蜂胶中的酚酸类化合物

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摘要：酚酸类化合物是蜂胶中的主要活性成分之一。本文根据结构所属的基本骨架对蜂胶中已发现的酚酸类化合物进行分类汇总，旨在为蜂胶化学成分的研究提供有价值的化学依据，为全面评价蜂胶的药用价值提供参考。

关键词：蜂胶；酚酸类化合物

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Phenolic Acid in Propolis

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ABSTRACT: Phenolic acids are the main active ingredients in propolis. In this article, we classified the phenolic acids in propolis according to their affiliate basic skeleton structures, that aimed to provide valuable chemical basis for investigating chemical composition and comprehensive assessing medicinal value of propolis.

KEY WORDS: propolis; phenolic acids

酚酸类化合物是含有酚羟基和羧基的一类代谢产物，广泛分布于植物界。迄今为止，已从蜂胶中鉴定出一百多种酚酸类化合物。这些酚酸类化合物被公认是蜂胶中的主要活性成分之一。蜂胶的抗氧化、抑菌、抗肿瘤等生物学活性均与其中所含的酚酸类物质有关，尤其是咖啡酸苯乙酯(caffeic acid phenethyl ester，CAPE)的生物学活性是近年来研究的热点[1-2]。

蜂胶中发现的酚酸类化合物的主要骨架类型有以下两类：一是 C6-C1 型，基本骨架是苯甲酸，如没食子酸等；二是 C6-C3 型，基本骨架是苯丙酸，如咖啡酸、阿魏酸等[3]。此外，从巴西蜂胶中还发现了许多绿原酸类化合物。本文根据结构所属的基本骨架对蜂胶中已发现的酚酸类化合物进行分类汇总，旨在为蜂胶化学成分的研究提供有价值的化学依据。

1　苯甲酸为母核的酚酸类成分

自然界中以苯甲酸为母核的酚酸类化合物主要是没食子酸及其衍生物。蜂胶中较为常见的酚酸类有没食子酸、原儿茶酸、香兰酸、龙胆酸等，见表 1。

表 1　以苯甲酸为母核的酚酸类成分

Tab 1　Benzoic acid derivatives

化学名称	常用名	参考文献
3,4-dihydroxybenzoic acid	原儿茶酸	[4]
4-methoxybenzoic acid	4-甲氧基苯甲酸	[5]
benzyl salicylate	水杨酸苄酯	[5]
3,4,5-trihydroxybenzoic acid	没食子酸	[6]
2,5-dihydroxybenzoic acid	龙胆酸	[5]
methyl salicylate	邻羟基苯甲酸甲酯	[7]
p-hydroxy benzoic acid	p-苯甲酸	[7]
2-hydroxybenzoic acid	水杨酸	[7]
acetyl salicylic acid	乙酰水杨酸	[8]
veratric acid	藜芦酸	[7]
4-hydroxy-3-methoxybenzoic	香兰酸	[7]
4-hydroxy-3-prenylbenzoic acid		[9]
4-hydroxy-3-prenylbenzoic acid		[9]

2　苯丙酸类化合物

苯丙酸类化合物的基本结构是由酚羟基取代的芳香环与丙烯酸构成的。蜂胶中最常见的苯丙酸类化合物是羟基肉桂酸类，如肉桂酸、*p*-香豆酸、咖啡酸、阿魏酸等结构单元及其衍生物见图 1。蜂胶中发现的苯丙酸类化合物见表 2。

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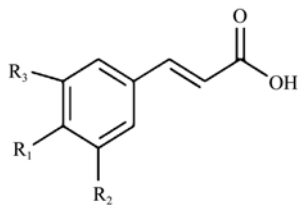


	R_1	R_2	R_3
肉桂酸	H	H	H
p-香豆酸	OH	H	H
咖啡酸	OH	OH	H
阿魏酸	OH	OCH_3	H
异阿魏酸	OCH_3	OH	H

图 1 蜂胶中主要酚酸的结构图

Fig 1 Chemical structure of major phenolic acid in propolis

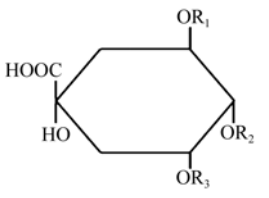
3 绿原酸类衍生物

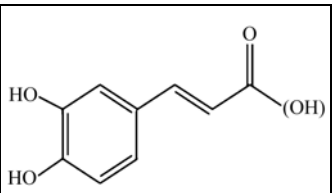
绿原酸类物质是由咖啡酸与奎尼酸组成的缩酚酸类物质，包括单咖啡酰奎尼酸(3-*O*-咖啡酰奎尼酸，及 4 或 5 位取代的衍生物)、双咖啡酰奎尼酸(1,5-双咖啡酰奎尼酸、3,5-双咖啡酰奎尼酸、4,5-双咖啡酰奎尼酸和 3,4-双咖啡酰奎尼酸)及三咖啡酰奎尼酸(如 3,4,5-三咖啡酰奎尼酸)等，结构见图 2。蜂胶中发现的绿原酸类化合物均从巴西蜂胶中分离得到，见表 3。这些成分，在其他地区来源的蜂胶中还未见报道。

