain the quantitative and fingerprinting data.

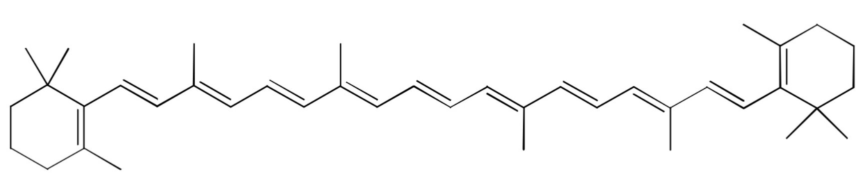
Chemical composition and biological activities of *Dipteryx odorata* ("cumaru")

Seeds of *D. odorata* are also known as tonka beans and contain an important chemical component for perfumes, coumarin (**63**), as a major compound with yields of 1 to 3%, and other minor compounds such as diterpene, flavonoid, lignan, etc. (**64–76**).[34,35]



55 **56** **57**

Figure 4. *Structures of compounds 55-57 from Bertholletia excelsa*



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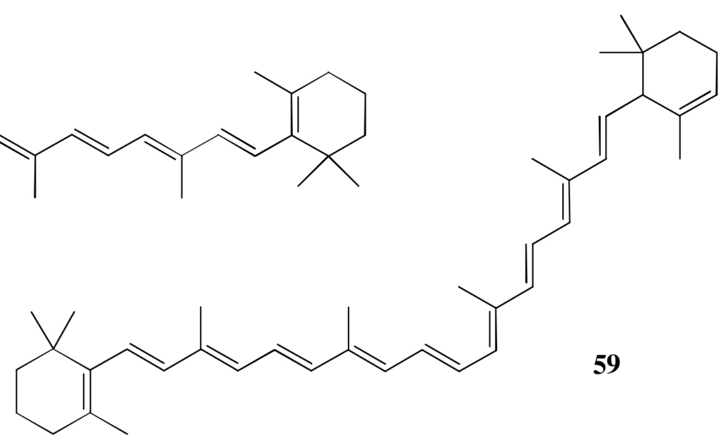

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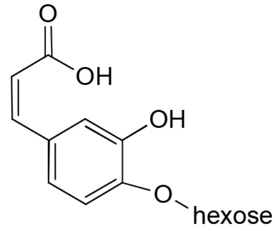

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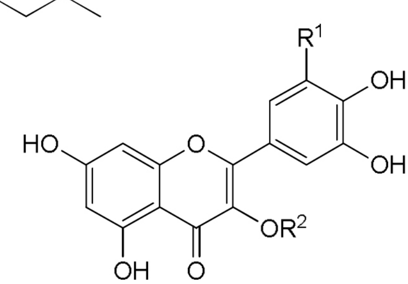

	R1	R2
61	OH	H
62	H	Glu-Rha

Figure 5. *Structures of compounds 58-62 from* Mauritia flexuosa *(or* M. vinifera*)*

Jang *et al.*[35] isolated four potential cancer chemopreventive compounds: isoliquiritigenin (**68**), 6,4´-dihydroxy-3´-methoxyaurone (**69**), sulfuretin (**70**), and (±)-balanophonin (**71**) by a bioassay-guided fractionation of an ethyl acetate-soluble extract of the seeds using the enzyme quinone reductase (QR) induction assay. With further analysis of selected compounds, **68** exhibited significant inhibition of carcinogen-induced preneoplastic lesion formation (76% at 10 μg mL^{-1}) in the mouse mammary organ culture (MMOC) assay.

Chemical composition and biological activities of *Theobroma grandiflorum* ("cupuaçu")

Fruits of *T. grandiflorum* are very much appreciated for its acidic and highly-flavored pulp, that is consumed as the ingredient of juices, ice-creams, jams, and candies.[69]

Phytochemical analyses demonstrated in the seeds the presence of xanthine alkaloids (**76–79**)[37,38] and flavonoids (**6**, **7**, **15**, **80–89**),[39,40] of which hypolaetin 8-*O*-β-D-glucuronide (**87**) and isoscutellarein 8-*O*-β-D-glucuronopyranoside 3″-*O*-sulfate (**84**) were dominant.[40] Activity-guided fractionation using DPPH method of the seeds identified 11 flavonoid antioxidants (**6**, **7**, **15**, **81–88**), of which quercetin (**15**) and its glycosides (**82**, **83**) were more potent with IC_{50} values of 39.7-44.4.[39]

