棘豆属植物化学成分研究概况*

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摘 要 本文概述了所研究过的二十余种棘豆属植物的化学成分,主要对其中的黄酮类、三萜皂甙类和生物碱类成分进行了归纳总结。

关键词 棘豆;黄酮类;三萜皂甙类;生物碱类

豆科(Leguminosae)棘豆属植物,全世界约300余种,主要分布在北半球[1],在我国棘豆属植物约有150余种,分布于西北、华北、东北、西南等地[2]。棘豆属植物中许多种有毒性,牲畜采食后往往引起中毒乃至死亡,给畜牧业造成极大损失,关于其毒性成分及中毒机理,至今尚未准确查明,有文献报道认为棘豆属植物中含有毒性生物碱,如所含喹啉里西定类生物碱(Quinolizidine alkaloids),对实验动物中枢神经产生抑制、呼吸抑制或兴奋、致幻、流产和致畸等作用[3],所含吲哚里西定类生物碱(Indolizidine alkaloids)使哺乳动物组织细胞产生空泡变性[4];另有文献报道认为含硒过多,牲畜采食后,由硒引起中毒;还有报道认为与其所含毒性蛋白(蛋白质类溶血毒素)有关[5,6];以及以上三种成分综合作用之结果[7]。该属植物也有一定的药用价值,有十余种棘豆在藏药、蒙药等中有一定的使用[8]。

棘豆属植物的化学成分,自1929年由Couch从*O. lambertii*中分离得到生物碱类成分起,经过化学工作者长期艰苦的工作,已从二十余种棘豆属植物中分离得到110多种化学成分,其主要化学成分为黄酮类、三萜皂甙类和生物碱类化合物[9,10,11],还有少量的木脂素[12],有机脂肪酸、醇、醛、烷类等化合物[13],以及氨基酸[14]等。

1 棘豆属植物黄酮类成分研究概况

黄酮类成分为棘豆属植物的主要化学成分,以黄酮醇甙类化合物尤为突出,有关棘豆属植物中黄酮类成分的研究,早在七、八十年代,前苏联及加拿大学者已作过综述性的报道[1,9,15],在该属植物中黄酮类化合物甙元主要为Apigenin、Chrysin、Luteolin(flavones)[1],Kaempferol、Quercetin、Myrecetin、Rhamnetin、Isorhamnetin、Rhamnazin[9,15]、Rhamnocitrin(flavonols)[16],糖取代基有D-glucose、L-rhamnose、D-galacotose、L-arabinose、D-xylose,其黄酮甙均为氧甙。从棘豆属植物中分离得到的黄酮类及衍生物共52个,其中黄酮17个;黄酮醇33个;异黄酮1个(Isoliquiritigenin)[17];异黄烷1个(3′7-dihydroxy-2′4′-dimethoxy-isoflavane)[18]。除由上述7种黄酮醇甙元在3、7、3′、4′、5′位与糖基形成的黄酮甙以外,李平等从*O. ochrocephala*种子中分离得到1个5位甲氧基取代的黄酮醇甙:5-methoxy-7-hydroxy-3-O-galactoside-4′-glucoside(Compd. 49),以及还有一种色酮类化合物:4H-Pyran-4-one,3-hydroxy-2-methyl[19]。黄酮类化合物的基本骨架见下图。

2 棘豆属植物三萜皂甙类成分研究概况

1974年,前苏联学者Iriste等从*O. lanata*中首次分离得到三萜皂甙类成分,经水解后得到甙元Soyasapogenol B,从水解液中检出D-galacotose、D-glucose、L-arabinose、L-rhamnose和D-galacturonic acid,因受当时条件限制,未能确定其准确的分子结构[10]。从1987年至今,我国学者先后从*O. ochrocephala*、*O. glabra*、*O. bicolor*三种棘豆中分离得到近13种三萜皂甙类成分[20,26,32,33,34,35],其分子骨架为齐墩果烷型(the oleanene-type)和五环三萜环丙烷型(the cyclopropane)两种,其中齐墩果烷型11种,环丙烷型2种。孙荣奇等从*O. ochrocephala*总皂甙酸水解产物中分离得到两种三萜皂甙元,即Soyasapogenol B和olean-13(18)-ene-22α-chloro-3β,

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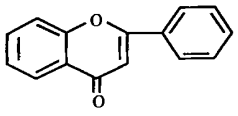
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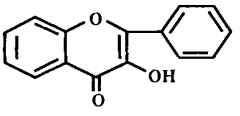
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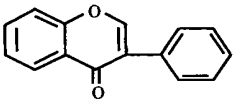
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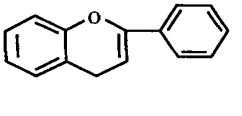
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表 1 棘豆属植物中的黄酮类化合物