表 2 蜂胶中的苯丙酸类化合物

Tab 2 Phenylpropionicacids in propolis

化合物名称	参考文献	化合物名称	参考文献
肉桂酸衍生物(cinnamic acid derivatives)：		咖啡酸类化合物(caffeic acid)：	[25]
cinnamic acid	[10]	caffeic acid	[18]
cinnamic acid ethyl ester	[5]	3-methyl-2-butenyl caffeate	[15]
cinnamic acid methyl ester	[5]	3-methyl-3-butenyl caffeate	[18]
cinnamic acid, 3,4 dimethoxy-tms-ester	[11]	butenyl caffeate	[26]
cinnamic acid, trimethylester	[11]	benzyl caffeate	[18]
3,4-dihydroxy-5-prenylcinnamic Acid	[12]	butyl caffeate	[12]
artepillin C	[13]	caffeic acid cinnamyl ester	[12]
3-prenyl cinnamic acid allyl ester	[14]	caffeic acid isoprenyl ester	[12]
3-prenyl-4-(2,3-dihydrocinnamoyloxy)cinnamic acid	[12]	caffeic acid phenethyl ester	[7,12]
3-prenyl-4-(2-methylpropionyloxy)cinnamic acid	[12]	cinnamyl caffeate	[27]
drupanin 3-prenyl-4-hydroxycinnamic acid	[13]	dimethylallyl caffeic acid	[28]
p-methoxycinnamic acid	[15]	dimethylcaffeic acid	[7]
allyl-3-prenyl cinnamate	[16]	ethyl caffeate	[10,26]
benzyl 3,4-dimethoxycinnamate	[4]	phenylethyl caffeate	[18]
benzyl-3,4-dimethoxycinnamate	[7]	pentyl caffeate	[18]
cinnamyl 3,4-dimethoxycinnamate	[17]	pentenyl caffeate	[15]
cinnamyl cinnamate	[17]	hexadecyl caffeate	[29]
3,5-dimethoxy-4-hydroxycinnamic acid	[6]	hydrocaffeic acid	[19]
cis-3-methoxy-4-hydroxy-cinnamic acid	[16]	isopentenyl-caffeate	[18]
dihydrocinnamic acid	[15]	β-phenylethyl caffeate	[25]
dimethoxycinnamic acid	[18]	ferulic acid	[18]
hydrocinnamic acid	[16]	3-methyl-2-butenyl ferulate	[17]
hexadecyl-4-methoxyhydrocinnamate	[19]	3-methyl-3-butenyl ferulate	[4]
hexadecenyl-4-methoxyhydrocinnamate	[19]	benzyl ferulate	[19]
octadecyl-4-methoxyhydrocinnamate	[19]	heindecenyl hydroferulate	[19]
p-hydroxycinnamic acid	[16]	octadecatrienyl ferulate	[19]
p-hydroxyhydrocinnamic acid	[16]	octenyl ferulate	[19]
p-methoxy-cinnamic acid cinnamyl ester	[12]	pentadecenyl hydroferulate	[19]
tetradecenyl-4-methoxyhydrocinnamate	[19]	pentadecyl hydroferulate	[4]
tetradecyl-4-methoxyhydrocinnamate	[19]	pentenyl ferulate	[7]
trans-3,4-Dimethoxycinnamic acid	[16]	prenyl ferulate	[19]
trans-3-methoxy-4-hydroxy-cinnamic acid	[16]	tridecatrienyl hydroferulate	[19]
trimethylsilyl 3-methoxy-4-cinnamate	[11]	tridecenyl hydroferulate	[19]
capillartemisin A	[20]	tridecyl hydroferulate	[17]
cinnamylidene acetic acid	[12]	2-methyl-2-butenyl ferulate	[18]
p-香豆酸及衍生物(*p*-coumaric acid and derivatives)：		isoferulic acid	[7]
p-coumaric acid	[21]	3-methyl-3-butenyl isoferulate	[15]
m-coumaric acid	[7]	3-methyl-2-butenyl isoferulate	[7]
o-coumaric acid	[7]	benzyl isoferulate	[4]
3,5-diprenyl-p-coumaric acid	[22]	cinnamyl isoferulate	[4]
3-prenyl-4-(2,3-dihydro-p-coumaric acid)	[23]	pent-4-enyl isoferulate	[7]
3-prenyl-p-coumaric acid	[22]	pentenyl isoferulate	[7]
Baccharin	[24]	phenylethyl isoferulate	[7]
coumaric acid methyl ester	[12]	prenyl isoferulate	[7]
p-coumaric acid ester	[12]	2-methyl-2-butenyl isoferulate	[17]
p-coumaric benzyl ester	[12]	cinnamyl isoferulate	
p-coumaric cinnamyl ester	[12]		
p-coumaric-methyl-butenyl ester	[12]		





