

巴西蜂胶化学成分的研究进展

申小阁, 张翠平, 胡福良

浙江大学动物科学学院, 杭州 310058

摘要: 巴西蜂胶植物来源广泛, 化学组成复杂, 具有丰富而突出的生物学活性。本文对巴西蜂胶中已发现的 362 种化学成分进行分类汇总, 并给出相应的蜂胶来源, 旨在为巴西蜂胶化学标准化及质量控制的研究提供有价值的化学依据, 并为全面评价蜂胶的药用价值以及开发利用提供参考。

关键词: 巴西蜂胶; 植物来源; 化学成分

中图分类号: R282.74; S896.6

文献标识码: A

DOI: 10.16333/j.1001-6880.2015.05.032

Chemical Constituents of Brazilian Propolis: A review

SHEN Xiao-ge, ZHANG Cui-ping, HU Fu-liang*

College of Animal Sciences, Zhejiang University, Hangzhou 310058, China

Abstract: With a wide botanical origin and complex chemical compositions, Brazilian propolis possesses various and prominent biological activities. In this article, we presented the identified 362 chemical compositions of Brazilian propolis in groups along with each corresponding sources. Aiming to provide valuable chemical basis for further research of chemical standardization and quality control, and also to provide a reasonable reference for comprehensively evaluating pharmacological values of Brazilian propolis for its exploitation and utilization.

Key words: Brazilian propolis; botanical origin; chemical composition

蜂胶 (Propolis) 是蜜蜂工蜂采集植物树脂等分泌物与其上颚腺、蜡腺等分泌物混合而成的一种天然粘稠物质。蜂胶的应用历史十分悠久, 早在公元前 300 年, 古埃及人就将其作为防腐物质及防治疾病的药物来使用。现代研究表明, 蜂胶含有丰富的黄酮类、酚酸类及萜烯类化合物^[1-3], 具有广泛的生物学活性和药理学活性, 如抗氧化、抗菌、抗病毒、抗炎、抗肿瘤、保肝、免疫调节等; 目前已广泛用于医药、保健品、化妆品等领域^[4]。

蜂胶在全世界范围内均有分布, 其中, 巴西因其得天独厚的地理位置和丰富的生物资源而成为蜂胶生产大国。巴西蜂胶种类繁多, 化学组成复杂, 具有丰富而突出的生物学活性。自 20 世纪 90 年代以来, 巴西蜂胶的化学组成及其生物学活性引起了国内外蜂胶研究者的广泛关注。目前, 已从中分离鉴定出了 300 多种化合物^[1-5]。本文对巴西蜂胶中已发现的化学成分进行分类总结, 以为巴西蜂胶的

药理活性、质量控制以及开发利用提供理论依据。

1 巴西蜂胶的植物来源及成分特征

巴西地处热带气候的南美洲, 植被种类繁多, 蜂胶资源丰富。Park 等 (2000) 曾根据巴西蜂胶地理来源的不同将其分为 12 种不同的类型: 5 种来自巴西南部, 6 种来自巴西东北部, 1 种来自巴西东南部及中西部地区^[6]。这些不同类型的蜂胶之间化学成分差异较大, 而胶源植物是造成这一差异性的直接因素。目前, 通过蜜蜂采胶行为的观察、蜂胶中花粉谱的显微检测以及两者化学成分的指纹图谱对比分析发现, 巴西蜂胶的植物来源主要有 *Baccharis dracunculifolia*^[6-9]、*Araucaria* spp.^[10-12]、*Eucalyptus* spp.^[10,13-16]、*Dalbergia ecastophyllum*^[17-18]、*Clusia* spp.^[12] 和 *Hyptis divaricata*^[6] 等 15 种, 其相应的化学成分也较为复杂 (表 1)。

酒神菊属型绿蜂胶是目前国际市场上最流行、研究最深入的巴西蜂胶。Bankova 等研究发现绿蜂胶的植物来源是 *Baccharis dracunculifolia*^[5-9]。Park 等 (2004) 进一步观察到蜜蜂主要采集该植物的幼芽和未展开的嫩叶, 很少采集展开的叶子^[19]。典型

表 1 巴西蜂胶的植物来源及相关化学成分

Table 1 Plant origin and chemical composition of Brazilian propolis

组别 Group	植物来源 Plant sources	蜂胶来源 Propolis sources	主要成分 Main components	参考文献 Ref.
G1	<i>Baccharis dracunculifolia</i>	东南部/中西部	异戊烯化苯丙素类, 咖啡酰奎宁酸, 萜烯类化合物	5, 7, 8, 9
G2	<i>Araucaria angustifolia</i>	东南部/南部	半日花烷型二萜酸类	10, 11, 12
G3	<i>Eucalyptus citriodora</i>	东南部/南部	无异戊烯基肉桂酸类衍生物, 山奈酚, 没食子酸	10, 13, 14
G4	<i>Poplar alba</i>	南部	B 环无取代基的黄酮类, 咖啡酸酯类化合物	5
G5	<i>Myrceugenia euosma</i>	南部	三萜类, 芳香族化合物	22
G6	<i>Citrus</i> spp.	南部	咖啡酰奎宁酸类衍生物	14, 15
G7	<i>Eupatorium</i> spp.	南部	-	14, 15
G8	<i>Hyptis divaricata</i>	东北部	脂肪酸类, 萜烯类化合物, hyperibone A	5
G9	<i>Dalbergia ecastophyllum</i>	东北部/北部	异黄酮, 查尔酮, 新黄酮类化合物	17
G10	<i>Clusia</i> spp.	东北部/北部	异戊烯化苯甲酮, 三萜类化合物	12
G11	<i>Acacia</i> spp.	-	-	14, 15
G12	<i>Mimosa</i> spp.	-	-	15, 16
G13	<i>Myrcia</i> spp.	-	-	15
G14	<i>Borreria</i> spp.	-	-	14, 15
G15	<i>Schinus</i> spp.	-	-	26, 27

的酒神菊属绿蜂胶质地坚硬易碎, 颜色从黄绿色到深绿色不等, 具有宜人的芳香气味, 同时还兼有其独特的辛辣味。酒神菊属型绿蜂胶主要分布于巴西东南部和中西部地区, 其主要成分为异戊烯化苯丙素类及其衍生物、咖啡酰奎宁酸类及一些萜烯类化合物, 而黄酮类化合物含量相对较低。阿替匹林 C (3, 5-二异戊烯基-4-羟基肉桂酸) 是酒神菊属型绿蜂胶的特征性成分, 其含量主要受地理来源、植物来源及采胶季节的影响^[20]。韩利文等还建立了反相高效液相色谱法测定蜂胶中阿替匹林 C 含量的方法^[21], 为酒神菊属型绿蜂胶的质量评价提供了可靠的理论依据。

除了 *Baccharis dracunculifolia* 外, *Araucaria* spp. 及 *Eucalyptus* spp. 也是巴西东南部及南部地区蜂胶的植物来源。Barth 及 Silva 等对圣保罗、里约热内卢地区多个蜂胶样中的花粉进行显微检测, 结果发现大量的桉属植物花粉粒^[13, 16], 进一步对桉属植物叶芽提取物的化学成分进行测定发现肉桂酸、p-香豆酸及没食子酸是其主要的化学成分^[10]。Bankova 等采用 GC-MS 技术对圣保罗地区的蜂胶样及南洋杉属植物叶芽分泌物的化学成分进行测定, 结果显示二者含有相同的二萜类化合物, 其中半日花烷型二萜酸类化合物(南洋杉酸、E/Z Communic acid) 是

其主要的组成成分^[10], 这也证实了 *Araucaria* spp. 是巴西蜂胶中二萜类化合物主要的植物来源。

杨树植物 (*Populus* spp.) 主要分布于温带地区, 杨树型蜂胶是温带地区典型的蜂胶类型。然而, Park 等在巴西南部地区也发现了少量的植物来源为 *Poplar alba* 的蜂胶类型, 其化学成分主要为短叶松素、乔松素、短叶松素-3-乙酸酯、柯因和高良姜素等几种 B 环无取代基的黄酮类化合物以及杨树型蜂胶中特有的致敏性物质—1, 1-二甲基烯丙基咖啡酸^[6]。

Ito 及 Junko 等在寻找有效的抗艾滋病药物过程中发现巴西南部的一种蜂胶具有显著的抗艾滋病活性, 经研究证实该蜂胶的植物来源为 *Myrceugenia euosma* (Myrtaceae), 主要的化学成分为三萜类化合物及芳香族化合物^[22]。