FA (**27**) and TAG (**29**) compositions of seed fats were compared among the eight species of the genus *Theobrama*.[41] Significant differences in these profiles were observed between species of

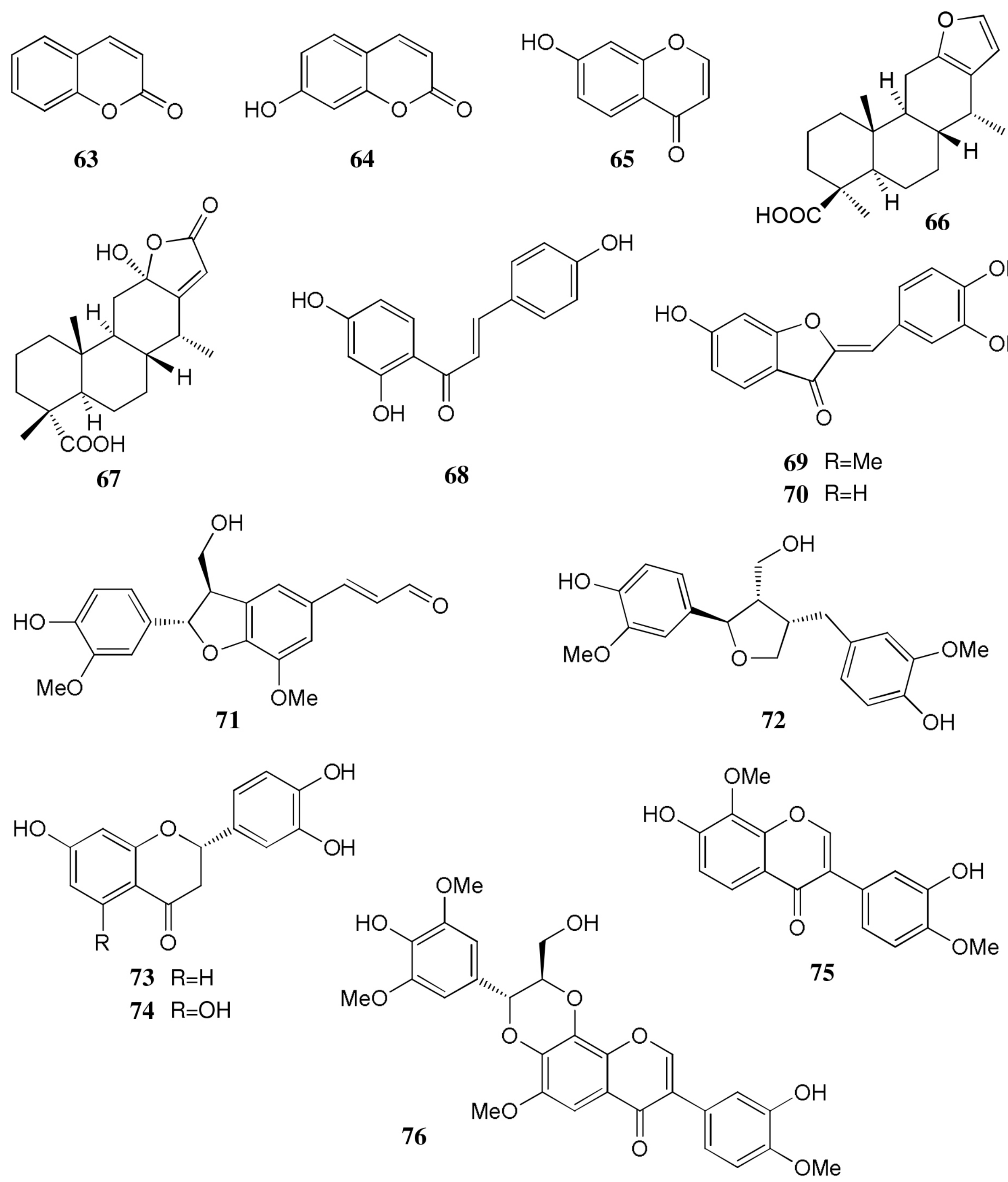

***Figure 6.** Structures of compounds 63-76 from* Dipteryx odorata

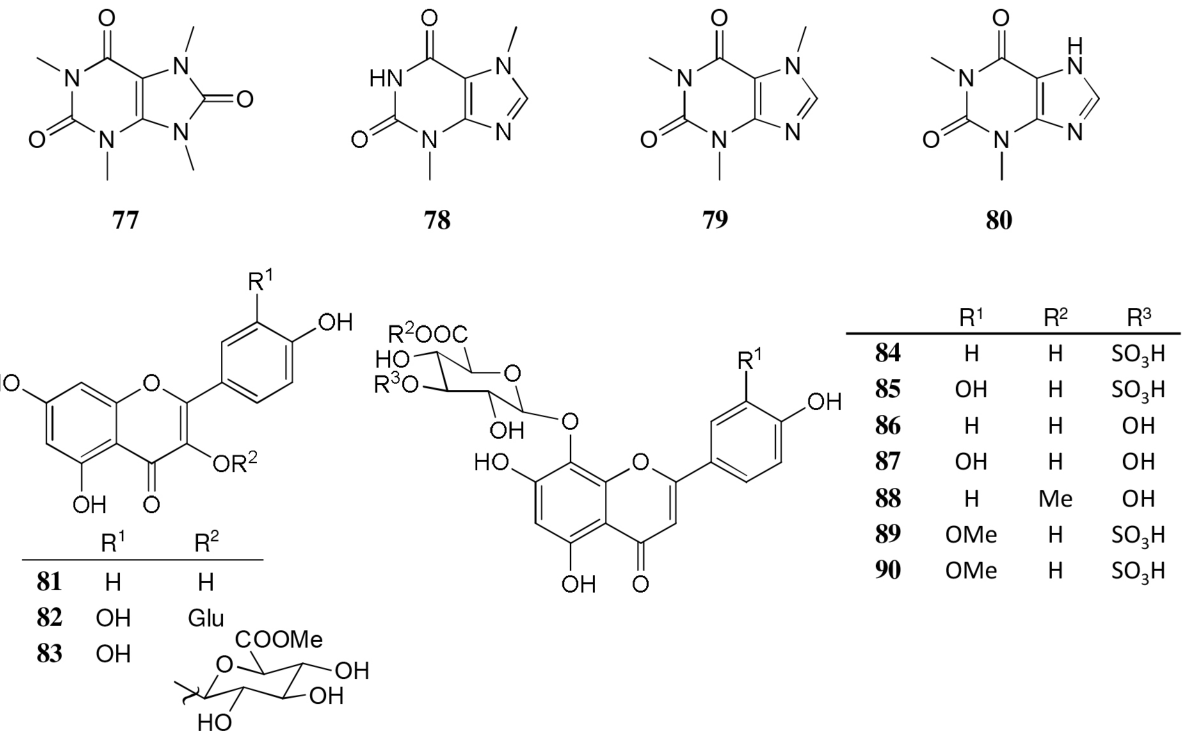

***Figure 7.** Structures of compounds 77-90 from* Theobroma grandiflorum *and* Paullinia cupana

distinct sections (subdivision of genus according to morphological characters), whereas the profiles of species from the same section were similar.

Chemical composition and biological activities of *Paullinia cupana* ("guarana")

P. cupana is widely consumed as an effective stimulant in dietary supplements and drinks. It is due to the highest content of caffeine (**78**) in its seed from 3 to 6% of dry weight,[42,81] but other minor compounds also contribute to pharmacological effects such as central nervous system stimulants of xanthine alkaloids (**79**, **80**), antioxidant flavonoids (**6**, **7**) and tannins.[43,45] In the cosmetic industry, the seed extracts are used in soap, cream, and shampoo.[82]

Majhenič *et al*.[83] reported that the seed extracts exhibited high antioxidant, antimicrobial, and antifungal activities, and had promising potentials as natural additives in food, cosmetic, and pharmaceutical industries. Also, because of the cellulite reduction effect of methylxanthines, such as **78–80**, *P. cupana* is used for cosmetic formulation.[84]

The seed powder and commercial tablets of *P. cupana* were characterized by capillary electrophoresis (CE) using caffeine (**78**) as a marker compound and the results were compared to those obtained by HPLC.[85] In this study, the CE technique showed good specificity, sensitivity and precision like HPLC and had advantages in the analysis time and solvent consumption as compared to HPLC.