Table 1 The flavonoids from Oxytropis species

编号 №	(类型)结构式 (Type) Structures	化合物名称 Names of compounds	植物来源 Natural sources	文献 Ref.
1	(A)5,7,4′-OH	Apigenin	*O. bicolor*	[20]
2	(A)5,4′-OH,7-O-β-D-glc	Apigenin 7-O-glucoside	*O. jordalii*	[1]
3	(A)5,4′-OH,7-O-β-D-glc(1→2)-β-D-glc	Apigenin 7-O-diglucoside	*O. jordalii*	[1]
4	(A)5,4′-OH,7-O-β-D-xyl(1→2)-β-D-glc	Apigenin 7-O-xylosylglucoside	*O. jordalii*	[1]
5	(A)5,4′-OH,7-O-α-L-rha(1→2)-β-D-glc	Apigenin 7-O-neohesperidoside	*O. varians*	[1]
6	(A)5,4′-OH,7-O-α-L-rha(1→6)-β-D-glc	Apigenin 7-O-rutinoside	*O. varians* *O. monticola*	[1]
7	(A)5,4′-OH,7-O-α-L-arb(1→6)-β-D-glc	Apigenin 7-O-arabinosylglucoside	*O. monticola*	[1]
8	(A)5,7-OH	Chrysin	*O. pseudoglandulosa*	[17]
9	(A)5,7,4′-OH,3′-OMe	Chrysoeriol		[1]
10	(A)5,4′-OH,3′-OMe,7-O-β-D-glc	Chrysoeriol 7-O-glucoside	*O. varian*, *O. monticola* *O. jordalii*	[1]
11	(A)5,4′-OH,3′-OMe,7-O-β-D-glc(1→2)-β-D-glc	Chrysoeriol 7-O-diglucoside	*O. monticola*	[1]
12	(A)5,4′-OH,3′-OMe,7-O-α-L-rha(1→6)-β-D-glc	Chrysoeriol 7-O-rutinoside	*O. monticola*	[1]
13	(A)5,7,3″,4′-OH,	Luteolin		[1]
14	(A)5,3″,4′-OH,7-O-β-D-glc	Luteolin 7-O-glucoside	*O. varians* *O. cusickii*	[1]
15	(A)5,3″,4′-OH,7-O-β-D-glc(1→6)-β-D-glc	Luteolin 7-O-diglucoside	*O. varians*, *O. jordalii* *O. monticola*	[1]
16	(A)5,3″,4′-OH,7-O-α-L-rha(1→6)-β-D-glc	Luteolin 7-O-rutinoside	*O. varian*	[1]
17	(A)5,7,4′-OH,3′-O-β-D-glc	Luteolin 3′-O-glucoside	*O. monticola*	[1]
18	(B)5,7,4′-OH	Kaempferol	O. thalassica	[21]
19	(B)5,7,4′-OH,3-O-β-D-glc	Astragalin	*O. lanata*	[22]
20	(B)5,4′-OH,7-O-α-L-rha	Kaempferol 7-O-rhamnoside	*O. glabra*	[23]
21	(B)5,7,4′-OH,3-O-β-D-glc(1→2)-β-D-glc	Kaempferol 3-O-diglucoside	*O. glabra*	[23]
22	(B)5,7,4′-OH,3-O-β-D-xyl(1→2)-β-D-glc	Kaempferol 3-O-xylosylglucoside	*O. cusickii*	[1]
23	(B)5,7,4′-OH,3-O-α-L-rha(1→6)-β-D-glc	Kaempferol 3-O-rutinoside	*O. glabra*	[24]
24	(B)5,4′-OH,7-O-α-L-rha(1→2)-β-D-glc	Kaempferol 7-O-glucorhamnoside	*O. komarovii*	[25]
25	(B)5,4′-OH,7-O-α-L-rha,3-O-α-L-rha(1→2)-β-D-glc	Kaempferol 3-O-glucorhamnoside-7-O-rhamnoside	*O. komarovii*	[25]
26	(B)5,4′-OH,3,7-O-β-D-glc	Kaempferol 3-O-glucoside-7-O-glucoside	*O. glabra*	[26]
