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云南牛蒡子的化学成分研究*

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摘 要: 从牛蒡子中分离得到6个化合物,分别鉴定为:β-谷甾醇(1),胡萝卜甙(2),牛蒡子甙(3),牛蒡酚A(4),牛蒡酚B(5),松脂醇(6).化合物6为首次从该种植物中分离得到.

关键词: 牛蒡子;牛蒡子甙;牛蒡酚
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牛蒡子(arctium lappaol.)是菊科(composite)牛蒡属植物牛蒡的种子.在我国此属分布在云南,四川等地[1],在民间牛蒡子常称为,"大力子"其性辛、苦,寒,具有归肺、胃经,疏散风热,宣肺透疹,解毒利咽之功效,治疗风热感冒,咳嗽痰多,麻疹,风疹,咽喉肿痛,痄腮丹毒,痈肿疮毒等多种疾病[2].药理研究表明其提取物具有抗肿瘤活性[3].笔者对牛蒡子的化学成分做了较为系统的研究,从中分得6个化合物.根据理化性质和波谱分析,分别鉴定为:β-谷甾醇(β-sitosterol),胡萝卜甙(daucosterol),牛蒡子甙(arctiin),牛蒡酚A(lappaol A),牛蒡酚B(lappaol B),松脂醇(pinoresinol).其中化合物6为首次从该种植物中分离得到.

1 试验部分

1.1 试验仪器和材料

熔点仪用Kofler显微熔点仪测定(温度未校正);旋光由JASCO-20旋光仪测定;红外光谱(IR)用KBr压片法由Bio-Rad FTS-135红外分光光度仪测定;紫外光谱(UV)用UV-210A紫外分光光度仪测定;质谱(MS)用VG Auto spec-3000型质谱仪测定,采用FAB技术测定;核磁共振谱(^{1}H NMR,^{13}C NMR,DEPT)用Bruker DRX-500超导核磁仪测定,TMS内标,化学位移δ,单位ppm,偶合常数J,单位Hz;薄层层析硅胶和柱层析硅胶均为青岛海洋化工厂产品.

1.2 提取和分离

牛蒡子(10kg,产地:云南),购于昆明菊花村药材市场,粉碎(100目),用90%甲醇回流热提(3×4小时),减压浓缩回收溶剂得甲醇浸膏(2kg).浸膏溶于水(2500ml),分别用乙酸乙酯和正丁醇萃取三次(3x2000ml),得乙酸乙酯部分(273g)和正丁醇部分(735g).取乙酸乙酯部分,甲醇溶解,300g硅胶拌样,进行硅胶柱层析共分得5个化合物,经各种波谱数据以及参考文献对照的方法鉴定化合物的结构.

2 结构鉴定

β-谷甾醇(1):白色针状结晶,易溶于氯仿,mp138-140c^0. mp及Rf值与标准品β-谷甾醇一致,鉴定为β-谷甾醇.

胡萝卜苷(2):白色块状结晶,易溶于甲醇,mp288-289c^0. mp及Rf值与标准样品对照一致,推断为胡萝卜甙.