Chemical composition and biological activities of *Calycophyllum spruceanum* ("mulateiro")

The wood of *C. spruceanum* (syn. *C. multiflorum*) has high economic value because of its resistance to deterioration and facility to work, being used in lumber and construction materials.[86] Local people apply the bark poultice to skin, as antifungal, contraceptive, emollient, and vulnerary or take the bark decoction for diabetes and eye infection.[87] The bark of *C. spruceanum* has recently attracted world attention as the ingredient for body care products.[86]

Phytochemical study showed that the ethanolic extracts of the wood bark yielded seco-iridoids and iridoids (**91**–**98**), of which 7-methoxydiderroside (**91**), 6´-acetyl-β-D-glucopyranosyldiderroside (**92**), secoxyloganin (**94**), and diderroside (**96**) exhibited weak *in vitro* antitrypanosomal activities.[46] Screening study for antifungal activity of forty five extracts of species used in traditional medicine demonstrated that the dichloromethane extract of the bark of *C. multiflorum* had the highest activity,[88] which may support the use for skin treatment.

Chemical composition and biological activities of *Astrocaryum murumuru* ("murumuru")

A distinguishing feature of the palm tree, *A. murumuru*, is innumerable thorns even on the seeds and flowers. The oil extracted from the seed is white and solid at room temperature.[61] The seed butter can be added to skin care products, shampoos, and conditioners because the oil has water-retention capacity.[89]

The chemical studies on saponifiable compositions of the seed butter demonstrated unique TAG (**29**) and FA (**26**) profiles with lauric (43-52%) and myristic (26-37%) acid as major fatty acids.[22,47]

Chemical composition and biological activities of *Oenocarpus bataua* ("patawa")

O. bataua (syn. *Jessenia bataua*) is one of the useful palm tree for Amazonian indigenous. The fruit is consumed as a nutritional beverage and the oil extracted from both fruit and kernel seed is traditionally used for medicinal, culinary, and cosmetic purposes, including for hair and skin care.[69,90]

The fruit oil has a profile of fatty acids similar to that of olive oil, with high oleic acid contents (77%), being considered to have nutritional value.[32,47,48] Because in the sterol composition, the percentage of Δ^5-avenasterol (**99**), known for effective antioxidant,[91] is high and that of campesterol (**100**) is relatively low, these compounds could