27	(B)5,4′-OH,7-O-α-L-rha,3-O-α-L-rha(1→6)-β-D-gal	robinin	*O. varlakovii*	[27]
28	(B)5,7,4′-OH,3-O-β-D-glc(6″-O-acetyl)	Kaempferol 3-O-glucoside(6″-O-malonyl)	*O. deflexa*	[12]
29	(B)5,7,4′-OH,3-O-β-D-glc(6″-O-malonyl)	Kaempferol 3-O-glucoside(6″-O-malonyl)	*O. deflexa*	[12]
30	(B)5,7,3″,4′-OH	Quercetin	*O. thalassica*	[21]
31	(B)5,7,3″,4′-OH,3-O-β-D-glc	Quercetin 3-O-glucoside	*O. glabra*	[26]
32	(B)5,7,3″,4′-OH,3-O-β-D-glc	Isoquercitrin	*O. ochrocephala*	[30]
33	(B)5,7,3″,4′-OH,3-O-β-D-glc(1→2)-β-D-glc	Ruercetin 3-O-diglucoside	*O. cusickii*	[1]
34	(B)5,7,3″,4′-OH,3-O-α-L-rha(1→6)-β-D-glc	Quercetin 3-O-rutinoside	*O. strobilacea*	[28]
35	(B)5,7,3″,4′-OH,3-O-β-D-xyl(1→2)-β-D-glc	Quercetin 3-O-xylosylglucoside	*O. cusickii*	[1]
36	(B)5,3″,4′-OH,3,7-O-β-D-glc	Quercetin 3,7-O-diglucoside	*O. cusickii*	[1]
37	(B)5,3″,4′-OH,7-O-α-L-rha,3-O-β-D-glc(1→2)-β-D-glc	Oxymyrioside	*O. myriophylla*	[31]
38	(B)5,3″,4′-OH,7-O-α-L-rha,3-O-β-D-glc(6″-O-acetyl)(1→2)-β-D-glc	Acetyloxymyrioside	*O. myriophylla*	[31]
39	(B)5,3″,4′-OH,7-O-α-L-rha,3-O-β-D-glc(6″-O-coumaroyl)(1→2)-β-D-glc	Coumaroylisooxymyrioside	*O. myriophylla*	[31]
40	(B)5,3″,4′-OH,7-OMe	Rhamnetin	*O. strobilacea*	[28]
41	(B)5,7,4′-OH,3′-OMe	Isorhamnetin	*O. villosa*	[29]
42	(B)5,3″,4′-OH,7-OMe,3-O-β-D-glc	Rhamnetin 3-O-glucoside	*O. strobilacea*	[28]
43	(B)5,3″,4′-OH,7-OMe,3-O-β-D-gal	Rhamnetin 3-O-galactoside	*O. ochrocephala*	[19]
44	(B)5,7,4′-OH,3′-OMe,3-O-β-D-glc	Isorhamnetin 3-O-glucoside	*O. bicolor*	[20]
45	(B)5,4′-OH,7-OMe	Rhamnocitrin	*O. ochrocephala*	[30]
46	(B)5,4′-OH,7-OMe,3-O-β-D-glc	Rhamnocitrin 3-O-glucoside	*O. ochrocephala*	[30]
47	(B)5,4′-OH,7-OMe,3-O-β-D-gal	Rhamnocitrin 3-O-galactoside	*O. ochrocephala*	[16]
48	(B)5-OH,7-OMe,3-O-β-D-gal,4′-O-β-D-glc	Rhamnocitrin 3-O-galactoside-4′-O-glucoside	*O. ochrocephala*	[16]
49	(B)5-OMe,7-OH,3-O-β-D-gal,4′-O-β-D-glc	5-methoxy-7-hydroxy-3-O-galactoside-4′-O-glucoside	*O. ochrocephala*	[19]
50	(B)5,7,3″,4″,5′-OH,3-O-β-D-glc	Myricitin 3-O-glucoside	*O. glabra*	[26]
51	(C)3″,7-OH,2″,4′-OMe	3″,7-dihydroxy-2″,4′-dimethoxy-isoflavane	*O. glabra*	[18]
52	(D)4′-OH	Isoliquiritigenin	*O. pseudoglandulosa*	[17]