近年来, 红色的蜂胶也越来越多地引起了人们的关注。最早报道的红色蜂胶是古巴蜂胶, 其植物来源是 *Clusia nemorosa* (Clusiaceae)^[23]; 而委内瑞拉红蜂胶的植物来源是 *Clusia scrobiculata*^[24]。目前发现巴西有 3 种不同植物来源的红色蜂胶。最初 Park 等在东北部巴伊亚州发现了一种红棕色的蜂胶样, 经蜜蜂采胶行为的观察和化学成分的对比较分析, 证实该蜂胶来源于 *Hyptis divaricata*, 含有少量的

萜烯类、长链脂肪酸及其酯类化合物等一些弱极性物质^[13]。而 Trusheva 等(2006)报道的巴西红蜂胶成分的色谱图与委内瑞拉红蜂胶类似,异戊烯基苯甲酮是其主要成分^[25],经花粉谱显微检测结果表明该蜂胶来源于 *Clusia* spp.^[12]。

另外一种红蜂胶是最近研究的热点,即典型的“巴西红蜂胶”;Park 等研究发现该蜂胶的植物来源是 *Dalbergia ecastophyllum*,并观察到蜜蜂整个的采胶行为,进一步对其化学成分进行测定发现黄酮类化合物是其特征成分,包括紫檀碱、黄烷醇、新黄酮、异黄烷醇、异黄烷酮、查耳酮、异黄烷、异黄酮、黄烷酮和黄酮醇等^[24]。

此外,巴西多个地区的蜂胶样中花粉谱的检测结果显示, *Vernonia*、*Hyptis*、*Myrcia*、*Schinus*、*Mimosa pudica*、*Eupatorium*、*Acacia*、*Citrus* spp. 和 *Borreria* 也是巴西蜂胶的胶源植物。

2 巴西蜂胶的化学组成

现已从巴西不同类型蜂胶中分离鉴定出 362 种化合物。其中黄酮类化合物 130 种、萜烯类化合物 99 种、酚酸类化合物 87 种、挥发油类 25 种、木质素类 6 种及其他类化合物 15 种。

2.1 黄酮类化合物

黄酮类化合物是蜂胶中最为活跃的一类生物活性物质,根据母核结构的不同可分为黄酮、黄酮醇、二氢黄酮、二氢黄酮醇、异黄酮、二氢异黄酮、查尔酮、二氢查尔酮及新黄酮类化合物等。

巴西蜂胶中已分离鉴定出的黄酮类化合物大都以游离黄酮苷元形式存在,表现出很强的抗氧化、抑菌、抗炎、护肝等生物学活性^[32,42];而黄酮苷类物质的报道较少。此前,Andreas 等^[17]曾从巴西 5 个不同地区的红蜂胶中分离鉴定出了芦丁;随后,Righi 等^[42]采用 HPLC-DAD-ESI-MS/MS 技术从巴西阿拉戈斯州的红蜂胶中检测到了一种新的黄酮己糖碳苷类化合物。最近,Righi 等又从巴西多个地区的蜂胶样中发现了大量的黄酮氧苷及碳苷类化合物^[58];通过进一步二级质谱图解谱发现这些黄酮苷类化合物多数由木樨草素、芹菜素、槲皮素、柚皮素与葡萄糖、阿拉伯糖、鼠李糖等单糖类通过“C-C”或“C-O”连接而成。其中,芹菜素-8-C-葡萄糖苷-6-C-阿拉伯糖苷首次在巴西绿蜂胶中发现。此外,该团队从中还分离到了 9 种异戊烯基黄酮类化合物,这也是首次从巴西蜂胶中检测到该类型物质的存在。巴西蜂胶中已分离鉴定的黄酮类化合物见表 2。

表 2 巴西蜂胶中的黄酮类化合物
Table 2 Flavonoids in Brazilian propolis

序号 No.	英文名称 English name	中文名称 Chinese name	蜂胶来源 Propolis sources	参考文献 Ref.
黄酮(醇)类化合物				
1	chrysin	柯因(白杨素)	G4, G1	5, 17
2	acacetin	金合欢素(刺槐素)	G1	19
3	apigenin	芹菜素	G4, G1	5, 12
4	tectochrysin	柚木柯因	G4, G1	17, 60
5	luteolin	木樨草素	G9	17
6	luteolin-5-methyl ether	木樨草素-5-甲醚	G1	43, 44
7	diprenyl chrysin	二异戊烯基柯因	G1	58
8	prenyl-trimethoxyluteolin	异戊烯基-三甲氧基木樨草素	G1	58
9	5,7,3',4'-tetramethoxyflavone	5,7,3',4'-四甲氧基黄酮	G9	42
10	isorhamnetin	异鼠李亭	G1	41
11	quercetin	槲皮素(栎精)	G1, G9	17, 41
12	rhamnetin	鼠李亭	G1	41
13	galangin	高良姜素	G4, G1	5, 60
14	kaempferol	山奈酚	G1	9, 19
15	kaempferide	山奈素	G1	36

16	3-methylkaempferol	山奈酚-3-甲基	G1	40
17	6-methoxykaempferol	6-甲氧基山奈酚	G1	33
18	3,5,7-trihydroxy-4'-methoxy-flavonol	3,5,7-三羟基-4'-甲氧基黄酮醇	G1	9,12
19	ermanin	5,7-二羟基-3,4'-二甲氧基黄酮醇	G1	32
20	4',6-dimethoxy-3,5,7-trihydroxyflavone(betuletol)	3,5,7-三羟基-6,4'-二甲氧基黄酮醇	G1	37
21	alnusin	赤杨黄酮	G9	31
22	quercetin-dimethyl ether	槲皮素二甲醚	G1	58
23	pentamethoxy hydroxy flavonol	五甲氧基羟基黄酮醇	G1	58
24	pentamethoxy flavonol	五甲氧基黄酮醇	G1	58
25	prenyl-methoxyquercetin	异戊烯基-甲氧基槲皮素	G1	58
26	prenyl-methoxykaempferol	异戊烯基-甲氧基山奈酚	G1	58
27	prenyl-dimethoxyquercetin	异戊烯基-二甲氧基槲皮素	G1	58
28	prenyl-dimethoxykaempferol	异戊烯基-二甲氧基山奈酚	G1	58
29	prenyl-trimethoxykaempferol	异戊烯基-三甲氧基山奈酚	G1	58
	二氢黄酮(醇)类化合物			
1	naringenin	柚皮素	G1	37
2	sakuranetin	樱花亭	G1	37
3	isosakuranetin	异樱花亭	G1	19,34
4	pinocembrin	松属素	G4, G9, G1	5,17,60
5	(2S)-liquiritigenin	(2S)-甘草素	G9	31
6	(2S)-7-hydroxyflavanone	(2S)-7-羟基二氢黄酮	G9	31
7	(2S)-7-hydroxy-6-methoxyflavanone	(2S)-7-羟基-6-甲氧基二氢黄酮	G9	31
8	(2S)-naringenin	(2S)-柚皮素	G9	31
9	(2S)-dihydrobaicalein	(2S)-二氢黄芩黄素	G9	31
10	(2S)-dihydroroxylin A	(2S)-二氢木蝴蝶素 A	G9	31
11	dihydroquercetin	二氢槲皮素	G1	58
12	pinobanksin	短叶松素	G4, G1, G9	5,17,60
13	methoxypinobanksin	甲氧基短叶松素	G9	43,44
14	pinobanksin-5-methyl ether acetate	5-甲醚短叶松素乙酸酯	G4	58
15	pinobanksin-3-acetate	短叶松素-3-乙酸酯	G4, G1, G9	5,17,60
16	dihydrokaempferol (aromadendrin)	二氢山奈酚	G1	33
17	dihydrokaempferide	二氢山奈素	G1	7
18	aromadendrin-4'-methyl ether	香树精-4'-甲醚	G9	38,39
19	(2R,3R)-3,7-dihydroxyflavanone	(2R,3R)-3,7-二羟基二氢黄酮醇	G9	31
20	garbanzol	3,7,4'-三羟基二氢黄酮醇	G9	31
21	(2R,3R)-3,7-dihydroxy-6-methoxyflavanone	(2R,3R)-3,7-二羟基-6-甲氧基二氢黄酮醇	G9	28
22	alnustinol	3,5,7-三羟基-6-甲氧基二氢黄酮醇	G9	28
23	laricitrin	3,5,7,4',5'-五羟基-3'-甲氧基二氢黄酮醇	G1	58
	异黄酮和二氢异黄酮类化合物			
1	biochanin	鹰嘴豆芽素	G9	52
2	biochanin A	鹰嘴豆芽素 A	G9	31
3	formononetin	芒柄花黄素	G9	31