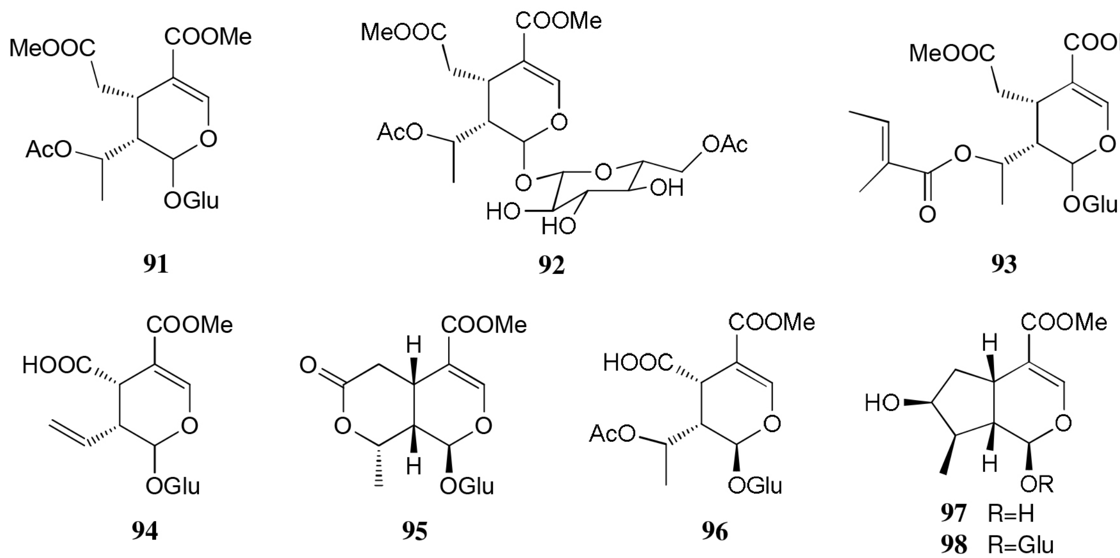

Figure 8. *Structure of compounds 91-98 from* Calycophyllum spruceanum

serve as markers for authentication of the oil.[49] The latest report by Rezaire *et al.*[50] dealing with the *in vitro* antioxidant tests showed the good activity of the fruit of *O. bataua* as compared to *E. oleracea* and other berries known as potential antioxidants. This activity could be accounted for by the presence of characteristic polyphenols like stilbenes (**101**, **102**), phenolic acids (**103**), and condensed tannins, identified by ultra-performance liquid chromatography/mass spectrometry (UPLC/MS). However, further experiments including structural elucidation and biological activity would be required.

Chemical composition and biological activities of *Pentaclethra macroloba* ("pracaxi")

Seed oil of *P. macroloba* is used in cosmetic industry and may have positive effects on wound healing.[92]

The oil is known to have the highest content of behenic acid, $C_{21}H_{43}COOH$, in natural products (10-25%),[51] while most fruits or nuts contain less than 1%.[27,48] Besides, the saponin (**104**) isolated from the seeds exhibited high larvicidal activity with LC_{50} = 18.6 µg mL^{-1}.[52]

Chemical composition and biological activities of *Aniba rosaeodora* (rosewood)

Essential oil of *A. rosaeodora* is worldly famous with pleasant rose-like aromas and is employed as fragrance in fine perfumery. European fragrance industry originally obtained the oil from French Guiana, but after the intensive exploitation, Brazilian rainforest is the main producer and *A. rosaeodora* is protected under international law.[93]

The oil is obtained from the wood chips and contains mainly linalool (**42**, 80-90%) with small amounts of (*Z*)- or (*E*)-linalool oxide (furanoid) (**43**, **44**), α- or β-selinene (**105**, **106**) and α-copaene (**107**).[53-55]

For the sustainable production of the oil, there are other sources including: the young leaves or branches of *A. rosaeodora*; synthetic linalool; another species with linalool-rich essential oils, such as *Cinnamomum camphora*[94] and *Croton cajucara*.[95] Yet sometimes, as obtained by low cost and considered low quality, they are used for product adulteration. Chemical study using comprehensive