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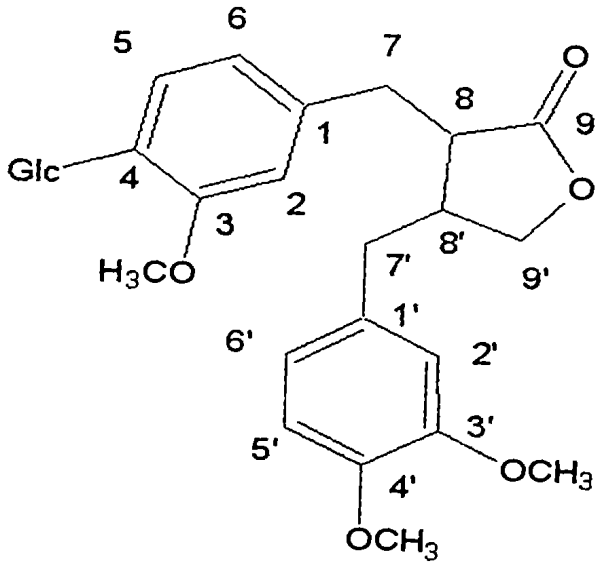
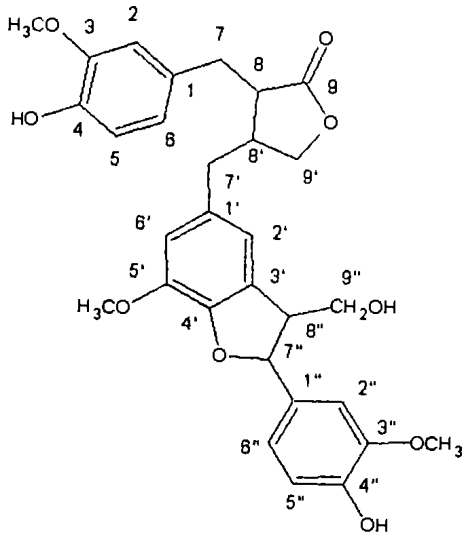
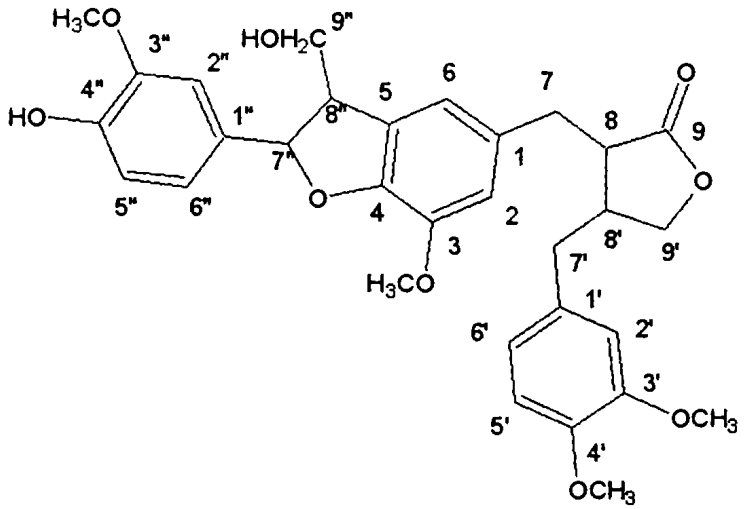


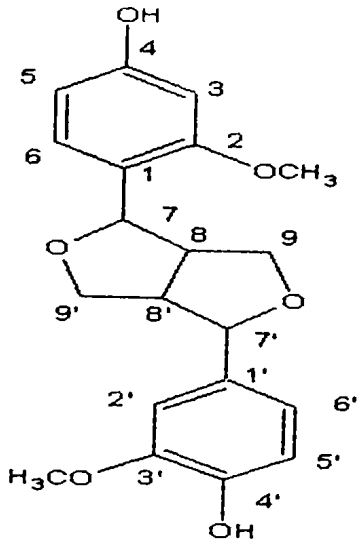
化合物 3:牛蒡甙



化合物 4:牛蒡酚 A



化合物 5:牛蒡酚 B



化合物 6:松脂醇

图 1　牛蒡子中几种化合物的结构

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表 1 化合物 3－5 的 ^{1}H－NMR 数据(in $CDCl_3$)

^{1}H－NMR	3	4	5	6
2	6.47(d, 2)	6.49 (d,2)	6.65(s)	6.86(s)
5	6.88(d,8)	6.97(d,8)		6.89(d,8)
6	6.53(dd,8,2)	6.55(dd,8,2)	6.25(d,2)	6.81(dd,8,2)
7	2.83(m)	2.89(m)	2.92(dd,14,5) 2.89(dd,14,7)	4.70(d,13)
8	2.51(m)	2.56(m)	2.52(m)	3.20(m)
9				3.80(m)
2'	6.64(s)	6.34(d,2)	6.63(d,2)	6.86(s)
5'	6.72(d,8)		6.82(d,8)	6.89(d,8)
6'	6.60(d,8)	6.46(d,2)	6.60(dd,8,2)	6.81(dd,8,2)
7'	2.62(dd,14,7) 2.45(dd, 14,7)	2.59(dd,14,7) 2.66(dd,14,6)	2.50(dd,14,8) 2.64(dd,14,6)	4.70(d,13)
8'	2.56(m)	2.48(m)	2.50(m)	3.20(m)
9'	4.07－4.09(m)	3.93(dd,9,7) 4.23(dd,9,8)	3.88(dd,9,7) 4.14(dd,9,7)	3.80(m)
2''		6.93(d,2)	6.94(d,2)	
5''		6.88(d,8)	6.88(d,8)	
6''		6.89(dd,8,2)	6.89(dd,8,2)	
7''		5.47(d,7)	5.48(d,7)	
8''		3.54(dd,13,6)	3.52(dd,13,6)	
9''		3.93－3.83(m)	3.90－3.82(m)	
OCH_3	3.85	3.84	3.85	3.87
	3.83	3.83	3.84	3.86
	3.84	3.80	3.84	
			3.82	

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表 2 化合物 3-5 的 ^{13}C-NMR 数据(in $CDCl_3$)

