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三分三的化学成分研究

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摘　要:对三分三(*Auisodus acutangulus* C..r. Wuet C..Chen)非生物碱成分进行研究。利用生物碱的酸碱性采用多次萃取的方法除去生物碱成分,运用柱层析等分离纯化方法从三分三的非生物碱成分中,分离并鉴定出5个化合物,分别是东莨菪素(**1**),东莨菪苷(**2**),皮契荔枝苷(**3**),β-谷甾醇(**4**),胡萝卜苷(**5**),5个化合物均为首次从该植物中分离得到。

关键词:三分三;化学成分;香豆素
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Study on the Chemical Constituentsof *Auisodus acutangulus*

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Abstract:Five compounds were isolated from the ethanol extract of *Auisodus acutangulus* C. Y. Wu et C. Chen. They were identified asscopoletin(**1**),scopolin(**2**),fabiatrin(**3**),β-sitisterol(**4**),and dancosterol(**5**),by using spectroscopic methods. All these compounds were isolated from this species for the first time.

Key words:*Auisodus acutangulus*;chemical constituents;coumarin

三分三(*Auisodus acutangulus* C..r. Wuet C..Chen)又名大搜山虎、山野烟、野烟、山茄子、野旱烟,多年生草本,分布于云南、四川等地。三分三具有麻醉镇痛的功效,临床广泛用于治疗胃痛、骨折、风湿痛、跌打损伤。通过文献检索,对三分三的报道主要是关于生物碱成分的药理作用,而对其化学成分报道甚少[1],因此我们对非生物碱成分作了一定的研究,从中分离到5个化合物。根据理化性质和图谱特征鉴定为东莨菪素(**1**),东莨菪苷(**2**),皮契荔枝苷(**3**),β-谷甾醇(**4**),胡萝卜苷(**5**),5个化合物均为首次从该植物中分离得到。

1　仪器与材料

Bruker DRX-500 核磁共振波谱仪,Bruker AV-400 核磁共振波谱仪,Bruker AVANCE III 600 核磁共振波谱仪,Bruker AVANCE III 400 核磁共振波谱仪,TMS 作为内标;ESIMS 用 Bruker HCT Esquire 3000 离子阱质谱仪;Waters 600 高效液相色谱仪;柱层析用硅胶 200~300 目,GF_{254} TLC 板(青岛海洋化工);Buchi R210 旋转蒸发仪。石油醚、丙酮、氯仿、甲醇、乙醇等均为工业纯试剂。

三分三 *Auisodus Acutangulus* 根由云南植物药业有限公司采购部采购自云南省大理州宾川县药材市场,由中国科院昆明植物研究所邓德山鉴定,标本收藏于云南植物药业有限公司质量部。

2　提取分离

三分三药材 20kg,粉碎后用75%乙醇热回流提取三次,浓缩至无醇水液,加碱调 PH=9,加水液3倍量的氯仿萃取,得水液部分和氯仿层部分,氯仿层再用2%的硫酸溶液萃取至氯仿层无生物碱,回收氯仿得到浸膏(110 g),经硅胶柱层析,以石油醚、丙酮,氯仿、甲醇梯度洗脱,得到东莨菪素、β-谷甾醇和胡萝卜苷。将 PH=9 的水液部分调节 PH 为中性,经大孔树脂分段得水和10%、20%、30%及70%乙醇部分,合并20%和30%乙醇部分,浓缩得浸膏200 g,用氯仿、甲醇不同比例梯度洗脱得到东莨菪苷和皮契荔枝苷。

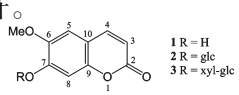

图1　化合物 1~3 的结构式

Fig. 1　Chemical Structures of compounds **1-3**

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表 1 化合物 1~3 的氢谱和碳谱数据

Table 1 ^{1}H and ^{13}C NMR Data of Compounds 1-3 (J in Hz)