4	daidzein	大豆黄素	G9	31
5	calycosin	毛蕊异黄酮	G9	31,42
6	2'-hydroxyformononetin (xenognosin B)	2'-羟基芒柄花黄素	G9	28
7	pratensein	红车轴草素	G9	31
8	2'-hydroxybiochanin A	2'-羟基鹰嘴豆芽素 A	G9	31
9	(3S)-vestitone	-	G9	31
10	(3S)-7,4'-dihydroxy-2'-methoxyisoflavan	(3S)-7,4'-二羟基-2'-甲氧基异黄酮	G9	56
11	(3S)-violanone	-	G9	31
12	(3S)-ferreirin	-	G9	31
13	(3R)-4'-methoxy-2',3,7-trihydroxy-isoflavanone	(3R)-4'-甲氧基-2',3,7-三羟基二氢异黄酮	G9	31
14	isosativan	-	G9	18
15	4',7-dimethoxy-2'-isoflavonol	4',7-二甲氧基-2'-异黄酮醇	G9	12
16	7,4'-dihydroxyisoflavone	7,4'-二羟基异黄酮	G9	12
17	retusapurpurin A	-	G9	86
18	retusapurpurin B	-	G9	86
	查尔酮类化合物			
1	isoliquiritigenin	异甘草素	G9	31
2	3,4,2',3'-tetrahydroxychalcone	3,4,2',3'-四羟基查尔酮	G9	42
3	4,4'-dihydroxy-2'-methoxychalcone	4,4'-二羟基-2'-甲氧基查尔酮	G9	31
4	(α S)- α ,2',4,4''-tetrahydroxydihydrochalcone	(α S)- α ,2',4,4''-四羟基二氢查尔酮	G9	31
5	2',4'-dihydroxychalcone	2',4'-二羟基查尔酮	38	22
6	methyl licochalcone B	甲基甘草查尔酮 B	G1	58
7	phloretin	根皮素	G1	58
8	2-hydroxy-4-methoxychalcone	2-羟基-4-甲氧基查尔酮	G9	31
9	pinostrobin chalcone	球松素查尔酮	G4	6
	紫檀素类化合物			
1	(6aS,11aS)-medicarpin	(6aS,11aS)-美迪紫檀素	G9	31
2	(6aS,11aS)-3,10-dihydroxy-9-methoxypterocarpan	(6aS,11aS)-3,10-二羟基-9-甲氧基紫檀素	G9	31
3	(6AR,11AR)-3-hydroxy-8,9-dimethoxypterocarpan	(6AR,11AR)-3-羟基-8,9-二甲氧基紫檀素	G9	31
4	(6AR,11AR)-3,4-dihydroxy-9-methoxypterocarpan	(6AR,11AR)-3,4-二羟基-9-甲氧基紫檀素	G9	31
5	(6aS,11aS)-6a-ethoxymedicarpin	(6aS,11aS)-6a-乙氧基美迪紫檀素	G9	31
6	5,6,7-trihydroxy-3,4'-dimethoxyflavanone	5,6,7-三羟基-3,4'-二甲氧基黄酮	G9	38
7	(6AR,11AR)-4-methoxymedicarpin	(6AR,11AR)-4-甲氧基紫檀素	G9	31
8	(6AR,11AR)-3,8-dihydroxy-9-methoxypterocarpan	(6AR,11AR)-3,8-二羟基-9-甲氧基紫檀素	G9	52
9	homopterocarpan	后莫紫檀素	G9	12
	新黄酮类化合物			
1	2-(2'-hydroxy-4'-methoxyphenyl)-3-methyl-6-methoxybenzofuran	-	G9	42
2	(3S)-mucronulatol	-	G9	31
3	(3S)-vestitol	-	G9	31
4	(3S)-isovestitol	-	G9	31
5	(3S)-7-O-methylvestitol	-	G9	31
6	dalbergin	黄檀素	G9	17

7	2,6-dihydroxy-2-[(4-hydroxyphenyl)-methyl]-3-benzofuranone	2,6-二羟基-2-[(4-羟基苯基)甲基]-3-苯并呋喃酮	G9	31
8	2-(2',4'-dihydroxyphenyl)-3-methyl-6-methoxybenzofuran	2-(2',4'-二羟基苯基)-3-甲基-6-甲氧基苯并呋喃	G9	31
9	(7S)-dalbergiphenol 双黄酮类化合物	-	G9	31
1	volkensiflavone	-	G9	42
2	gliricidin 黄酮苷类化合物	-	G9	42
1	rutin	芦丁	G1, G9	17,60
2	methylkaempferol- <i>O</i> -rutinoside	甲基山奈酚- <i>O</i> -芸香糖苷	G1	58
3	naringenin- <i>C</i> -glucoside	柚皮素- <i>C</i> -葡萄糖苷	G1	58
4	quercetin- <i>O</i> -glucoside	槲皮素- <i>O</i> -葡萄糖苷	G1	58
5	luteolin- <i>O</i> -glucuronide	木樨草素- <i>O</i> -葡萄糖酸苷	G1	58
6	delphinidin arabinoside	花翠素-阿拉伯糖苷	G1	58
7	catechin arabinoside	儿茶素-阿拉伯糖苷	G1	58
8	apigenin- <i>O</i> -rutinoside	芹菜素- <i>O</i> -芸香糖苷	G1	58
9	apigenin-di- <i>C</i> -glucosyl rhamnoside	芹菜素 2 <i>C</i> -葡萄糖鼠李糖苷	G1	58
10	apigenin-6,8-di- <i>C</i> -glucoside(vicenin-2)	葫芦巴苷-2	G1	46,47
11	apigenin- <i>C</i> -rhamnosyl arabinoside	芹菜素- <i>C</i> -鼠李糖阿拉伯糖苷	G1	58
12	apigenin-6- <i>C</i> -glucosyl-8- <i>C</i> -arabinose (isoschaftoside)	异夏佛塔苷	G1	48
13	apigenin- <i>C</i> -rhamnoside	芹菜素- <i>C</i> -鼠李糖苷	G1	58
14	apigenin-8- <i>C</i> -glucosyl-6- <i>C</i> -arabinose (schaftoside)	夏佛塔苷	G1	48
15	luteolin-6,8-di- <i>C</i> -glucoside(lucenin-2)	木樨草素-6,8-2 <i>C</i> 葡萄糖苷	G1	58
16	pentosyl orientin	戊糖基-荛草素	G1	58
17	apigenin 8- <i>C</i> -glucoside (vitexin)	牡荆素	G1	58
18	quercetin- <i>O</i> -glucoside	槲皮素- <i>O</i> -葡萄糖苷	G1	58
19	luteolin acetyl glucoside	木樨草素乙酰基-葡萄糖苷	G1	58
20	chrysoeriol- <i>C</i> -glucoside	金圣草素- <i>C</i> -葡萄糖苷	G1	58
21	dimethoxy naringenin-diglucoside	二甲氧基柚皮素-二葡萄糖苷	G1	58
22	apigenin-di- <i>O</i> -glucoside	芹菜素-2- <i>O</i> -葡萄糖苷	G1	58
23	quercetin- <i>O</i> -arabinoside	槲皮素- <i>O</i> -阿拉伯糖苷	G1	58
24	quercetin- <i>O</i> -rhamnoside	槲皮素- <i>O</i> -鼠李糖苷	G1	58
25	isorhamnetin-glucoside	异鼠李亭-葡萄糖苷	G1	58
26	apigenin- <i>O</i> -glucuronide	芹菜素- <i>O</i> -葡萄糖苷酸	G1	58
27	naringenine-7-rhamnosidoglucoside(nobiletin)	川陈皮素	G1	58
28	chrysin rhamnoside	柯因-鼠李糖苷	G1	58
29	dimethoxyluteolin-glucoside	二甲氧基木樨草素-葡萄糖苷	G1	58
30	naringenin- <i>C</i> -hexoside	柚皮素- <i>C</i> -己糖苷	G9	42
31	hesperetin 7-rhamnoglucoside	橙皮素-7-鼠李葡萄糖苷	G1	87,88

