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云木香根中一新的巴卡林烷型三萜*

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摘要 从云木香(*Saussurea lappa* C.B.Clarke)根中分得一新的巴卡林烷型三萜化合物 3β-acetoxy-9(11)-baccharene(**1**)和一已知三萜化合物 α-amyrin(**2**)。它们的结构通过波谱方法得到鉴定。
关键词 云木香,菊科,巴卡林烷型三萜,3β-乙酰氧基-9(11)-巴卡林烯

A NEW BACCHARANE-TYPE TRITERPENOID ISOLATED FROM THE ROOTS OF *SAUSSUREA LAPPA* C.B.CLARKE*

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Abstract A new baccharane-type triterpene, 3β-acetoxy-9(11)-baccharene(**1**), as well as a known compound, α-amyrin(**2**), has been isolated from the ether extract of the roots of *Saussurea lappa* C.B.Clarke. The structure of the new compound was identified by spectrum analysis.
Key words *Saussurea lappa*, Compositae, Baccharane-type triterpenoid, 3β-acetoxy-9(11)-baccharene

Saussurea lappa C.B.Clarke introduced from India has been cultivated in many places of China, particularly in Yunnan and Gansu Province. It has been used as a traditional Chinese medicine and also an important fragrance since ancient times[1]. It possesses the function of spasmolysis, antihypertension and antibacteria infection. The chemical constitutents of this plant have been studied by some research groups during the past four decades, and many sesquiterpenes, sesquiterpene lactones and some other substances have been reported[2~4]. With the objective of focusing attention on the minor constituents of this plant, the roots of *S. lappa* (produced in Lijiang, Yunnan Province) were investigated. In the present communication, we report here the isolation and the structure elucidation of a new baccharane-type triterpene, 3β-acetoxy-9(11)-baccharene(**1**), as well as a known compound, α-amyrin(**2**).

RESULTS AND DISCUSSION

Compound **1** produced $[M]^+$ ion at m/z 470 in EI mass spectra. The combination of EI mass and ^{13}C-NMR spectra (including DEPT technique) (Table 1) suggested a formula of **1** as $C_{32}H_{54}O_2$,

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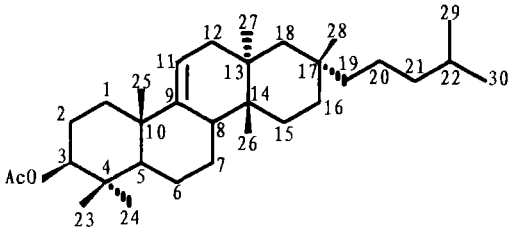
Table 1 ^{13}C-NMR spectral data of 3β-acetoxy-9(11)-baccharene(1)*

C	1	C	1	C	1	C	1
1	41.41t	9	158.14s	17	28.84s	25	21.21q
2	23.56t	10	37.79s	18	29.71t	26	29.71q
3	81.10d	11	117.01d	19	37.79t	27	25.94q
4	39.10s	12	36.79d	20	18.79t	28	29.94q
5	55.81d	13	35.25s	21	37.55t	29	16.60q
6	17.56t	14	38.02s	22	49.03d	30	15.50q
7	35.25t	15	33.81t	23	28.03q	acetoxy	170.84s
8	49.34d	16	33.23t	24	21.33q		33.38q

* 100MHz, $CDCl_3$, TMS, taken on Bruker spectrospin AM-400 spectrometer.

which was confirmed by HRMS spectrum (found m/z 470.414 5, calculated 470.412 4 for $C_{32}H_{54}O_2$). The fragmentation pattern of EI mass of **1** (Fig.1) indicated **1** to be a baccharene having a double bond at 9(11)(m/z 325, 327 and 329 for tetracyclic part; 189, 203, 204, 231, 243 and 257 for 9(11) ene[5]). IR absorption band pointed to the presence of an ester carbonyl(1 715 cm^{-1}). The ^{1}H-NMR spectrum (Table 2) of **1** exhibited the presence of six tertiary methyl groups (C-23 to C-28), two secondary methyl groups (C-29, C-30) and one methyl group (C-2′) adjacent to the carbonyl. A proton (δ 5.51, dd, J = 8.0, 2.8 Hz, H-11) of a trisubstituted double bond and a proton (δ 4.43, dd, J = 10.6, 5.4 Hz, H-3) of a methine connected acetoxy group, which was supported by the tertiary carbon signal at δ 81.10(C-3). In addition, the ^{13}C-NMR indicated the presence of six quaternary carbons and the functional groups predicted by the ^{1}H-NMR spectrum, suggesting that **1** is a tetracyclic triterpene having one acetoxy group, one double bond and an isohexyl side chain.