24-diol,并发现两种甙元的相对含量与盐酸浓度有关,进一步研究发现两种甙元在一定条件下可相互转化[33]。从 *O. bicolor* 中分离得到的三萜皂甙(Compd. 13)经盐酸水解得到甙元 3β,16β,25-trihydroxy-(20R,24S)-20,24-epoxy-9β,19-cylolanostane。从 *O. glabra* 的三萜皂甙成分经水解得甙元 Oxytrogeol、3β, 22β, 24-trihydroxyolean-12-en-oic acid、Soyasapogenol E、Soyasapogenol B[34]; Azukisapogenol[20]、Azukisapogenol methyl ester、Azukisapogenol amide[35]。三萜皂甙类化合物的基本骨架见下图。

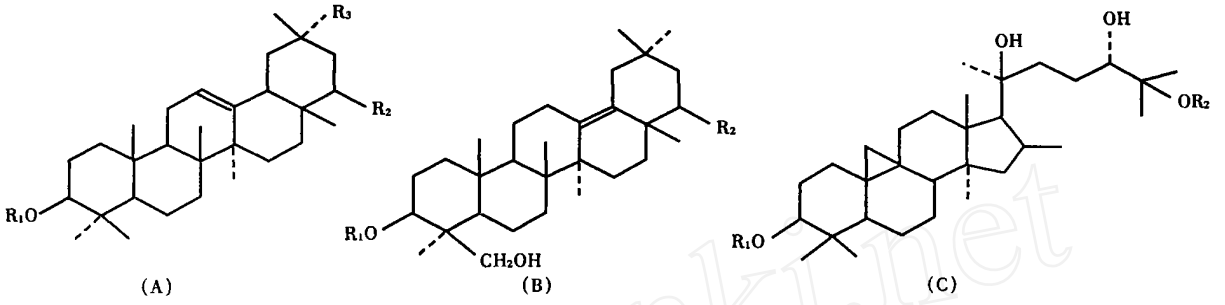

表 2 棘豆属植物中的三萜皂甙类化合物

Table 2 The triterpenoids from Oxytropis species

编号 №	类型 Type	取代基位置 Substituted position			化合物名称 Names of Compounds	植物来源 Natural sources	文献 Ref.
		R_1	R_2	R_3			
1	A	α-L-rha(1→3)-β-D-glc(1→6)-β-D-gluA	OH	CH_3	3-O-[α-L-rhamnopyranosyl-(1→3)-β-D-glucopyranosyl(1→6)-β-D-glucuronopyranosyl]soyasapogenol B	*O. glabra*	[26]
2	A	α-L-rha(1→2)-β-D-glc(1→4)-β-D-gluA	OH	CH_3	3-O-[α-L-rhamnopyranosyl-(1→2)-β-O-glucopyranosyl(1→4)-β-D-glucuronopyranosyl]soyasapogenol B	*O. ochrocephala* *O. glabra* *O. bicolor*	[36] [34] [20]
3	A	α-L-rha(1→2)-β-D-arb(1→4)-β-D-gluA	OH	CH_3	3-O-[α-L-rhamnopyranosyl-(1→2)-β-D-arabinopyranosyl(1→4)-β-D-glucuronopyranosyl]soyasapogenol B	*O. ochrocephala*	[36]
4	A	β-D-glc(1→2)-β-D-gluA	H	COOH	3-O-[β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]azukisapogenol	*O. bicolor*	[20]
5	A	β-D-glc(1→2)-β-D-gluA	OH	CH_3	3-O-[β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]soyasapogenol B	*O. ochrocephala*	[33]
6	A	β-D-glc(1→2)-β-D-gluA	H	CO_2CH_3	3-O-[β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]azukisapogenol methyl ester	*O. glabra*	[35]
7	A	β-D-glc(1→2)-β-D-gluA	H	$CONH_2$	3-O-[β-D-glucopyranosyl(1→2)-β-D-glucuronopyranosyl]azukisapogenol amide	*O. glabra*	[35]
8	A	α-L-rha(1→2)-β-D-glc(1→4)-β-D-gluA	OH	CH_2OH	Oxytrogenol, 3-O-α-L-rhamnopyranosyl(1→2)-β-D-glucopopyranosyl(1→4)-β-D-glucuronopyanoside	*O. glabra*	[34]
9	A	α-L-rha(1→2)-β-D-glc(1→4)-β-D-gluA	OH	COOH	3β,22β,24-trihydroxyolean-12-en-oic acid, 3-O-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl(1→4)-β-D-glucuronopyranoside	*O. glabra*	[34]
10	A	α-L-rha(1→2)-β-D-glc(1→4)-β-D-gluA	O	CH_3	Soyasapogenol E,3-O-α-L-rhamnopyranosyl(1→2)-β-D-glucopyranosyl(1→4)-β-D-glucuronopyranoside	*O. glabra*	[34]
11	A	[β-D-glc(1→4)][α-L-rha(1→2)-β-D-glc(1→4)]-β-D-gluA	OH	CH_3	Soyasapogenol E, 3-O-[β-D-glucopyranosyl(1→2)][α-L-rhamnopyanosyl(1→2)-β-D-glucopyranosyl(1→4)]-β-D-glucuronopyranoside	*O. glabra*	[34]
12	B	H	Cl		olean-13(18)-ene-22α-chloro-3β,24-diol	*O. ochrocephala*	[33]
13	C	β-D-glc(1→2)-β-D-glc	H		3-O-[β-D-glucopyranosyl(1→2)-β-D-glucopyranosyl](20S,24S)-9,19-cycloanostane-3,16,20,24,25-pentaol	*O. bicolor*	[20]
14	C	β-D-glc(1→2)-β-D-glc	α-L-rha		3-O-[β-D-glucopyranosyl(1→2)-β-D-glucopyranosyl]-25-O-α-L-rhamnopyranosyl-(20S,24S)-3β,16,20,24,25-pentahydroxy-9,19-cycloanostane	O. bicolor	[32]

