鳞毛蕨属植物化学成分研究进展

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摘要: 目的: 对鳞毛蕨属植物化学成分的研究进展进行综述。方法: 总结有关鳞毛蕨属植物化学成分的研究文献, 综述鳞毛蕨属植物所含化学成分的种类、数量、结构、提取分离方法及结构鉴定。结果: 到目前为止已从鳞毛蕨属植物中分离出间苯三酚类化合物 58 种, 萜类化合物 13 种, 黄酮类化合物 4 种, 而且该属植物具有多种生理活性。结论: 我国鳞毛蕨属植物资源丰富, 应将化学成分的研究与药理活性的研究紧密结合, 从而更好地开发利用该属的植物资源。

关键词: 鳞毛蕨属; 化学成分; 粗茎鳞毛蕨
中图分类号: R284.1 **文献标识码**: A **文章编号**: 1005-9903(2003)03-0050-06

Progress in Chemical Constituents of Genus *Dryopteris*

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Abstract: Objective: To review the chemical studies progress of genus *Dryopteris*. Methods: To review the types of compounds, and their structures, isolation and identification from the reference. Results: 58 Phloroglucinol derivatives, 13 terpenoids and 4 flavonoids were isolated and identified from plants of genus *Dryopteris*. Conclusion: The resources of genus *Dryopteris* are very abundant in China. To full use of this resource, the chemical studies should be closely combined with pharmacological screening.

Key words: Genus *Dryopteris*; Chemical components; crassirhizoma

鳞毛蕨科(*Dryopteridaceae*)的鳞毛蕨属(*Dryopteris*)植物, 在全世界有 450 余种, 我国就有 300 余种之多, 药用的有 21 种[1], 分布全国各地。该属植物含有多种间苯三酚类化合物, 且有多种生理活性, 一直被各国药学和化学工作者所关注, 尤其近来日本学者又从 *Dryopteris crassirhizoma* 中分出了具有抗 HIV 活性的黄酮类化合物, 使该属植物具有更大的研究和开发价值。本文综述了该属植物的化学成分研究概况, 为进一步开发利用该属植物资源提供参考。

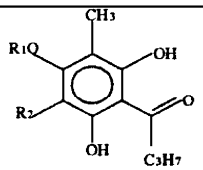
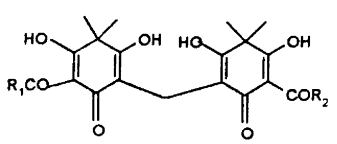
1 化学成分种类

迄今为止从鳞毛蕨属植物中分得了多种类型的化学成分, 其中主要有间苯三酚类、萜类以及黄酮类等。

1.1 间苯三酚类 经总结到目前为止已从该属植物中分离得到 58 种间苯三酚类化合物, 其中单环化合物 2 个(编号为 1~ 2), 双环化合物 32 个(编号为 3~ 34), 三环化合物 15 个(编号为 35~ 48), 四环化合物 4 个(编号为 49~ 52), 五环化合物 1 个(编号为 53), 六环化合物 2 个(编号为 54~ 55), 含倍半萜取代的特殊间苯三酚化合物 3 个(编号为 56~ 58), 其名称、结构、植物来源及文献见表 1。

1.2 萜类 到目前为止已从该属植物中分离得到 13 种萜类化合物, 其中倍半萜 1 个(编号为 59), 五环三萜 12 个(编号为 60~ 71), 其名称、结构、植物来源及文献见表 1。

表 1 鳞毛蕨属植物化学成分名称、结构、植物来源及文献

编号	化合物名称和结构、植物来源[文献]
	
1	aspidinol R_1= CH_3 R_2= H Dryopteris dilatata [4]
2	dimethylphlorobutyrophenone R_1= H R_2= CH_3 D. abbreviata [5]
	