Quinic acid: R_1=R_2=R_3	Caffeoyl(caffeic acid)		
	R_1	R_2	R_3
Chlorogenic acid	Caffeoyl	H	H
4,5-dicaffeoylquinic acid	H	Caffeoyl	Caffeoyl
4,5-dicaffeoylquinic acid	Caffeoyl	H	Caffeoyl
3,4,5-tri-caffeoylquinic acid	Caffeoyl	Caffeoyl	Caffeoyl

图 2　蜂胶中的绿原酸类化合物基本骨架

Fig 2　The basic skeleton of chlorogenic acids in propolis

表 3　蜂胶中的绿原酸类化合物

Tab 3　Chlorogenic acid derivatives in propolis

化学名称	参考文献
3,4-dicaffeoylquinic acid	[30,31]
3,5-dicaffeoylquinic acid	[30,31]
3-caffeoylquinic acid	[30,31]
4,5-dicaffeoylquinic acid	[30,31]
4-caffeoylquinic acid	[30,31]
4-feruoylquinic acid	[31]
5-caffeoylquinic acid	[30,31]
5-ferruoyl quinic acids	[31]
dicaffeoyl quinic acid	[10,32]
mono-caffeoylquinic acid	[32]
tricaffeoyl quinic acid	[10]
3,4,5-tri-caffeoylquinic acid	[33]

4　其他酚酸类衍生物

随着研究的不断深入，人们还从蜂胶中发现了许多复杂的酚酸类衍生物，见表 4。

表 4　蜂胶中的复杂酚酸类化合物

Tab 4　Complex phenolic acid derivatives in propolis

化学名称	参考文献
6-(2-carboxyethenyl)-2,2-dimethyl-2H-1-benzopyran	[9]
6-propenoic-2,2-dimethyl-8-prenyl-2H-1-benzopyran acid	[34]
8-(methyl-butanechromane)-6-propenoic acid	[16]
methyl3-[4-hydroxy-3-(3-methyl-2-butenyl)phenyl]-2-(*E*)-propenoate	[20]
1,3-diferuloyl-2-acetylglycerol	[5]
1-feruloyl-3p-coumaroyl-2-acetylglycerol	[5]
2,2-dimethyl-6-carboxyethenyl-2H-1-benzopyran	[13]
2,2-dimethyl-6-carboxyethenyl-8-prenyl-2H-1-benzopyran	[22]
2,2-dimethyl-6-carboxyethnyl-2H-1-benzopyran	[34]
2,2-dimethyl-8-prenylchromene	[14]
3-hydroxy-2,2-dimethyl-8-prenylchromane-6-propenoic acid	[16]
2,2-dimethyl-8-prenylchromene-6-propenoic acid	[16]
2,2-dimethylchromene-6-propenoic acid	[16]

5　结语

蜂胶的化学成分由蜜蜂采集的胶源植物决定，不同来源的蜂胶中酚酸类化合物的种类及含量差异显著。目前蜂胶质量主要以总黄酮含量高低为衡量指标，而酚酸类化合物在蜂胶质量控制方面的作用还未引起足够重视[35]。

迄今为止，绿原酸类化合物仅在巴西蜂胶中发现，是否其他类型蜂胶中也含有绿原酸需进一步研究证实。这方面的研究不仅能为蜂胶药理活性的开发提供基础，而且也能为蜂胶植物源的分类提供依据。

目前，蜂胶产品的研究开发主要针对其中的类黄酮化合物[36]，而蜂胶中还含有大量的酚酸类化合物及萜类化合物[37]。因此，对蜂胶中不同类型化合物进行提取、分离以及药理活性的深入研究，将为蜂胶的深入研究开发奠定基础。

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