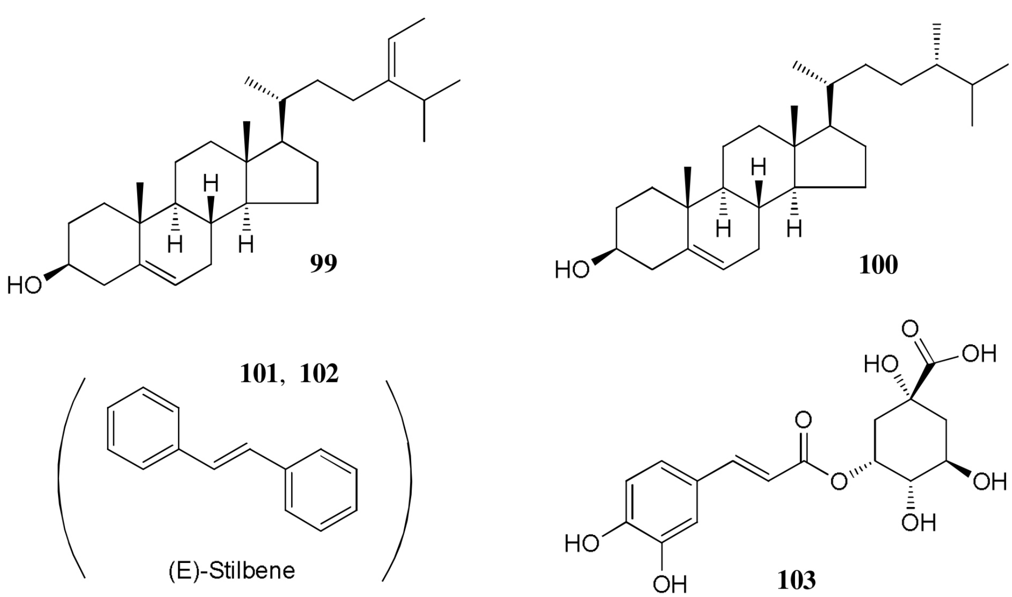

Figure 9. *Structures of compounds 99-103 from* Oenocarpus bataua

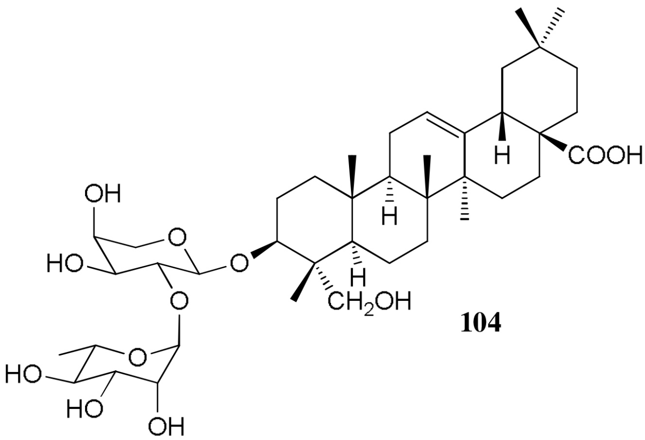

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Figure 10. Structure of compound 104 from Pentaclethra macroloba

two-dimensional gas chromatography coupled with quadrupole mass spectrometric detection (GC×GC–qMS) identified major and minor chemical compositions of the oils extracted from the leaves collected from trees with different ages (four, ten and twenty year old) and few differences in constituents were found among all samples.[96] Souza *et al.*[97] characterized the oils from the wood and leaves by ESI-MS and the adulteration with synthetic linalool could be detected by fingerprinting.

Linalool (**42**) has two enantiomeric forms due to a stereogenic center at C_3 (Figure 3). (*R*)-(-)-linalool has a woody lavender scent while (*S*)-(+)-linalool has a sweet floral scent and both forms can be found at various proportions according to the geographic origin and part of the tree.[53,55,98] Linalool has a diversity of pharmacological properties,[99] but the chiral influence to the properties is not clear.[55,100]

Chemical composition and biological activities of *Virola sebifera* ("ucuuba")

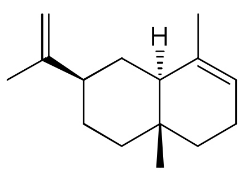
Yellow and aromatic fat extracted from the seeds of *V. sebifera* has some cosmetic properties such as emollient, moisturizer, skin conditions and antiseptic, and due to that, it is used for industrial products such as soap, cleansing, massage lotion and hair care products.[69] The fat has high content of myristic (72.9%) and lauric (17.3%) acids[56] and the former has high absorption into the skin.[101]

Study on the secondary metabolites of the seeds showed the accumulation of a variety of lignans (**109**–**112**) such as aryltetralone (**109**), dibenzylbutyrolactone (**110**), arylindan (**111**), and furofuran (**112**) type lignans.[57-60]

ANALYTICAL TECHNIQUES FOR QUALITY CONTROL OF COSMETIC PRODUCTS AND OTHER APPROACHES

Reported chemical constituents of Amazonian species were classified from an analytical point of view:

1) TAG and FA - Major constituents of oils and fats are triacylglycerols, which are esters derived from glycerol and three fatty acids. FA analysis by gas chromatography with flame ionization detection (GC-FID) is a broadly accepted official method to characterize quality and a specific oil,[102] but the analysis needs a conversion of TAG to fatty



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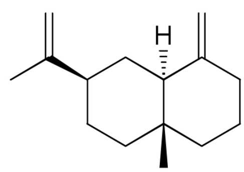

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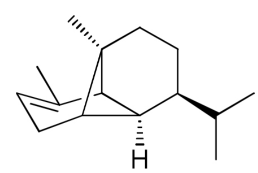

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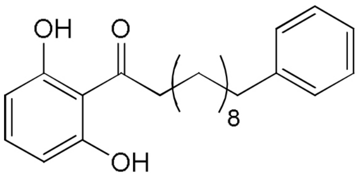
Figure 11. Structures of compounds 105-107 from Aniba rosaeodora



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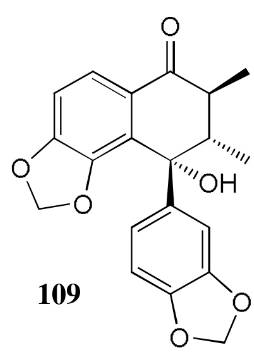