2.2 酚酸类化合物

研究发现,巴西蜂胶中酚酸类化合物含量丰富,种类繁多,在其抗氧化、抗菌、抗肿瘤、细胞毒性等生

物学活性方面发挥着极其重要的作用^[20,25]。

酚酸类化合物按其母核结构的不同可分为苯酚类、苯甲酸类、苯丙酸类、咖啡酰奎宁酸类以及其他

较为复杂的酚酸类物质。其中,苯丙酸类化合物是存在于巴西蜂胶中最为普遍的一种酚酸类化合物,迄今已从中鉴定到了40种该类型的化合物;而以羟基肉桂酸类衍生物尤其是异戊烯基 *p*-香豆酸类化合物(阿替匹林 C、3-异戊烯基肉桂酸烯丙酯)为代表的苯丙酸类物质在巴西绿蜂胶中最为常见,也是其典型的代表性成分,引起了人们的普遍关注。

其次,以绿原酸为代表的咖啡酰奎宁酸类化合物在巴西蜂胶中的含量也较为丰富,这包括单咖啡

酰奎宁酸、双咖啡酰奎宁酸及三咖啡酰奎宁酸等化合物,研究表明该类物质具有强效的抗氧化及细胞毒性作用^[25]。Righi 等通过 HPLC 分离技术结合二级质谱又从巴西蜂胶中发现了几种新的阿魏酰-咖啡酰奎宁酸、阿魏酰奎宁酸类化合物以及一种新的甘油酯类化合物—二氢咖啡酸-二氢肉桂酸甘油酯^[58]。

巴西蜂胶中已分离鉴定的酚酸类化合物见表 3。

表 3 巴西蜂胶中的酚酸类化合物

Table 3 Phenolic acid in Brazilian propolis

序号 No.	英文名称 English name	中文名称 Chinese name	蜂胶来源 Propolis sources	参考文献 Ref.
苯丙酸类衍生物				
1	benzenepropanoic acid	苯丙酸	G1	5
2	3,5-diprenyl-4-hydroxycinnamic acid (artepillin C)	阿替匹林 C	G1	30
3	4-dihydrocinnamoyloxy-3-prenylcinnamic acid	3-异戊烯基-4-二氢肉桂酰肉桂酸	G1	32
4	(<i>E</i>)-3-prenyl-4-(dihydrocinnamoyloxy)-cinnamic acid	-	G1	30
5	4-hydroxy-3-prenylcinnamic acid (drupanin)	4-羟基-3-异戊烯基肉桂酸	G1	12
6	dihydrocinnamic acid	二氢肉桂酸	G1	8
7	<i>p</i> -coumaric acid	<i>p</i> -香豆酸	G1	5
8	<i>p</i> -hydroxyhydrocinnamic acid	对羟基氢肉桂酸	G1	8
9	methyl hydrocinnamate	氢化肉桂酸甲酯	G4, G8, G1	5, 59
10	ethyl hydrocinnamate	氢化肉桂酸乙酯	G1	59
11	ferulic acid	阿魏酸	G4, G8, G1	5
12	caffeic acid	咖啡酸	G4, G1	5
13	<i>p</i> -methoxycinnamic acid	4-甲氧基肉桂酸	G1	8
14	cis-3-methoxy-4-hydroxy-cinnamic acid	顺式-3-甲氧基-4-羟基肉桂酸	G1	8
15	trans-3-methoxy-4-hydroxy-cinnamic acid	反式-3-甲氧基-4-羟基肉桂酸	G1	8
16	cis-3,4-dimethoxycinnamic acid	顺式-3,4-二甲基肉桂酸	G1	8, 45
17	trans-3,4-dimethoxycinnamic acid	反式-3,4-二甲基肉桂酸	G1	45
18	3,4-dihydroxy-5-prenylcinnamic acid	3,4-二羟基-5-异戊烯基肉桂酸	G1	40
19	4-hydroxy-3-(<i>E</i>)-(4-hydroxy-3-methyl-2-butenyl)-5-prenylcinnamic acid (capillartemisin A)	茵陈蒿酸 A	G1	34
20	benzyl <i>p</i> -coumarate	<i>p</i> -香豆酸苯甲酯	G1	33
21	phenethyl <i>p</i> -coumarate	<i>p</i> -香豆酸苯乙酯	G1	33
22	3-prenyl-4-hydroxycinnamic acid methyl ester (plicatin B)	3-异戊烯基-4-羟基肉桂酸甲酯	G1	33
23	allyl-3-prenylcinnamate	3-异戊烯基肉桂酸烯丙酯	G1	62
24	dihydrocinnamic acid ethyl ester	二氢肉桂酸乙酯	G1	45
25	dihydroconiferyl <i>p</i> -coumarate	(<i>E</i>)-2,3-二氢松柏基 <i>p</i> -香豆酸	G1	7
26	(<i>E</i>)-2,3-dihydroconiferyl <i>p</i> -coumarate	(<i>E</i>)-2,3-二氢松柏基 <i>p</i> -香豆酸	G1	33
27	3-[4-hydroxy-3-(3-oxobut-1-enyl)-phenyl] acrylic acid	-	G1	72
28	(<i>E</i>)-3-prenyl-4-(2-methylpropionyloxy)-cinnamic acid	-	G1	7
29	dimethylallyl caffeic acid	二甲基烯丙基咖啡酸	G4	5
30	dimethylallyl caffeic acid ester	-	G4	5

31	3-prenyl-4-(2-methylpropionyloxy)-cinnamic acidmethyl ester	-	G1	58
32	ferulic acid-methoxy trihydroxy phenyl ethyl ester	阿魏酸-甲氧基三羟基苯乙酯	G1	58
33	caffeic acid-dihydroxy phenyl ethyl ester	咖啡酸-二羟基苯乙酯	G1	58
34	carbomethoxy benzyl caffeate ester	甲酯基苄基咖啡酸酯	G1	58
35	caffeic acid 4-O-arabinoside	咖啡酸 4-O-阿拉伯糖苷	G1	58
36	cinnamoyl hexoside	肉桂酸己糖苷	G1	58
37	caffeic acid 4-O-glucoside	咖啡酸 4-O-葡萄糖苷	G1	58
38	caffeic acid 4-O-xyloside	咖啡酸 4-O-木糖苷	G1	58
39	ferulic acid octene ester	阿魏酸辛烯酯	G1	58
40	ferulic acid octadiene ester	阿魏酸辛二烯酯	G1	58
	咖啡酰奎宁酸类			
1	3-caffeoylquinic (chlorogenic) acid	绿原酸	G1	73
2	4-caffeoylquinic acid	4-咖啡酰奎宁酸	G1	73
3	5-caffeoylquinic acid	5-咖啡酰奎宁酸	G1	73
4	3,5-dicaffeoylquinic acid	3,5-二咖啡酰奎宁酸	G1	73
5	4,5-dicaffeoylquinic acid	4,5-二咖啡酰奎宁酸	G1	73
6	4,5-dicaffeoylquinic acid methyl ester	4,5-二咖啡酰奎宁酸甲酯	G1	73
7	3,4-dicaffeoylquinic acid	3,4-二咖啡酰奎宁酸	G1	73
8	3,4-dicaffeoylquinic acid methyl ester	3,4-二咖啡酰奎宁酸甲酯	G1	74
9	3-O-feruloyl-5-O-caffeoylquinic acid	3-氧-阿魏酰-5-氧-咖啡酰奎宁酸	G1	77,78
10	didihydrocaffeoylquinic acid	二(二氢咖啡酰)奎宁酸	G1	77,78
11	feruloylquinic acid	阿魏酰奎宁酸	G1	58
12	4-feruoylquinicacid	4-阿魏酰奎宁酸	G1	25
13	5-feruoylquinicacid	5-阿魏酰奎宁酸	G1	25
14	dihydrocaffeoyl-dihydrocinnamoyl-glyceride	甘油酯	G1	58
	其它酚酸类物质			
1	6-propenoic-2,2-dimethyl-8-prenyl-2H-1-benzopyran acid	-	G1	75
2	6-(2-carboxyethyl)-2,2-dimethyl-2H-1-benzopyran	6-(2-羧基乙烯基)-2,2-二甲基色烷	G1	30
3	3-hydroxy-2,2-dimethyl-8-prenylchromane-6-propenoic acid	3-羟基-2,2-甲基-8-异戊烯基色烷-6-丙烯酸	G1	12
4	8-(methyl-butanechromane)-6-propenoic acid	8-(异戊基色烷)-6-丙烯酸	G1	8
5	2,2-dimethyl-8-prenylchromene-6-propenoic acid	2,2-二甲基-8-异戊烯基苯并吡喃-6-丙烯酸	G1	12
6	2,2-dimethylchromene-6-propenoic acid	2,2-二甲基苯并吡喃-6-丙烯酸	G1	12
7	2,2-dimethylchromene-6-carboxylic acid	2,2-二甲基苯并吡喃-6-羧酸	G1	80
8	3-(2,2-dimethyl-2H-1-benzopyran-6-yl)-2-propenoic acid	-	G1	33
9	(E)-3-[2,3-dihydro-2-[2-[(E)-p-coumaroyloxy]-1-methylethyl]-5-benzofuranyl]-2-propenoic acid	-	G1	33
10	(E)-4-(2,3-dihydrocinnamoyloxy)cinnamic acid	-	G1	33
11	(E)-3-(2,2-dimethyl-3,4-dihydro-3-hydroxy-2H-1-benzopyran-6-yl)-2-propenoic acid	-	G1	33
12	(E)-3-[2,3-dihydro-2-(1-methylethenyl)-5-benzofuranyl]-2-propenoic acid	-	G1	33
13	(E)-3-[2,3-dihydro-2-(1-methylethenyl)-7-prenyl-5-Benzofuranyl]-2-propenoic acid	-	G1	33
14	(E)-3-[4-hydroxy-3-[(E)-4-(2,3-dihydrocinnamoyloxy)-3-methyl-2-butenyl]-5-prenylphenyl]-2-propenoic acid	-	G1	33
15	(E)-3-(2,2-dimethyl-3,4-dihydro-3-hydroxy-8-prenyl-2H-1-benzopyran-6-yl)-2-propenoic acid	-	G1	7