Compound 1

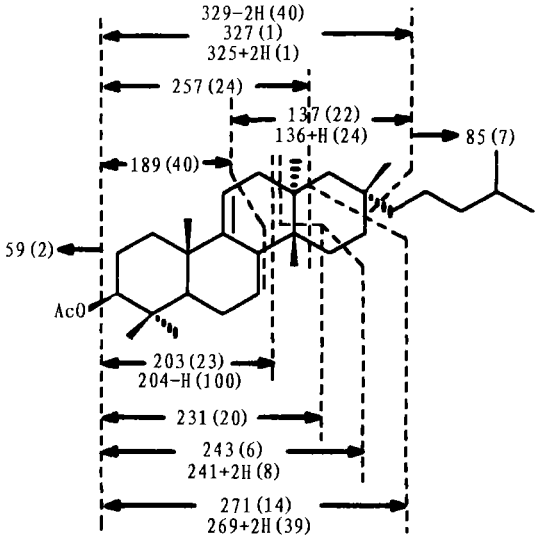


Fig. 1 Fragmentation pattern of EI mass of compound 1

From the above data and discussion, compound **1** has the structure of 3β-acetoxy-9(11)-baccharene(**1**). Comparisons of-NMR and MS spectra of **1** with those of its counterparts bacchara-12, 21-diene, lemmaphylla-9(11), 21-diene[5] and actinostemmoside F[6] gave good evidence to confirm the structure of **1**. The occurrence of a baccharane-type triterpene in plants is very rare, and

the isolation of this type of triterpene from the *S. lappa* is the only instance so far reported.

Table 2 ^{1}H-NMR spectral data of 3β-actoxy-9(11)-baccharene(1)*

H	δ_H(J in Hz)	H	δ_H(J in Hz)
3α	4.43(dd, 10.7, 5.4, 1H)	27	0.73(s, 3H)
11	5.51(dd, 8.0, 2.8, 1H)	28	0.93(s, 3H)
23	1.59(s, 3H)	29	0.84(d, 7.2, 3H)
24	1.07(s, 3H)	30	0.84(d, 7.2, 3H)
25	1.21(s, 3H)	acetoxy	2.02(s, 3H)
26	0.88(s, 3H)		

* 400 MHz, $CDCl_3$, TMS, taken on Bruker spectrospin AM-400 spectrometer.

The structure of the known compound was identified on the basis of physical constants and spectral data as α-amyrin(**2**).

EXPERIMENTAL

Mp: uncorr; MS: 70 eV; NMR: ^{1}H at 400 MHz, ^{13}C at 100 MHz. The multiplicities of ^{13}C-NMR spectral data were determined with the aid of 1 D Distortionless Enhancement Polarization Transfer (DEPT) spectra.

Plant material *S. lappa* was grown in Lijiang, Yunnan, China. Research samples were obtained from the Yunnan Native Products Branch of China National Native Products & Animal By-products Import & Export Corporation.

Extraction and isolation The air-dried powdered roots (2.5 kg) of *S. lappa* were extracted with Et_2O (5 × 4 000 mL) at room temperature within 3 weeks. The extract was evaporated to dryness *in vacuo* and the residue (142.0 g) was chromatographed on a silica gel column (200 to 300 mesh, 470.0 g, 120 × 4 cm) and successively eluted with petrol-ether (1:0, 9:1, 3:1, 1:1, and 0:1) to give fractions A (20.2 g), B (82.7 g), C (6.5 g), D (6.8 g) and E (5.5 g). From fr. B, 3β-acetoxy-9(11)-baccharene(**1**)(8 mg), α-amyrin(**2**)(34 mg) and other compounds[3,4] were obtained by CC on silica gel eluting with petrol-ether and petrol-chloroform, respectively.

3β-acetoxy-9(11)-baccharene(1) Colorless needles (petrol), mp 104.5 to 105.5 ℃. $[\alpha]_D$ (13.3) + 55.5°(c = 0.067, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 2 960, 2 920, 1 715, 1 620, 1 450, 1 360, 1 242, 1 020, 980, 810. For its EIMS, ^{1}H- and ^{13}C-NMR data, see Fig.1, Table 1 and Table 2, respectively.

α-amyrin (2) Colourless oil. Its physical constants and spectral data accord with the authentic sample.

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