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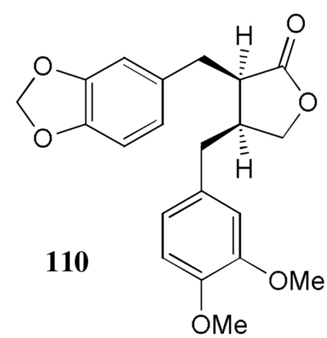

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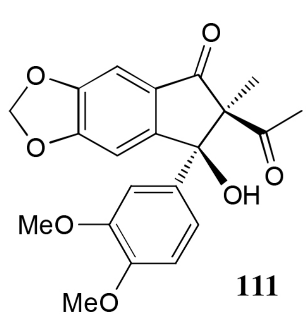

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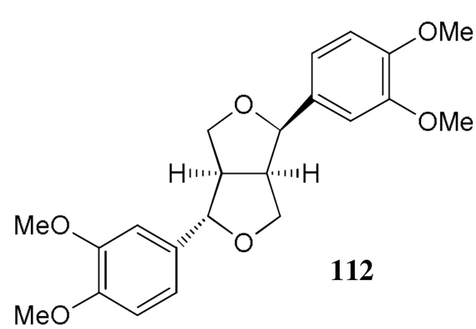

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Figure 12. Structures of compounds 108-112 from Virola sebifera

acid methyl esters by acid or base, and provides only total percentage of FA.[103] The separation of TAG can be achieved by HPLC,[104] but diverse factors, sample preparations, stationary and mobile phases, columns and detectors, have to be considered depend on the number of carbon atoms and their saturation.[105] A refractive index (RI) was the most widely used detector for the HPLC analysis despite its low sensibility.[106,107] Recently, advance of mass spectrometry has enabled the direct analysis of TAG in Amazon oils. First, Saraiva *et al.*[22] characterized Amazon vegetable oils (andiroba, Brazil nut, buriti, passion fruit, cupuaçu, and ucuuba) via dry matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) without pre-separation or derivatization. Easy ambient sonic-spray ionization mass spectrometry (EASI-MS) has, then, realized instantaneous analysis of Amazon vegetable oils, including açaí, andiroba, Brazil nut, and buriti, by both TAG and free fatty acid profiles.[16] Moreover, several samples of Brazil Nut oil (authentic oils of different geographic origin, commercial oils) were evaluated using EASI-MS TAG profiles and adulteration of Brazil nut oil with soy bean oil could be detected at a level of 5% or higher.[108]

2) Unsaponifiable fraction or minor components - This fraction contains minor constituents, which have also been employed for oil characterization. Tocopherols, carotenoids, and sterols are usually contained in any oils, but its amount varies depending on species and environmental conditions. Their qualitative and quantitative analyses can be performed by chromatographic methods such as HPLC coupled with photodiode array detection (DAD), fluorescence detection (FLD) or MS for tocopherol or carotenoid[30,109,110] and GC-FID for sterols.[49,109] Phenolic compounds have also been investigated because they are responsible for the antioxidant potential, stability and organoleptic characteristics and the use of these compounds would permit the authentication and quality assessment.[11,50]

3) Volatile constituents- Volatile compounds obtained from *D. odorata* and *A. rosaeodora* are ingredients of perfumes. The universally adapted analytical technique is GC including GC-FID and GC-MS. These techniques have recently been substituted by direct infusion mass spectrometry without or with simple pre-treatment because of the fast and simple measurement.[97]

Besides these techniques mentioned above, infrared[111] and NMR[112] spectroscopy have been applied to the authentication of natural products. Analyses of stable isotope ratio and trace element have also allowed us to determine the origin of food products.[113]

The fingerprinting techniques have become more and more popular for the purpose of quality control.[16,22,23,108] They enable the handling of a large amount of data and provide quantitative and qualitative information of the compounds as well as the relationship between chemical information and efficacy with the aid of chemometric tools.[114]