16	(<i>E</i>)-3-[2,3-dihydro-2-(1-hydroxy-1-methylethyl)-7-prenyl-5-benzofuranyl]-2-propenoic acid	-	G1	7
	苯甲酸类			
1	4-hydroxy-3-prenylbenzoic acid	4-羟基-3-异戊烯基苯甲酸	G1	33
2	benzoic acid	苯甲酸	G4, G8	68
3	methoxy-dihydroxy benzoic acid	甲氧基-二羟基苯甲酸	G9	44
4	3,4-dihydroxybenzoic acid	3,4-二羟基苯甲酸	G1	34
5	benzoic acid, 4(4-hydroxybenzoyl)-methyl ester	-	G1	58
6	benzoic acid, 2(4-hydroxybenzoyl)-methyl ester	-	G1	58
7	benzoic acid, 2-propoxy-(4-hydroxybenzoyl)-methyl ester	-	G1	58
	苯酚类物质			
1	<i>p</i> -vinylphenol	对乙烯基苯酚	G1	8
2	<i>p</i> -vinyl- <i>O</i> -prenylphenol	4-乙烯基-2-异戊烯基苯酚	G1	8
3	ethylphenol	乙基苯酚	G1	8
4	2,4,6-trimethylphenol	2,4,6-三甲基苯酚	G1, G9	12
5	benzene-3,3-dimethyl-4-pentenyl	-	G1	8
6	homovanillic acid(4-hydroxy-3-methoxyphenylacetic acid)	高香草酸	G1, G9	42, 58
7	benzyl alcohol, 2-propoxy-(4-hydroxybenzoyl)-methyl ester	-	G1	58
8	methyl <i>o</i> -orsellinate	苔色酸甲酯	G9	12
9	resorcinol	间苯二酚	G9	42

2.3 萜烯类化合物

目前从巴西蜂胶中共分离到了 97 种萜烯类化合物,包括 10 种单萜类、34 种倍半萜类、24 种二萜类及 29 种三萜类物质(表 4)。其中,倍半萜类化合物在巴西绿蜂胶中含量及种类最为丰富,也是其挥发油的主要组成成分,具有较强的抗菌活性。倍半萜类化合物基本的碳骨架主要为无环金合欢烷、单环没药烷、蛇麻烷,双环桉叶烷、石竹烷及三环柏木烷、香兰烷及其含氧衍生物;最近又从巴西红蜂胶中分离鉴定出了愈创木醇(酚)和 isomaternin 等物质。单萜类化合物是巴西蜂胶具有芳香气味及抗菌活性的另一主要活性成分,其含量相对较低,主要是无环月桂烯烷、单环薄荷烷类,以及少量的蒎烷及葑烷类化合物。蜂胶中的二萜类化合物类型较多,包括单

环二萜、双环二萜、三环二萜及四环二萜,而巴西蜂胶中最常见的二萜类化合物主要为双环半日花烷型、克罗烷型及三环枞酸型,研究发现这些二萜类物质具有强效的护肝、抗癌等生物学活性^[32,54]。三萜类化合物在巴西蜂胶萜类物质中含量及种类也较为丰富,主要以四环环菠萝蜜烷型、五环羽扇豆醇型及乌苏烷型为主,尤其是羽扇豆醇和香树精类衍生物。Junko 等还曾从巴西 G5 蜂胶甲醇提取物中分离到了一种新的三萜类化合物—melliferone 以及另外 3 种三萜酸类化合物^[22]。巴西绿蜂胶中三萜类物质的含量高低可以直接通过蜂胶样的物理性状来判断,随着三萜类物质含量的上升,蜂胶的硬度变小,绿色变浅,其典型的苯丙素类衍生物含量也随之下降。

表 4 巴西蜂胶中的萜烯类化合物

Table 4 Terpenoids in Brazilian propolis

序号 No.	英文名称 English name	中文名称 Chinese name	蜂胶来源 Propolis sources	参考文献 Ref.
	单萜类			
1	linalool	芳樟醇	G1	59
2	β -myrcene	月桂烯	G1	60

3	limonene	柠檬烯	G1	59
4	α -terpineol	α -松油醇	G1	59,60
5	4-terpineol	4-松油醇	G1	60
6	α -pinene	α -蒎烯	G1	6
7	β -pinene	β -蒎烯	G1	6
8	1,8-cineole	1,8 - 桉叶素	G1	91
9	exo-fenchol	小茴香醇	G1	91
10	p-cimen-8-ol	-	G1	8
	倍半萜类			
1	farnesol	金合欢醇	G1, G9	12,42
2	farnesyl acetate	金合欢乙酸酯	G1	45
3	β -farnesene	β -金合欢烯	G1	59
4	viridiflorol	白千层醇	G1	45
5	ledol	喇叭茶醇	G1	57
6	ledene	喇叭烯	G1	11
7	palustrol	喇叭茶碱	G1	11
8	guaiol	愈创木醇	G1, G9	12
9	methylguaiacol	甲基愈创木酚	G9	42
10	α -caryophyllene	α -石竹烯	G1	59
11	β -caryophyllene	β -石竹烯	G8, G1	59,60
12	caryophyllene oxide	石竹烯氧化物	G1	45
13	nerolidol	橙花叔醇	G1	60
14	α -humulene	α -蛇麻烯	G1	60
15	γ -elemene	榄香烯	G1	59
16	γ -cadinene	γ -杜松烯	G1	59
17	δ -cadinene	杜松烯	G1	59,60
18	epi-alpha-cadinol	香榧醇	G1	60
19	valencene	瓦伦烯	G1	59
20	spatulanol	斯巴醇	G1	11
21	isopatulanol	异斯巴醇	G1	11
22	α -copaene	胡椒烯	G1	11
23	α -ylangene	依兰烯	G1	59
24	α -muurolene	α -依兰油烯	G1	59
25	γ -muurolene	γ -依兰油烯	G1	59
26	aromadendrene	香木兰烯	G1	59,60
27	spathulenol	匙叶桉油烯醇	G1	59,60
28	globulol	蓝桉醇	G1	60
29	dehydrocostus lactone	去氢木香内酯	G1	59
30	isomaturmin	-	G1	8
31	longipinene	长叶蒎烯	G1	89
32	α -eudesmol	α -桉叶醇	G1	89
33	β -eudesmol	桉叶醇	G1	89