^{13}C-NMR	3	4	5	6
1	132.7	131.2	128.2	133.2
2	113.0	112.5	111.2	108.9
3	149.5	144.4	146.9	147.1
4	147.5	146.7	146.7	145.8
5	111.0	119.1	133.0	114.5
6	120.8	121.9	114.3	119.4
7	38.3	34.6	34.6	86.2
8	41.1	46.6	46.6	54.6
9	178.9	178.7	178.7	72.1
1'	130.1	128.3	130.8	133.3
2'	112.0	111.7	113.1	109.0
3'	149.1	132.9	144.0	147.2
4'	145.2	145.5	145.4	145.7
5'	116.0	146.6	119.1	114.5
6'	122.3	114.2	121.2	119.4
7'	34.5	38.4	38.4	86.3
8'	46.8	41.1	41.1	54.6
9'	179.5	71.3	71.3	72.1
1''		129.5	129.8	
2''		108.8	108.8	
3''		146.5	146.8	
4''		144.1	144.3	
5''		114.3	114.6	
6''		116.4	117.1	
7''		87.9	87.9	
8''		53.5	53.5	
9''		63.9	63.9	
OCH3	56.3	56.7	56.7	56.4
	56.2	56.6	56.6	56.4
	56.2	56.4	56.5	
			56.4	
Glc-1	101.6			
Glc-2	73.2			
Glc-3	76.3			
Glc-4	69.3			
Glc-5	76.1			
Glc-6	61.1			

牛蒡子甙(3):无色块状结晶,易溶于氯仿.$[\alpha]D^{23}$ = -48.6(MeOH, c 0.1). UVλ_{max}^{EtOH}(logε)nm:279(3.3),230(3.7),280(3.2). IR(KBr)cm^{-1}:3400(OH),1760(C=O),1600(C=C). ^1H-NMR(见表 1),^{13}C-NMR(见表 2). EI-MSm/z(%):535(M+,50),372(90), 151(95),137(100).以上波谱数据与参考文献[3]相符.因此,该化合物推断为牛蒡子甙(arctiin).

牛蒡酚 A(4):白色无定性粉末,易溶于仿.$[\alpha]D^{20}$ = -17.2°(MeOH, C 0.1). UVλ_{max}^{MeOH}(logε)nm:235(3.0),280(3.1). IR(KBr)cm^{-1}:3400(OH),1765(C=O),1600(C=C). ^1H-NMR(见表 1),^{13}C-NMR(见表 2). EI-MSm/z(%):536(M^+,50),298(10),137(70).根据文献[4]数据,确定该化合物为牛蒡酚 A.

牛蒡酚 B(5):白色无定性粉末,易溶于仿.$[\alpha]D^{20}$ = -19.2°(MeOH, C 0.1). UV$\lambda_{max\,MeOH}$(logε)nm:233(3.0),282(3.1). IR(KBr)cm^{-1}:3400(OH),1765(C=O),1600(C=C). ^1H-NMR(见表 1). ^{13}C-NMR(见表 2). EI-MSm/z(%):550(M^+,55),298(10),177(15),151(45).根据文献[5]数据,确定该化合物为牛蒡酚 B.

松脂醇(6):无色结晶($CHCl_3$). ^1H-NMR(见表 1),^{13}C-NMR(见表 2). EI-MSm/z(%):358M^+.根据文献[6]数据,确定该化合物为松脂醇.

3 结论

通过对云南牛蒡子的化学成分分析研究,掌握了云南牛蒡子大致化学成分,为云南牛蒡子的运用开发提供了一定的科学依据.

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Study on Compositions of Arctium Lappa

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Abstract: From The seed of Arctium lappa, six compounds were isolated. On the basis of the spectrospic analysis, the compounds were identified as: β - sitosterol(1), daucosterol(2), arctiin(3), lappaolA (4), lappaolB(5), pinoresinol (6).

Key words: Arctiumlappaol; Arctiin; Lappaol

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Formation and Property Studies of $Al_{87}Ce_3Ni_{8.5}Mn_{1.5}$ Nanophase Amorphous Composites

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Abstract: The higher mechanical strength $Al_{87}Ce_3Ni_{8.5}Mn_{1.5}$ nanophase amorphous composites have been produced with two methods. The first nanophase amorphous composites directly are produced by melt spinning without any further heat treatment. The approach taken for the second nanophase amorphous composites is to first obtain wholly amorphous material through melt spinning, followed by isothermal annealing at different temperatures. The formative condition, the microstructure. the particle size, the volume fraction of α - Al phase and microhardness of nanophase amorphous composites have been investigated and compared by X - ray diffractometry (XRD), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). The microstructure of composites produced by the second method is more homogeneous than former. The microhardness of composites produced the second method is higher than the former. The control of experiment conditions is easer in the latter.

Key words: rapid solidification; Al - Ce - Ni - Mn amorphous alloy; nanophase amorphous compoites