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续表 1

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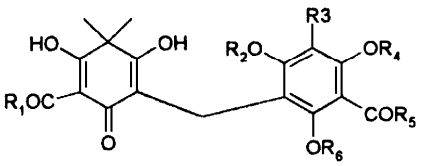
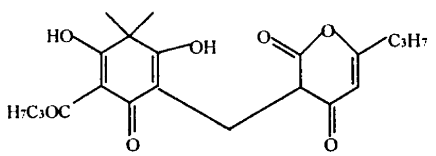
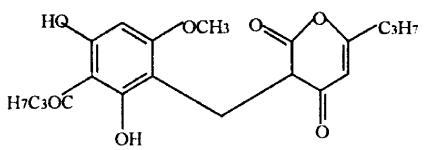
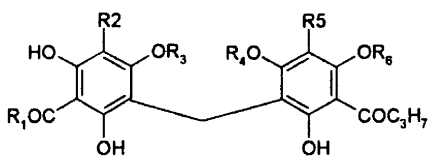
编号	化合物名称和结构、植物来源[文献]
3	albaspidin BB R_1= R_2= C_3H_7 D. villarii; D. patula; D. aitoniana; D. spinulosa; D. chrysocome; D. assimilis [6~10]
4	albaspidin PB R_1= C_2H_5 R_2= C_3H_7 D. chrysocome; D. villarii [6, 9]
5	albaspidin PP R_1= R_2= C_2H_5 D. chrysocome; D. villarii [6, 9]
6	albaspidin AB R_1= CH_3 R_2= C_3H_7 D. chrysocome; D. villarii [6, 9]
7	albaspidin AP R_1= CH_3 R_2= C_2H_5 D. chrysocome; D. villarii [6, 9]
8	albaspidin AA R_1= R_2= CH_3 D. patula; D. villarii [6, 7] D. crassirhizoma [11]
	
9	aspidin BB R_1= R_5= C_3H_7 R_2= R_6= H R_3= R_4= CH_3 D. assimilis; D. intermedia; D. patula [4, 7, 10] D. dilatata; D. gymnosora; D. fragrans [12~14]
10	aspidin AB R_1= R_3= R_4= CH_3 R_2= R_6= H R_5= C_3H_7 D. intermedia; D. fragrans [4, 10, 14] D. crassirhizoma [15]
11	aspidin PB R_1= C_2H_5 R_2= R_6= H R_3= R_4= CH_3 R_5= C_3H_7 D. fragrans [14, 16]
12	aspidin AA R_1= R_3= R_4= R_5= CH_3 R_2= R_6= H D. gymnosora [13]
13	para-aspidin BB R_1= R_5= C_3H_7 R_4= R_6= H R_2= R_3= CH_3 D. campyloptera [4]
14	para-aspidin AA R_1= R_2= R_3= R_5= CH_3 R_4= R_6= H D. arguta [6]
15	flavaspidic acid BB R_1= R_5= C_3H_7 R_2= R_4= R_6= H R_3= CH_3 D. abbreviata; D. patula; [7, 10] D. aitonianna; D. chrysocome [8, 9]
16	flavaspidic acid PB R_1= C_2H_5 R_2= R_4= R_6= H R_3= CH_3 R_5= C_3H_7 D. abbreviata [5, 10]
17	flavaspidic acid AB R_1= R_3= CH_3 R_2= R_4= R_6= H R_5= C_3H_7 D. abbreviata [5, 10]

续表 1

表 1 鳞毛蕨属植物化学成分名称、结构、植物来源及文献

编号	化合物名称和结构、植物来源[文献]
	D. paralloegramme; D. crassirhizoma [7, 15]
18	lavaspidic acid AP R_1= R_3= CH_3 R_2= R_4= R_6= H R_5= C_2H_5 D. goldiana [4]
19	norflavaspidic acid AB R_1= CH_3 R_2= R_3= R_4= R_6= H R_5= C_3H_7 D. dickinsii [17]
20	desaspidin BB R_1= R_5= C_3H_7 R_2= CH_3 R_3= R_4= R_6= H D. assimilis; D. patula [4, 7, 10]
21	desaspidin AB R_1= R_2= CH_3 R_3= R_4= R_6= H R_5= C_3H_7 D. arguta [6]
22	desaspidin PB R_1= C_2H_5 R_2= CH_3 R_3= R_4= R_6= H R_5= C_3H_7 D. arguta [6]
23	desaspidin AP R_1= R_2= CH_3 R_3= R_4= R_6= H R_5= C_2H_5 D. arguta [6]
24	desaspidin AA R_1= R_2= R_5= CH_3 R_3= R_4= R_6= H D. arguta [6]
	
25	phloropyron D. assimilis; D. campylopter [4, 10]
	
26	phloraspyron D. austriaca [18]
	
27	hloraspidinol BB R_1= C_3H_7 R_2= R_3= R_4= CH_3 R_5= R_6= H D. austriaca [18]
28	phloraspidin BB R_1= C_3H_7 R_2= R_4= CH_3 R_3= R_5= R_6= H D. marginalis [4, 10]
29	margaspidin BB R_1= C_3H_7 R_2= R_4= R_5= CH_3 R_3= R_6= H D. marginalis [4, 10]
30	aemulin BB R_1= C_3H_7 R_2= R_5= R_6= CH_3 R_3= R_4= H D. aemula; D. crassirhizoma [10, 15]
31	methylene-bis-aspidinol BB R_1= C_3H_7 R_6= H R_2= R_3= R_4= R_5= CH_3 D. marginalis [10]