34	selina-3,7(11) diene 二萜类	γ -芹子烯	G1	93
1	isocupressic acid	异柏酸	G1	12
2	15-acetoxyisocupressic acid	15-乙酰氧基异柏酸	G1	12
3	agathic acid (8(17),13E-labdadien-15,19-dioic acid)	贝壳松烯二酸	G1	12
4	agathic acid 15-methyl ester	贝壳松烯二酸-15-甲酯	G1	33
5	communic acid	璎柏酸	G1	33
6	dehydroabietic acid	去氢松香酸	G1	33
7	agathalic acid	-	G1	12
8	cupressic acid	柏酸	G1	12
9	ent-17-hydroxy-3,13Z-clerodadien-15-oic acid	-	G1	53
10	15-oxo-3,13Z-kolavadiene-17-oic acid	-	-	54
11	15-oxo-3,13E-kolavadiene-17-oic acid	-	-	54
12	imbricatoloic acid	南洋杉酸	G1	11
13	kaurenoic acid	含异贝壳杉烯酸	G1	9
14	ent-15 β -hydroxyl-16-kauren-19-oic acid	-	-	67
15	ent-15 β -(3-methylbutanoyloxy)-16-kauren-19-oic acid	-	-	67
16	labdane type diterpenic acid	半日花烷型二萜酸	G1	38
17	13-symphoreticolic acid	-	G1	12
18	methyl abietate	松香酸甲酯	G9	12
19	methyl dehydroabietate	脱氢松香酸甲酯	G1	11
20	ethyl dehydroabietate	脱氢松香酸乙酯	G1	11
21	12,16-epoxy-6-hydroxy-(15-16)-abeo-5,8,11,13-abietatetraene-7-one	-	G1	11
22	1,4 $\alpha\beta$ -dimethyl-7-isopropyl-2,3,4,-4a,9,10-hexahydrophenanthrene	1 α ,4 β -二甲基-7-异丙基-2,3,4,4a,9,10-六氢菲	G1	8
23	manool	泪杉醇	-	90
24	totarol	桃柝酚	-	90
	三萜类			
1	α -amyrin	α -香树精	G1, G9	42,57
2	β -amyrin	β -香树精	G1, G9	42,57
3	α - amyrinone	α -白檀酮	G1	55
4	β -amyrinone	β -白檀酮	G1	55
5	α -amyrin acetate	α -香树精乙酸酯	G1	55
6	β -amyrin acetate	β -香树精乙酸酯	G1	55
7	β -amyrin alkanoates	β -香树精烷酸酯	G1	57,68
8	cycloartenol	环阿乔醇	G1, G9	18,55
9	melliferone	-	G5	22
10	moronic acid	-	G5	22
11	anwuweizonic acid	-	G5	22
12	betulonic acid	桦桐酸	G5	22
13	lupeol(20(29)-lupen-3 β -ol)	羽扇醇	G1, G9	42,57
14	lupenone(20(29)-lupen-3-one)	羽扇豆烯酮	G1, G9	18,57
15	lupeol acetate	羽扇醇乙酯	G1	55

16	lupeol alkanooates	羽扇醇烷酸酯	G1	57
17	bauer-7-en-3-en-3 β -yl acetate	-	G1	8
18	lanosta-7,24-diene-3 β -ol	-	G1	69
19	24-methylene-9,19-ciclolanostan-3 β -ol	-	G1	57
20	taraxerone	蒲公英萜酮	G1	57
21	oleanene	土当归烯	G1	57
22	squalene	鲨烯	G1	45
23	obtusifoliol	钝叶醇	G1	45
24	pteron-14-en-7-one	-	G1	59
25	olean-14-en-3,28-dione	-	G1	45
26	2-t-butylnaphto-[2,3-b]-furan-4,9-dione	-	G1	8
27	2-hydroxy-7,12-dimethyl-benzanthracene	2-羟基-7,12-二甲基苯蒽	G1	8
28	1-hydroxy-2-(1-methoxyethyl)-3-methoxyanthraquinone	1-羟基-2-(1-甲氧乙基)-3-甲氧基蒽醌	G1	8
29	ergosterol	麦角固醇	G1	58
30	lupeol 3-(39R-hydroxy)-hexadecanoate	-	G1	69
31	3-(39R-hydroxy)-octadecanoate	-	G1	69

2.4 木脂素类化合物

木脂素类化合物广泛分布于包括食用植物在内的多数木本植物组织中,具有多种生理药理活性,特

别是抗肿瘤及抗病毒活性,引起了人们的极大关注。

目前在巴西蜂胶中共发现了6种木脂素类化合物(表5)。

表5 巴西蜂胶中的木脂素类化合物

Table 5 Ligans in Brazilian propolis

序号 No.	英文名称 English name	中文名称 Chinese name	蜂胶来源 Propolis sources	参考文献 Ref.
1	1-(4-hydroxy-3-methoxyphenyl)-1,2-bis[4-(<i>E</i>)-3-acetoxypropen-1-yl]-2-methoxyphenoxy}-propan-3-ol acetate	-	G1	33,70
2	3-acetoxymethyl-5-[(<i>E</i>)-2-formylethen-1-yl]-2-(4-hydroxy-3-methoxyphenyl)-7-methoxy-2,3-dihydrobenzofuran	-	G1	12,36
3	dimeric coniferyl acetate	乙酸二聚松柏酯	G1	12
4	(+)-pinoresinol dimethyl ether	(+)-松脂二甲基酯	G9	31
5	(+)-pinoresinol	(+)-松脂醇	G9	31
6	(+)-syringaresinol	(+)-丁香脂素	G9	31

2.5 挥发油类化合物(非萜类)

巴西蜂胶中挥发油含量虽然不高,但成分相当复杂。除了上述主要的单萜及倍半萜外,还含有其他类有机化合物,主要包括芳香族苯甲酮、苯乙酮及其异戊烯化衍生物、苯丙烷类衍生物、酚类化合物

或其酯类,以及一些小分子脂肪族醇、醛、酮及酸类化合物(表6)。其中,异戊烯基苯甲酮类化合物主要存在于红蜂胶中,对多种细菌、真菌具有强效的抑菌活性,并具有较强的肿瘤细胞毒性作用^[18,28]。

表6 巴西蜂胶中的挥发油类化合物(非萜类)

Table 6 Volatile oils in Brazilian propolis (non-terpenoid)

序号 No.	英文名称 English name	中文名称 Chinese name	蜂胶来源 Propolis sources	参考文献 Ref.
1	4-hydroxy-3-methoxybenzaldehyde (vanillin)	香草醛	G5, G1	12,22

2	3-Methoxy-4-hydroxycinnamaldehyde(coniferyl aldehyde)	松柏醛	G1	12
3	2-[1-hydroxymethyl]-vinyl-6-acetyl-5-hydroxycumarane (viscidone)	-	G1	32
4	2-[1-acetoxymethyl]-vinyl-6-acetyl-5-hydroxycumarane (12-acetoxyviscidone)	-	G1	32
5	methoxyeugenol	甲氧基丁香酚	G9	42
6	anisylacetone	茴香酮	G9	42
7	elimicin	榄香素	G9	18
8	cis-asarone	顺式-细辛脑	G9	42
9	acetophenone	苯乙酮	G9	59
10	prenylacetophenone	异戊烯基苯乙酮	-	56
11	diprenylacetophenone	二异戊烯基苯乙酮	-	56
12	benzaldehyde	苯甲醛	G9	59
13	nonanal	正壬醛	G9	59
14	benzyl benzoate	苯甲酸苄酯	G9	7
15	3-phenylpropanol	3-苯丙醇	-	56
16	α -methyl benzylalkohol	α -甲基苯甲醇	-	56
17	hyperibone A	-	G8	29
18	guttiferone E	-	G9	18
19	xanthochymol	大叶藤黄醇	G9	18
20	trans-anethol	反式-茴香脑	G9	18
21	methyleugenol	甲基丁香酚	G9	18
22	isoeugenol	异丁香酚	G9	56
23	trans-methyl isoeugenol	反式-异丁香酚甲醚	G9	18
24	trans-isoelemicin	反式异榄香素	G9	18
25	oblongifolin A	-	G9	86

2.6 其它类化合物

少量的环氧醌、香豆酮以及其他一些未能明确分类

随着研究的深入,人们还从巴西蜂胶中发现了 的化学成分(表7)。

表7 巴西蜂胶中的其他类化合物

Table 7 Other organic compounds in Brazilian propolis

序号 No.	英文名称 English name	中文名称 Chinese name	蜂胶来源 Propolis sources	参考文献 Ref.
1	4-hydroxy-3-methoxypropiofenone	3-甲氧基-4-羟基苯丙酮	G5	22
2	3-(3,4-dimethoxyphenyl)-2-propenal	-	G5	22
3	2-[1-methyl]-vinyl-5-acetylcumarane(tremetone)	白蛇根毒素	G1	12
4	12-acetoxytremetone	12-乙酰氧基白蛇根毒素	G5	22
5	benzofuran A	香豆酮 A	G1	81
6	benzofuran B	香豆酮 B	G1	81
7	2-[1-hydroxymethyl] vinyl-6-acetyl-5-hydroxycumarane	-	-	82
8	1,7,7-trimethyl-3-phenyl-2-oxabicyclo-(4.4.0)-deca-3,5-diene	-	G1	8
9	4,8-dimethyl-5-hydrindacene	-	G1	8
10	2-propoxy-(4-hydroxybenzoyl)-methyl ester	-	G1	58
11	2,3-epoxy-2-(3-methyl-2-butenyl)-1,4-naphthalenedione	-	G9	18