3 棘豆属植物生物碱成分研究概况

有关棘豆属植物中生物碱类成分的研究,起始于其毒性活性成分的发现,1929 年 Couch 由 *O. lambertii* 中分离得到一种多羟基含氮类化合物[37],这是最早报道由棘豆属植物中分离出的生物碱成分,受当时条件的限制未能确定其结构。至二十世纪九十年代末,从该属植物中分离得到 20 种生物碱类成分,其中喹啶里西定类(quinolizidine akaliods)8 种,吲哚里西定类(Indolizidine alkaloids)1 种,喹啉类(quinoline alkaloids)1 种,有机酰胺类 8 种,其它类 2 种。

表 3 棘豆属植物中的生物碱类成分

Table 3 The alkaloids from Oxytropis species

生物碱类结构类型 Types of alkaloids in structure	化合物名称 Names of compounds	植物来源 Natural sources	文献 Ref.
喹啶里西定类	Anagyrine, thermopsine, sparteine, lupanine, N-formyl-cytisine, 13-hydroxysparteine, N-methyl-cytisine, baptifoline	*O. ochrocephala*	[40] [46]
		O. glabra	[39]
吲哚里西定类	Harmine(banisterine)	*O. plabra*	[44]
喹啉类	Dictamnine	*O. glabra*	[39]
有机酰胺类	(-)-N-nicotionyl-2-hydroxyphenethylamine	*O. puberula*	[41]
		O. muricata	[44]
	(-)-N-benzoyl-2-phenyl-2-hydroxyethylamine	*O. trichophysa*	[42]
		O. muricata	[44]
	N-benzoylphenylaminomethylcarbinol Muricatide(N-benzoyl-2-acetoxyphenethylamine)	*O. muricata*	[38]
	Trichophidine (2-O-benzoyloxy-(β)-phenylethylamine)	*O. trichophysa*	[43]
	(-)-(R)-N-benzoyl-2-phenyl-2-hydroxyethylamine (+)-(R)-O-benzoyl-2-phenyl-2-hydroxyethylamine Cinnamoyl-β-phenylethylamine	*O. pseudoglandulosa*	[36]
其它含氮类化合物	Admidopurine	*O. glabra*	[39]
	Oxytriphine	*O. trichophysa*	[40]

4 棘豆属植物其它类化学成分的研究概况

李玉林等从 *O. deflexa* 中分离得到木脂素类化合物 Schisantherin A[12];梁斌等从 *O. kansuensis* 的精油中得到 Cis-farnesol、lauric acid、myristic acid、12-methylmyristic acid、6,10,14,-trimethyl-2-pentadecanon、nonadienoic aldehyde、palmitic acid[13];于荣敏等从 *O. glabra* 中得到 1,1,1,7,7,7-hexachloro-2,6-dihydroxy-heptan-4-one、2,2,2-trichloracetaldehyde hemiethyl acetal、daucosterol、tetratriacontane[45];Fedorova 等对棘豆属植物的氨基酸成分进行了分析,其中含 Lys, His, Glu, Thr, Ala, Tyr, Val, Met 和 Phe[14]。

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A SURVEY OF THE STUDIES ON CHEMICAL CONSTITUENTS OF OXYTROPIS SPECIES

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Abstract This paper reviews about 20 species of naturally occurring Oxytropis on the chemical Components. Flavonoids, triterpenoids and alkaloids are mainly listed.

Key words Oxytropis; flavonoids; triterpenoids; alkaloids