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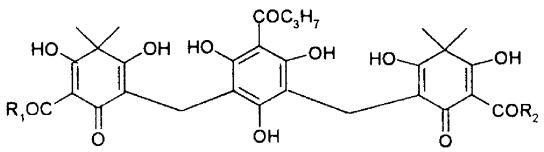
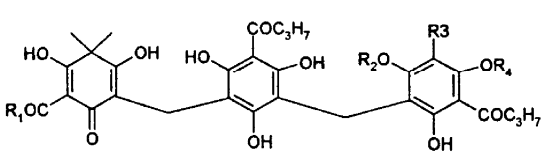
32	methylene-bis-desaspidinol BB R_1= C_3H_7 R_2= R_5= R_6= H R_3= R_4= CH_3 D. austriaca [18]
33	abbreviatin BB R_1= C_3H_7 R_2= R_5= CH_3 R_3= R_4= R_6= H D. abbreviata [5, 19]
34	abbreviatin PB R_1= C_2H_5 R_2= R_5= CH_3 R_3= R_4= R_6= H D. abbreviata [5]
	
35	filixic acid BBB R_1= R_2= C_3H_7 D. filix-mas; D. austriaca [10, 20~22] D. dickinsii; D. villarii [17, 22] D. crassirhizoma; D. chrysocome [9, 22]
36	filixic acid PBB R_1= C_2H_5 R_2= C_3H_7 D. filix-mas; D. chrysocome [9, 10, 20]
37	ilixic acid PBP R_1= R_2= C_2H_5 D. filix-mas; D. chrysocome [9, 10, 20]
38	filixic acid ABB R_1= CH_3 R_2= C_3H_7 D. arguta; D. dickinsii [10, 17] D. filix-mas; D. crassirhizoma [15, 20] D. chrysocome [9]
39	filixic acid ABP R_1= CH_3 R_2= C_2H_5 D. arguta; D. chrysocome [9, 10] D. filix-mas; D. crassirhizoma [15, 20]
40	filixic acid ABA R_1= R_2= CH_3 D. arguta; D. dickinsii [10, 17, 22] D. filix-mas; D. crassirhizoma [11, 20, 22] D. parallelogramme [7, 22]
	
41	tris-paraaspidin BBB R_1= C_3H_7 R_2= R_3= CH_3 R_4= H D. pallida; D. aitoniana [8, 10]
42	trisflavaspidic acid BBB R_1= C_3H_7 R_2= R_4= H R_3= CH_3 D. austriaca; D. aitoniana [8, 21]
43	tris-paraaspidin PBB R_1= C_2H_5 R_2= R_3= CH_3 R_4= H D. pallida [10]

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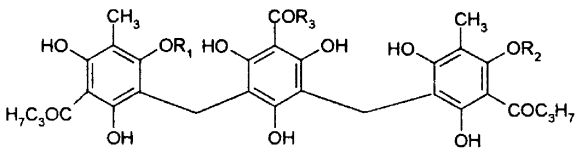
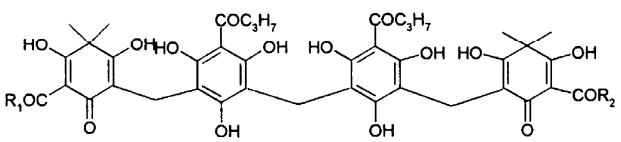
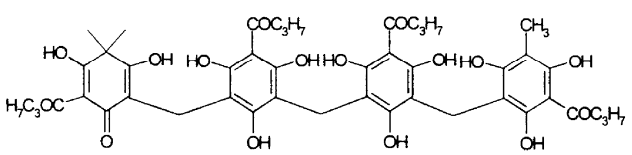
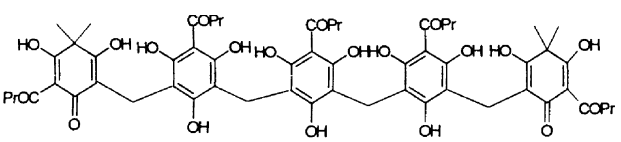
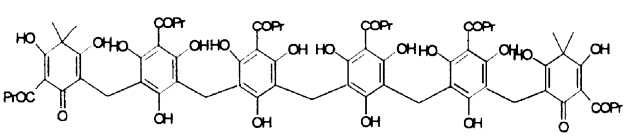
44	trisdesaspidin BBB R_1= C_3H_7 R_2= CH_3 R_3= R_4= H D. assimilis; D. austriaca [10, 21]
45	trisaspidin BBB R_1= C_3H_7 R_2= H R_3= R_4= CH_3 D. austriaca [21]
	
