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毛萼香茶菜中的新二萜化合物——毛萼晶 P

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摘要 从毛萼香茶菜(*Isodon eriocalyx*)的叶的甲醇提取物中分离得到两个二萜化合物, coetsoidin A 和毛萼晶 P. 它们是目前从香茶菜属植物中分离到的仅有的两个 B 环具有 α, β -不饱和酮结构的对映-贝壳杉烷型二萜化合物, 其中毛萼晶 P 为新化合物。

关键词 唇形科、毛萼香茶菜、二萜、毛萼晶 P

A NOVEL DITERPENOID FROM ISODON ERIOCALYX

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Abstract From the dried leaves of *I. eriocalyx*, one new *net*-kaurane diterpenoid named maoecrystal P and a known compound coetsoidin A were isolated. They have been the only two *ent*-kaurane diterpenoids possessing α, β -unsaturated ketone functional group in ring B isolated from *Isodon* genus plants so far.

Key words Labiatae, *Isodon eriocalyx*, Diterpenoid, Maoecrystal P

Isodon eriocalyx (Dunn) Hara, a perennial herb or shrub of Labiatae family, has long been used as folk medicine to cure sore throat, inflammation and interdigital disease (中国科学院中国植物志编辑委员会, 1997).

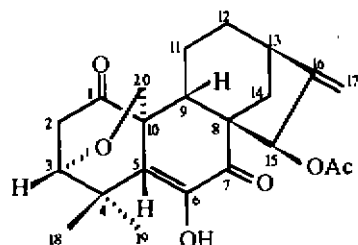
One new *ent*-kaurane diterpenoid named maoecrystal P and a known compound coetsoidin A were isolated from the dried leaves of *I. eriocalyx* collected in Jiangchuan County, Yunnan Province.

Coetsoidin A(1) (Wang *et al.* 1989) was the first example of *ent*-kaurane diterpenoid possessing α, β -unsaturated ketone functional group in ring B isolated from *Isodon* genus plants. Its structure was established unambiguously by spectroscopic and X-ray diffraction analysis. Coetsoidin A(1) was also obtained from *Isodon eriocalyx* (Dunn) Hara by us. The ^1H NMR and ^{13}C NMR data of 1 were consistent with those of the reported one. But the careful study of the assignment of carbon and proton signals in literature revealed that there was something wrong with the assignment at C-5, 6, 9 and 13 positions. This was proved by 2D NMR spectra. In the ^1H - ^{13}C COSY spectrum of 1, the proton signals ascribable to H-9 β (δ 3.72) and H-13 α (δ 2.66), both of which were determined by ^1H - ^1H COSY spectrum, showed correlation spots with C-9(δ 28.0) and C-13(δ 41.6), respectively. Thus, the carbon signal attributed to C-9(δ 41.6) and C-13(δ 28.0) in literature should be interchanged. Moreover, among the long-range couplings observed

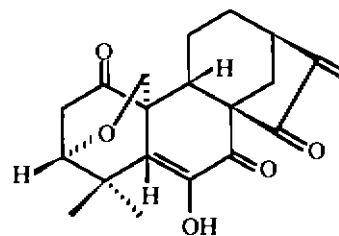
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in the COLOC spectrum, the proton signal at H-3, Me-18 and Me-19 showed significant correlations with C-5(δ 133.1) respectively. So the signals originally attributed to C-6(δ 133.1) and C-5(δ 146.1) also should be interchanged. The revised assignment of ^{13}C NMR data were listed in Table 1.



Coetsoidin A (1)



Maoecrystal P (2)

Table 1 ^{13}C NMR data of compounds 1 and 2 in $\text{C}_5\text{D}_5\text{N}$
(100 MHz, δ with reference to the signal of $\text{C}_5\text{D}_5\text{N}$)

Carbon	1	2	Carbon	1	2	Carbon	1	2
1	206.2 s	205.4 s	9	28.0 d	32.6 d	17	108.5 t	116.0 t
2	42.0 t	41.9 t	10	53.9 s	54.9 s	18	23.6 q	23.4 q
3	77.9 d	78.0 d	11	19.7 t	19.6 t	19	21.9 q	22.0 q
4	40.8 s	40.9 s	12	32.1 t	30.8 t	20	67.4 t	66.9 t
5	133.1 s	133.4 s	13	41.6 d	38.0 d	OAc	170.5 s	
6	146.1 s	147.0 s	14	38.1 t	38.1 t		20.7 q	
7	194.4 s	192.9 s	15	76.4 d	203.4 s			
8	54.4 s	59.7 s	16	152.5 s	149.0 s			