12	6-acetyl-2,2-dimethyl-3-hydroxy-chroman	-	G9	85,87
13	7-epi-nemorosone	-	G9	94
14	7-epi-clusianone	-	G9	94
15	gambogenone	-	G9	94

此外,在巴西蜂胶中还存在着微量的糖类、烃类、矿物元素和维生素等物质^[95-96]。Pereira 等通过 HT-HRGC-MS 技术分析,从里约热内卢和圣保罗地区采集的蜂胶中鉴定出一些糖类化合物,这些物质多数为单糖类,其中肌糖是首次在蜂胶中发现的单糖类化合物^[97]。最近,Mayworm 等在巴西蜂胶中还检测到了单宁酸类物质的存在,其中,红蜂胶中含量最高,绿蜂胶中次之^[98]。

3 结语

巴西因其得天独厚的地理位置和丰富的植物资源而成为蜂胶生产大国之一,在世界蜂胶市场上备受瞩目。巴西蜂胶的化学成分极其复杂,目前已从中分离鉴定到了 300 多种化合物;而受蜂种、地理来源、植物来源及采胶季节等多种因素的影响,巴西蜂胶的化学成分又具有多变性,不同蜂胶之间成分差异较大。因此,根据不同的地理位置和植物来源对巴西蜂胶进行分类研究,并结合多指标指纹图谱分析技术将更利于巴西蜂胶的标准化使用和质量控制。

巴西蜂胶具有多种生理药理学活性,但目前大部分的研究仍以巴西绿蜂胶中的酚酸类化合物为主,而其他类型的蜂胶仍含有黄酮类、萜烯类等多种生物学活性物质。此外,还有部分类型的蜂胶样的研究处于空白阶段,与其相关的胶源植物的确定也有待于进一步深入研究。

参考文献

- Zhang CP (张翠平), Hu FL (胡福良). Flavonoids in propolis. *Nat Prod Res Dev* (天然产物研究与开发), 2009, 21: 1084-1090.
- Zhang CP (张翠平), et al. Phenolic acid in propolis. *Chin J Mod Appl Pharm* (中国现代应用药学), 2013, 30: 102-105.
- Zhang CP (张翠平), Hu FL (胡福良). Terpenoids in propolis. *Nat Prod Res Dev* (天然产物研究与开发), 2012, 24: 976-984.
- Bankova VS, et al. Propolis: recent advances in chemistry and plant origin. *Apidologie*, 2000, 31: 3-15.
- Park YK, et al. Botanical origin and chemical composition of Brazilian propolis. *J Agric Food Chem*, 2002, 50: 2502-2506.
- Park YK, et al. Evaluation of Brazilian propolis by both physicochemical methods and biological activity. *Honeybee Sci*, 2000, 21(2): 85-90.
- Kumazawa S, et al. Direct evidence for the plant origin of Brazilian propolis by the observation of honeybee behavior and phytochemical analysis. *Chem Pharm Bull*, 2003, 51: 740-742.
- Teixeira éW, et al. Plant origin of green propolis: bee behavior, plant anatomy and chemistry. *Evid-based Compl Alt*, 2005, 2: 85-92.
- Midorikawa K, et al. Liquid chromatography-mass spectrometry analysis of propolis. *Phytochem Anal*, 2001, 12: 366-373.
- Bankova V, et al. Phytochemical evidence for the plant origin of Brazilian propolis from São Paulo State. *Z Naturforsch C*, 1999, 54: 401-405.
- Bankova V, et al. Antibacterial diterpenic acids from Brazilian propolis. *Z Naturforsch C*, 1996, 51: 277-280.
- Banskota AH, et al. Chemical constituents of Brazilian propolis and their cytotoxic activities. *J Nat Prod*, 1998, 61: 896-900.
- Lopes FC, et al. Effect of three vegetal sources of propolis on macrophages activation. *Phytomedicine*, 2003, 10: 343-343.
- Silva CRB, et al. Pollen spectrum of propolis samples from São Paulo State, Brazil. *Acta Sci Anim Sci*, 2013, 35: 297-300.
- Matos VR, et al. Pollen types and levels of total phenolic compounds in propolis produced by *Apis mellifera* L. (Apidae) in an area of the Semiarid Region of Bahia, Brazil. *An Acad Bras Ciênc*, 2014, 86: 407-418.
- Barth OM. Pollen analysis of Brazilian propolis. *Grana*, 1998, 37: 97-101.
- Daugusch A, et al. Brazilian red propolis-chemical composition and botanical origin. *Evid-based Compl Alt*, 2008, 5: 435-441.
- Trusheva B, et al. Bioactive constituents of Brazilian red propolis. *Evide-based Compl Alt*, 2006, 3: 249-254.
- Park YK, et al. Chemical constituents in *Baccharis dracunculifolia* as the main botanical origin of Southeastern Brazilian propolis. *J Agric Food Chem*, 2004, 52: 1100-1103.
- Wang K (王凯), et al. Research progress on the leading bio-

- active constituents of Brazilian green propolis. *Nat Prod Res Dev* (天然产物研究与开发), 2013, 25:140-145.
- 21 Han LW (韩利文), et al. Determination of Artepillin C in propolis by HPLC. *Chin Pharm Affairs* (中国药事), 2008, 22:312-314.
- 22 Ito J, et al. Anti-HIV activity of moronic acid derivatives and the new melliferone-related triterpenoid isolated from Brazilian propolis. *J Nat Prod*, 2001, 64:1278-1281.
- 23 Cuesta-Rubio O, et al. Polyisoprenylated benzophenones in Cuban propolis; biological activity of nemorosone. *Z Naturforsch C*, 2002, 57:372-378.
- 24 Trusheva B, et al. New polyisoprenylated benzophenones from Venezuelan propolis. *Fitoterapia*, 2004, 75:683-689.
- 25 dos Santos PA, et al. Distribution of quinic acid derivatives and other phenolic compounds in Brazilian propolis. *Z Naturforsch C*, 2003, 58:590-593.
- 26 Barth OM, da Luz CFP. Palynological analysis of Brazilian red propolis samples. *J Apicult Res*, 2009, 48:181.
- 27 Santos FA, et al. Brazilian propolis: physicochemical properties, plant origin and antibacterial activity on periodontopathogens. *Phytother Res*, 2003, 17:285-289.
- 28 Awale S, et al. Constituents of Brazilian red propolis and their preferential cytotoxic activity against human pancreatic FAMC-I cancer cell line in nutrient-deprived condition. *Bioorg Med Chem*, 2008, 16:181-189.
- 29 Castro ML, et al. Identification of a bioactive compound isolated from Brazilian propolis type 6. *Bioorg Med Chem*, 2009, 17:5332-5335.
- 30 Aga H, et al. Isolation and identification of antimicrobial compounds in Brazilian propolis. *Biosci Biotech Biochem*, 1994, 58:945-946.
- 31 Li F, et al. Cytotoxic constituents from Brazilian red propolis and their structure-activity relationship. *Bioorg Med Chem*, 2008, 16:5434-5440.
- 32 Banskota AH, et al. Hepatoprotective and anti-*Helicobacter pylori* activities of constituents from Brazilian propolis. *Phyto-medicine*, 2001, 8:16-23.
- 33 Tazawa S, et al. Studies on the constituents of Brazilian propolis. II. *Chem Pharm Bull*, 1999, 47:1388-1392.
- 34 Tazawa S, et al. Studies on the constituents of Brazilian propolis. *Chem Pharm Bull*, 1998, 46:1477-1479.
- 35 Hernandez J, et al. Sonoran propolis: chemical composition and antiproliferative activity on cancer cell lines. *Planta Medica*, 2007, 73:1469.
- 36 Bankova V, et al. A new lignan from Brazilian propolis. *Z Naturforsch C*, 1996, 51:735-737.
- 37 Horie T, et al. Studies of the selective O-alkylation and dealkylation of flavonoids. XXII. A convenient method for synthesizing 3, 5, 7-trihydroxy-6-methoxyflavones. *Chem Pharm Bull*, 1997, 45:446-451.
- 38 Popova S. Seasonal variations of the chemical composition of Brazilian propolis. *Apidologie*, 1998, 29:361-367.
- 39 Boudourova-Krasteva G, et al. Phenolics from Brazilian propolis. *Z Naturforsch C*, 1997, 52:676-679.
- 40 Hayashi K, et al. Isolation of antioxidative compounds from Brazilian propolis; 3, 4-dihydroxy-5-prenylcinnamic acid, a novel potent antioxidant. *Chem Pharm Bull*, 1999, 47:1521.
- 41 Koo H, et al. Effect of *Apis mellifera* propolis from two Brazilian regions on caries development in desalivated rats. *Caries Res*, 1999, 33:393-400.
- 42 Righi AA, et al. Brazilian red propolis: unreported substances, antioxidant and antimicrobial activities. *J Sci Food Agric*, 2011, 91:2363-2370.
- 43 Gardana C, et al. Analysis of the polyphenolic fraction of propolis from different sources by liquid chromatography-tandem mass spectrometry. *J Pharm Biomed*, 2007, 45:390-399.
- 44 Fernandes-Silva CC, et al. Chemical profiling of six samples of Brazilian propolis. *Quim Nova*, 2013, 36:237-240.
- 45 Teixeira EW, et al. Seasonal variation, chemical composition and antioxidant activity of Brazilian propolis samples. *Evidence-based Compl Alt*, 2010, 7:307-315.
- 46 Piccinelli AL, et al. HPLC PDA-MS and NMR characterization of C-glycosyl flavones in a hydroalcoholic extract of *Citrus aurantifolia* leaves with antiplatelet activity. *J Agr Food Chem*, 2008, 56:1574-1581.
- 47 Piccinelli AL, et al. Flavonoid profile and radical-scavenging activity of Mediterranean sweet lemon (*Citrus limetta* Risso) juice. *Food Chem*, 2011, 129:417-422.
- 48 Figueirinha A, et al. *Cymbopogon citratus* leaves: characterization of flavonoids by HPLC-PDA-ESI/MS/MS and an approach to their potential as a source of bioactive polyphenols. *Food Chem*, 2008, 110:718-728.
- 49 Djoukeng JD, et al. Flavonoid profiling in leaves of citrus genotypes under different environmental situations. *J Agric Food Chem*, 2008, 56:11087-11097.
- 50 Greenaway W, et al. The composition and plant origins of propolis: a report of work at oxford. *Bee World*, 1990, 71:107-118.
- 51 Kumazawa S, et al. A new prenylated flavonoid from propolis collected in Okinawa, Japan. *Biosci Biotechnol Biochem*, 2004, 68:260-262.
- 52 Campo Fernández M, et al. GC-MS determination of isoflavonoids in seven red Cuban propolis samples. *J Agric Food*