46	trisaemulin BBB R_1= R_2= CH_3 R_3= C_3H_7 D. aemula [13]
47	trisabbreviatin BBB R_1= R_2= H R_3= C_3H_7 D. abbreviata [8]
48	trisaemulin BAB R_1= R_2= R_3= CH_3 D. aemula [26]
	
49	dryocrassin ABBA R_1= R_2= CH_3 D. crassirhizoma; D. polylepis [10, 11, 22, 24]
50	dryocrassin ABBP R_1= CH_3 R_2= C_2H_5 D. crassirhizoma [10]
51	tetra-albaspidin BBBB R_1= R_2= C_3H_7 D. austriaca; D. aitoniana [22, 8]
	
52	tetraflavaspidic acid BBBB D. filix-max; D. aitoniana [8]
	
53	penta-albaspidin BBBBB D. aitoniana [8]
	

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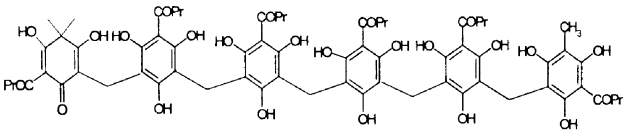
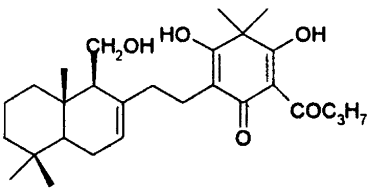
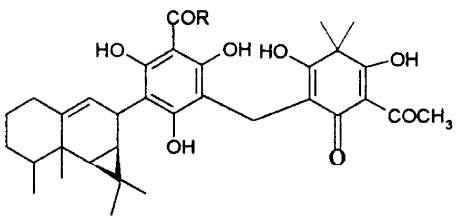
54 hexa-albaspidin BBBBBB D. aitoniana [8]



55 hexaflavaspidic acid BBBBBB D. aitoniana [8]

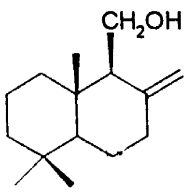


56 dryofragin d. fragrans [14, 16]

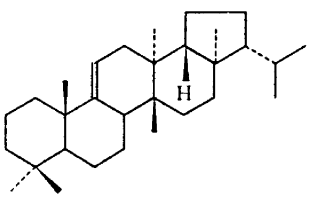


57 atrata-phloroglucinol A R= CH_3 D. atrata [25]

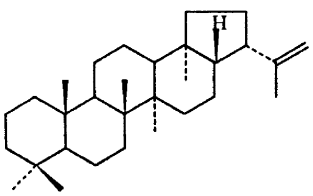
58 atrata-phloroglucinol B R= C_3H_7 D. atrata [25]



59 albicanol D. fragrans [14]



60 fern-9(11)-ene D. crassirhizoma [26]



61 hop-22(29)-ene D. crassirhizoma [26]

续表 1

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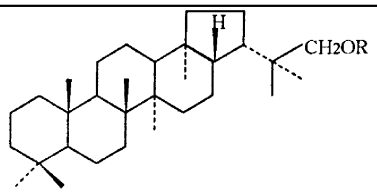
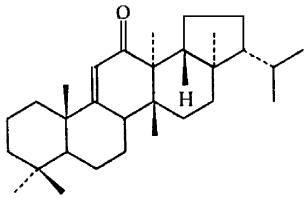
编号	化合物名称和结构、植物来源[文献]

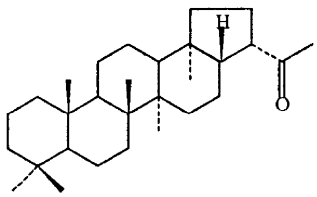


62 dryocrassyl acetate R= $COCH_3$ D. crassirhizoma [26]

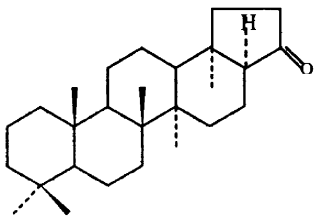
63 dryocrassol R= H D. crassirhizoma [26]