No.	1[a]		2[b]		3[b]	
	δ_H[c]	δ_C[d]	δ_H[e]	δ_C[d]	δ_H[e]	δ_C[d]
2		162.6 s		160.6 s		160.6 s
3	6.22 (d,9.6)	111.2 d	6.32 (d,9.5)	113.3 d	6.32 (d,9.5)	113.4 d
4	7.86 (d,9.6)	144.7 d	7.96 (d,9.5)	144.3 d	7.95 (d,9.5)	144.2 d
5	7.12 (s)	108.5 d	7.28 (s)	109.6 d	7.29 (s)	109.6 d
6		145.7 s		146.0 s		146.0 s
7		151.5 s		149.9 s		149.7 s
8	6.78 (s)	102.6 d	7.15 (s)	103.0 d	7.18 (s)	103.0 d
9		150.0 s		148.9 s		149.0 s
10		111.1 s		112.3 s		112.3 s
1′			5.07 (overlap)	99.5 d	5.09 (d,6.64)	99.4 d
2′			3.15 (m)	73.0 d	2.95 (overlap)	73.3 d
3′			3.27 (overlap)	77.1 d	3.04 (m)	76.6 d
4′			3.43 (overlap)	69.6 d	2.95 (overlap)	69.4 d
5′			3.27 (overlap)	76.8 d	3.26 (overlap)	75.3 d
6′a			3.68 (m)	60.6 t	3.88 (m)	68.2 t
6′b			3.43 (overlap)		3.60 (overlap)	
1″					4.10 (d,7.5)	104.1 d
2″					3.26 (overlap)	73.0 d
3″					3.26 (overlap)	76.6 d
4″					3.60 (overlap)	69.2 d
5″a					3.67 (m)	65.7 t
5″b					3.26 (overlap)	
OMe	3.92 (3H,s)	55.4 q	3.80 (3H,s)	56.0 q	3.80 (3H,s)	56.0 q
OH-7	4.87 (s)					
OH-2′			5.07 (overlap)		5.13 (d,4.8)	
OH-3′			5.13 (s)		5.20 (d,3.4)	
OH-4′			5.36 (s)		5.39 (d,4.4)	
OH-6′			4.58 (d,4.6)			
OH-2″					4.83 (d,4.8)	
OH-3″					4.87 (d,4.7)	
OH-4″					4.91 (d,4.9)	

[a]Recorded in MeOD; [b]Recordedin DMSO-d_6; [c]Recorded at 600 MHz; [d]Recorded at 100 MHz; [e]Recorded at 500 MHz.

3 结构鉴定

化合物 1 黄色粉末,紫外灯下有较强荧光,溶于甲醇,溶于氯仿;ESI$^+$-MS:m/z 215[M + Na]$^+$;详细的 NMR 数据归属见表 1,通过与文献数据仔细比对,最终确定该化合物为东莨菪素[2]。

化合物 2 白色粉末,紫外灯下有较强荧光,溶于甲醇,难溶于氯仿;ESI$^+$-MS:m/z 377[M + Na]$^+$;详细的 NMR 数据归属见表 1,通过与文献数据仔细比对,最终确定该化合物为东莨菪苷[3-5]。

化合物 3 白色粉末,紫外灯下有较强荧光,微溶于甲醇,难溶于氯仿、乙酸乙酯;ESI$^+$-MS:m/z

509[M+Na]$^+$;详细的 NMR 数据归属见表 1,通过与文献数据仔细比对,最终确定该化合物为皮契荔枝苷[5,6]。

化合物 4 白色针状针晶,溶于氯仿,ESI$^+$-MS:*m/z* 437[M+Na]$^+$;^{13}C NMR(100 MHz,pyridine-d_6),δ:37.9(t,C-1),32.3(t,C-2),71.3(d,C-3),43.6(t,C-4),140.2(s,C-5),121.3(d,C-6),32.7(t,C-7),32.2(d,C-8),50.5(d,C-9),36.9(s,C-10),21.4(t,C-11),40.0(t,C-12),42.5(s,C-13),56.9(d,C-14),24.6(t,C-15),28.6(t,C-16),56.3(d,C-17),12.0(q,C-18),19.7(q,C-19),36.5(d,C-20),19.2(q,C-21),34.2(t,C-22),26.4(t,C-23),46.0(d,C-24),29.5(d,C-25),19.0(q,C-26),20.0(q,C-27),23.4(t,C-28),12.2(q,C-29),与文献数据仔细比对,最终确定该化合物为 β-谷甾醇[7]。

化合物 5 白色粉末,溶于氯仿,ESI$^+$-MS:*m/z*599[M+Na]$^+$;^{13}C NMR(100 MHz,pyridine-d_6) δ:37.5(t,C-1),30.3(t,C-2),78.6(d,C-3),40.0(t,C-4),140.9(s,C-5),122.0(d,C-6),32.1(t,C-7),32.1(d,C-8),50.4(d,C-9),37.0(s,C-10),21.3(t,C-11),39.4(t,C-12),42.5(s,C-13),56.8(d,C-14),24.5(t,C-15),28.4(t,C-16),56.2(d,C-17),12.2(q,C-18),19.5(q,C-19),36.4(d,C-20),19.2(q,C-21),34.2(t,C-22),29.4(t,C-23),46.0(d,C-24),26.4(d,C-25),19.0(q,C-26),20.0(q,C-27),23.4(t,C-28),12.0(q,C-29),102.6(d,C-1′),75.4(d,C-2′),78.7(d,C-3′),71.7(d,C-4′),78.1(d,C-5′),62.8(t,C-6′),与文献数据仔细比对,最终确定该化合物为胡萝卜苷[8]。

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