- Chem, 2008, 56:9927-9932.
- 53 Matsuno T. A new clerodane diterpenoid isolated from propolis. *Z Naturforsch C*, 1995, 50:93-97.
- 54 Matsuno T, et al. Isolation and characterization of cytotoxic diterpenoid isomers from propolis. *Z Naturforsch C*, 1997, 52:702-704.
- 55 Marcucci MC, et al. Chemical composition of Brazilian propolis from São Paulo state. *Z Naturforsch C*, 1998, 53:117-119.
- 56 Bankova V, et al. Chemical composition and antibacterial activity of Brazilian propolis. *Z Naturforsch C*, 1995, 50:167-172.
- 57 Pereira AS, et al. Lupeol alkanooates in Brazilian propolis. *Z Naturforsch C*, 2002, 57:721-726.
- 58 Righi AA, et al. Comparative chemistry of propolis from eight Brazilian localities. *Evid-based Compl Alt*, 2013.
- 59 Oliveira AP, et al. Chemical composition and antibacterial activity of Brazilian propolis essential oil. *J Venomous Animals and Toxins including Tropical Diseases*, 2010, 16:121-130.
- 60 Maróstica Junior MR, et al. Comparison of volatile and polyphenolic compounds in Brazilian green propolis and its botanical origin *Baccharis dracunculifolia*. *Food Sci Technol Res*, 2008, 28:178-181.
- 61 Maárquez Hernaández I, et al. Studies on the constituents of yellow Cuban propolis: GC-MS determination of triterpenoids and flavonoids. *J Agric Food Chem*, 2010, 58:4725-4730.
- 62 Koo H, et al. Effects of compounds found in propolis on *Streptococcus mutans* growth and on glucosyltransferase activity. *Antimicrob Agents Ch*, 2002, 46:1302-1309.
- 63 Uchiyama N, et al. Trypanocidal terpenoids from *Laurus nobilis* L. *Chem Pharm Bull*, 2002, 50:1514-1516.
- 64 Ghisalberti EL. Propolis review. *Bee World*, 1979, 60:59-84.
- 65 Krol W, et al. Inhibition of neutrophils chemiluminescence by ethanol extract of propolis (EEP) and phenolic components. *J Ethnopharmacol*, 1996, 45:19-25.
- 66 Negri G, et al. Green propolis: unreported constituents and a novel compound from chloroform extracts. *J Apicult Res*, 2003, 42:39-41.
- 67 Velikova M, et al. Antibacterial ent-kaurene from Brazilian propolis of native stingless bees. *Fitoterapia*, 2000, 71:693-696.
- 68 Pereira AS, et al. Rapid screening of polar compounds in Brazilian propolis by high-temperature high-resolution gas chromatography-mass spectrometry. *J Agric Food Chem*, 2000, 48:5226-5230.
- 69 Furukawa S, et al. Two novel long-chain alkanolic acid esters of lupeol from Alecrim-propolis. *Chem. Pharm Bull*, 2002, 50:439-440.
- 70 Valcic S, et al. Lignans from Chilean propolis. *J Nat Prod*, 1998, 61:771-775.
- 71 Schmitt A, Telikepalli H, Mitscher LA. Plicatin B, the antimicrobial principle of *psoralea juncea*. *Phytochemistry*, 1991, 301:3569-3570.
- 72 Basnet P, et al. Potent free radical scavenging activity of propol isolated from Brazilian propolis. *Z Naturforsch C*, 1997, 52:828-833.
- 73 Tatefuji T, et al. Isolation and identification of compounds from Brazilian propolis which enhance macrophage spreading and mobility. *Biol Pharm Bull*, 1996, 19:966-970.
- 74 Basnet P, et al. Potent antihepatotoxic activity of dicaffeoyl quinic acids from propolis. *Biol Pharm Bull*, 1996, 19:1479-1484.
- 75 Marcucci MC, et al. Evaluation of phenolic compounds in Brazilian propolis from different geographic regions. *Z Naturforsch C*, 2000, 55(1/2):76-81.
- 76 Marcucci MC, et al. Phenolic compounds from Brazilian propolis with pharmacological activities. *J Ethnopharmacol*, 2001, 74:105-112.
- 77 Takemura T, et al. 3,4-dicaffeoylquinic acid, a major constituent of Brazilian propolis, increases TRAIL expression and extends the lifetimes of mice infected with the influenza A virus. *Evid-based Compl Alt*, 2012, 2012:1-7.
- 78 Moura SAL, et al. Aqueous extract of Brazilian green propolis: primary components, evaluation of inflammation and wound healing by using subcutaneous implanted sponges. *Evid-based Compl Alt*, 2011, 2011:1-8.
- 79 Nunes CA, Guerreiro MC. Characterization of Brazilian green propolis throughout the seasons by headspace GC/MS and ESI-MS. *J Sci Food Agri*, 2012, 92:433-438.
- 80 De Sousa JPB, et al. A reliable quantitative method for the analysis of phenolic compounds in Brazilian propolis by reverse phase high performance liquid chromatography. *J Sep Sci*, 2007, 30:2656-2665.
- 81 Banskota AH, et al. Two novel cytotoxic benzofuran derivatives from Brazilian propolis. *J Nat Prod*, 2000, 63:1277-1279.
- 82 Salomao K, et al. Brazilian propolis: correlation between chemical composition and anti-microbial activity. *Evid-based Compl Alt*, 2008, 5:317-324.
- 83 Li F, et al. Study on the constituents of Mexican propolis and their cytotoxic activity against PANC-1 human pancreatic cancer cells. *J Nat Prod*, 2010, 73:623-627.
- 84 Bankova V, et al. New developments in propolis chemical diversity studies (since 2000). *Scientific Evidence of the Use of Propolis in Ethnomedicine*, 2008:1-13.