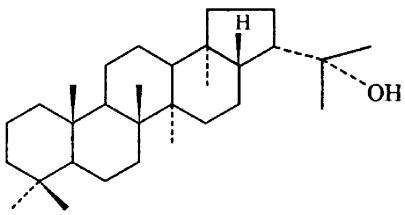
64 fern-9(11)-en-12-one D. crassirhizoma [26]



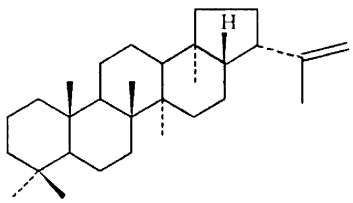
65 soadiantone D. crassirhizoma [26]



66 17 α H-trisnorhopanone D. crassirhizoma [26]



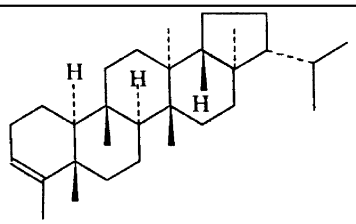
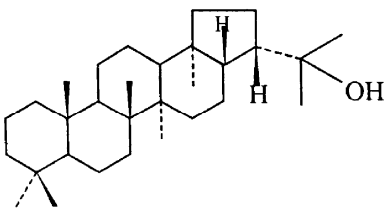
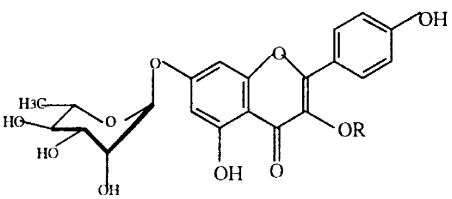
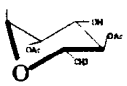
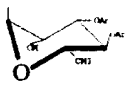
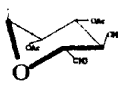
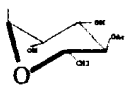
67 hydroxyhopane D. crassirhizoma [26]



68 diploptene D. crassirhizoma [26]

续表 1

表 1 鳞毛蕨属植物化学成分名称、结构、植物来源及文献

编号	化合物名称和结构、植物来源[文献]
69	filicene D. crassirhizoma [11] 
70	adiantone D. crassirhizoma [11, 26] 
71	diplopterol D. crassirhizoma [11] 
72	crassirhizomoside A R=  D. crassirhizoma [27]
73	crassirhizomoside B R=  D. crassirhizoma [27]
74	crassirhizomoside C R=  D. crassirhizoma [27]
75	sutchuenoside A R=  D. crassirhizoma [27]

1.3 黄酮类 到目前为止已从该属植物中分离得到 4 种黄酮苷类化合物(编号为 72~ 75),其名称、结构、植物来源及文献见表 1。

1.4 其他成分 除以上成分外,还从该属植物中分离得到了 β-谷甾醇(β-sitosterol)和菜油甾醇(campesterol)的混合物[2]、质体蓝素(plastocyanin)[3]等。

2 化学成分提取分离方法

早在 19 世纪初,由于该属植物具有良好的驱虫作用,就引起了药物化学工作者的广泛关注,并开始对其化学成分进行研究,当时人们用经典的氧化镁法提取分离间苯三酚粗品,并进行了一些初步化学结构的研究,70 年代 Penttila 和 Widen 等人作过综述[28,29]。到 80 年代,关于该属植物化学成分的研究有了很大突破,对于间苯三酚类成分的分离,抛弃了经典的氧化镁法,采用不同 pH 值缓冲液处理后的硅胶进行柱层析,分离得到了多种间苯三酚类化合物[12],于此同时对该属植物其他成分的研究也已开始,从粗茎鳞毛蕨的正己烷提取物中,经硅胶柱层析,正己烷—苯—乙醚梯度洗脱,得到了多个五环三萜类化合物[2]。90 年代后,随着科学技术的发展和实验条件的改善,从常规柱层析分离方法发展到了用半制备型和制备型反相高效液相色谱法分离,不仅可得到间苯三酚类化合物,还分离出了多个黄酮类化合物[8]。

3 化学成分结构鉴定

80 年代以前,间苯三酚类成分的结构鉴定主要依靠质谱和氢谱[6,7,12,19],90 年代以来,随着核磁技术的发展,碳谱及二维谱也得到了应用[8],使间苯三酚类成分的结构鉴定更准确、方便、快捷。

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