Table 2 ^1H NMR data of compounds 1 and 2 in $\text{C}_5\text{D}_5\text{N}$
(400 MHz, δ with reference to the signal of $\text{C}_5\text{D}_5\text{N}$, J in Hz, * overlap)

proton	1	2	proton	1	2
2 α	3.03(dd, 3.2, 19.2)	2.93(dd, 3.2, 19.6)	14 β	1.54(dd, 12.0, 4.8)	1.98(dd, 11.6, 4.8)
2 β	2.89(dd, 3.2, 19.2)	2.85(dd, 3.2, 19.6)	15 α	6.83(t, 2.0)	
3 β	3.86(br.s)	3.84(t, 3.2)	17Hb	5.02(br.s)	6.09(br.s)
9 β	3.72(d, 7.6)	3.48(d, 8.0)	17Ha	5.24(br.s)	5.23(br.s)
11 α	1.43~1.47(m, *)	1.42~1.50(m, *)	18Me	1.80(s)	1.78(s)
11 β	2.19(m)	1.71(m)	19Me	1.30(s)	1.29(s)
12 α	1.28(m)	1.42~1.50(m, *)	20b	4.36(d, 8.8)	4.75(d, 8.8)
12 α	1.43~1.47(m, *)	1.42~1.50(m, *)	20a	4.47(d, 8.8)	4.33(d, 8.8)
13 α	2.66(br.s)	2.95(br.s)	OAc	1.96(s)	
14 α	1.80(d, 12.0)	2.12(d, 11.6)	OH-6	11.00(s)	11.25(s)

Maoecrystal P(2) had a molecular formula of $\text{C}_{20}\text{H}_{22}\text{O}_5$ concluded from the HR EIMS(342.1465[M] $^+$, calc. 342.1467), mp 234.0~236.0 $^{\circ}\text{C}$, $[\alpha]_{\text{D}}^{25}$ -141.7 $^{\circ}$ (CH_2Cl_2 , c0.30).

A comparison of the ^1H and ^{13}C NMR spectral data of 2 with those of 1 indicated that 2 was quite similar to 1 except for ring D. The carbon signal assigned to C-15 at δ 76.4 in 1 was replaced by a ketonic signal at δ 203.4 in 2 and the proton signal ascribable to H-15 α at δ 6.83 (1H, t, J=2.0 Hz) in 1 was disappeared in

2. Meanwhile, the signals assigned to acetyl group in 1 were also absent in 2. All these facts revealed that the structure of 2 was 6-hydroxy-3 α , 20-epoxy-*ent*-kaura-5,16-diene-1,7,15-trione.

Compound 2 was the second instance of *ent*-kaurane diterpenoid possessing α,β -unsaturated ketone functional group in ring B isolated from *Isodon* genus plants so far.

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滇产刺果番荔枝种子中的 acetogenin 类化合物*

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ACETOGENINS FROM SEED OF ANNONA MURICATA

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关键词 番荔枝科, 刺果番荔枝, 刺果番荔枝丁素

Key words Annonaceae, *Annona muricata*, Muricatin D

化学成分

刺果番荔枝(*Annona muricata* Linn.)为番荔枝科植物。西双版纳地区有栽培, 为寻找其生理活性成分, 我们对该植物种子进行化学成分分析, 从中分到若干具有抗肿瘤活性的 acetogenins 类化合物。前文(Li *et al*, 1994)已报道其中的 4 个化合物。本文报道另外 2 个 acetogenin 衍生物。经风干粉碎的 3.5 kg 刺果番荔枝种子, 石油醚脱脂, 然后用乙醇于室温下浸提, 所得乙醇提取物, 经水和氯仿分配。氯仿萃取物经硅胶柱层析, 依次用石油醚、乙酸乙酯-石油醚, 甲醇-乙酸乙酯梯度洗脱, 收集流分。乙酸乙酯-石油醚 2:8 流份得 AM-C(100 mg), 被鉴定为 epoxyrolin B(Laprevote, 1990)(2), 乙酸乙酯-石油醚 1:1 流份得 Au-50D(109 mg), 鉴定为 murisolin(3), (Myint *et al*, 1990) 甲醇-乙酸乙酯 0.5:95 流份得 Au-125

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