Even though chemical composition analyses have been a great success to detect adulteration, there are difficulties in the discrimination of cultivars because of the high variability influenced by environmental conditions. In order to overcome this problem, molecular approach has been used in food[115] and medicine[116] traceability. In particular, for complex matrix like olive oil, molecular markers techniques such as random amplified polymorphic DNA (RAPD), amplified fragment length polymorphism (AFLP), and simple sequence repeat (SSR) are useful.[117] Special attention has, however, to be paid for extraction and purification of DNA because samples (oil or extract) are usually complex and highly processed.[118]

CONCLUDING REMARKS

Table 2 summarized possible chemical markers of reviewed Amazonian species for control purpose of cosmetic products. Chemical markers have been used in the regulatory agencies of herbal medicines or by scientists and each agency or scientist has own classification.[4] With reference to them, the following criteria were used to select chemical markers: (a) the constituents have biological activities which are or are not related to efficacy as cosmetics; (b) their biological activities are not known, but they are abundant or the isolation yield was the highest; (c) they are not abundant, but characteristic (not common); (d) the fingerprintings (or profiles) of the groups of constituents are distinguishable when compared to those of other species.

Table 2. Selected chemical markers for quality control of cosmetic products containing extracts of Amazonian species

Species	Chemical markers
E. oleracea	cyanidin 3-rutinoside (**2**)[b]/phenolic compounds[d]/oleic and linoleic acids[a]/ β-sitosterol (**27**)[a]
C. guianensis	limonoids (**30**-**41**)[c], especialy, 7-desacetoxy-7-oxogedunin (**33**)[b]
P. insignis	linalool[b]/α- and γ-mangostin (**52**, **53**)[a,b]/garcinielliptone FC (**54**)[a]
B. excelsa	squalene (**55**)[a]/ tocopherol (**28**)[a,d]/ TAG (**29**)[d]
M. flexuosa	carotenoids (**58**,**59**)[a,d]/phenolic compounds[d]
D. odorata	coumarin (**63**)[b]/isoliquiritigenin (**68**)[a]
T. grandiflorum	quercetin (**15**)[a]/hypolaetin 8-*O*-β-D-glucuronide (**87**)[b]/ theograndin I (**84**)[b]
P. cupana	caffeine (**78**)[a,b]/theobromine (**79**)[a]/theophylline (**80**)[a]/ (+)-catechin (**6**)[a]/(-)-epicatechin (**7**)[a]
C. spruceanum	seco-iridoid and iridoid (**91**-**98**)[c]
A. murumuru	TAG (**29**)[d]/FA (**26**)[d]
O. bataua	sterols[d] , especially, Δ5-avenasterol (**99**)[a] and campesterol (**100**)/polyphenols (**101**-**103**)[d]
P. macroloba	FA (**26**)[d]/saponin (**104**)[a]
A. rosaeodora	linalool (**42**)[b]/volatile compounds[d]
V. sebifera	FA (**26**)[d]/lignans (**109**-**112**)[c,d]

[a,b,c,d] The selection criteria for chemical markers: [a]The constituent has biological activity; [b]The constituent is abundant; [c]The constituent is characteristic; [d]Fingerprinting of the group of constituents is distinguishable.

These chemical markers have been proposed based on the reviewed articles. It is noted that markers have different role according to the type. When the markers don´t have biological activities, they can provide quantitative information. It seems that the fingerprintings of TAG would be applicable to most of the fixed oils for quantitative assessment, especially identification and detection of adulteration. Essential fatty acids such as linoleic acid may be useful as chemical markers to evaluate efficacy, but they would not be adequate for the use of authentication purpose or stability test due to the susceptibility to autoxidation.[119]

In view of increasing demand for Amazon cosmetics, little data are available about the chemical studies on Amazonian species. Even though chemical constituents of some species, such as *E.oleracea*, *C. guianensis*, have been studied by many researchers, their biological activities, especially cosmetic efficacies, have hardly been evaluated. Furthermore, there are few studies focused on the origin of extract and in many cases researchers have obtained or purchased previously prepared extracts because of the difficulty of access to the Amazon raw materials. This problem has to be overcome to study geographical origin, seasonality, cultivar, and extraction method that affect the quality of natural cosmetics.

Thus, it is essential that quality control of natural products would be accomplished by multi/interdisciplinary approaches including chemistry, biology, and agriculture. In addition, the access to the Amazon biodiversity should be controlled properly by international regime[120] for further research and development.

ACKNOWLEDGMENTS

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