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瘿花香茶菜的微量成分

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摘要 从唇形科瘿花香茶菜(*Rabdosia rosthornii*)叶的乙醚抽出物中分出2个新的微量成分, 瘿花丙素和丁素。基于详细的光谱分析, 包括应用二维核磁共振数据, 瘿花丙素和丁素的化学结构分别确定为对映-11α-乙酰氧基-7β,13β,19-三羟基贝壳杉-16-烯-15-酮(1)和对映-11α-乙酰氧基-7β,12β,14α-三羟基贝壳杉-16-烯-15-酮(2)。

关键词 瘿花丙素, 瘿花丁素, 瘿花香茶菜, 唇形科 化学成分

Minor Constituents from Rabdosia rosthornii

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Abstract Two new ent-kaurenoids, rosthornin C and D, with rosthornin A and B, have been isolated from the ethereal extract of the leaves of *Rabdosia rosthornii*. The chemical structures of the two minor constituents have been established as ent-11α-acetoxy- 7β,13β,19-trihydroxykaur-16-en-15-one (1) and ent-11α-acetoxy-7β,12β,14α-trihydroxykaur-16-en-15-one (2), respectively, on the basis of detailed spectroscopic analysis, including 2D NMR data.

Key words Rosthornin C and D, *Rabdosia rosthornii*, Labiatae

INTRODUCTION

Rabdosia rosthornii is distributed mainly over southwestern Sichuan and northern Guizhou. The decoctions of this plant are used in Chinese traditional medicine against pyrexia, oedema and abdominal distension (Wu *et al*, 1977). As a constitution of our phytochmical investigations for the biologically active constituents from *Rabdosia* plants, the structures of two new diterpenoids, rosthornin A and B, isolated from the leaves of *R. rosthornii* was reported previously (Xu et al, 1989). The present paper was described the isolation and the structural determination of minor constituents, rosthornin C and D, from same source.

RESULTS AND DISCUSSION

Rosthornin C (1), $C_{22}H_{32}O_6$, M 392, showed the presence of two methyl groups, seven methylene

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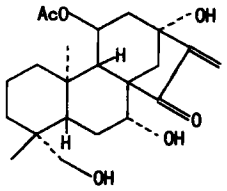
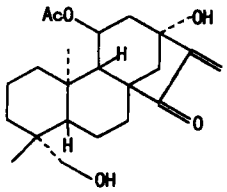
groups, four methine groups, four quaternary carbons, two olefinic carbons, one ketonic carbon and one acetoxy signal in the ^{13}C NMR (DEPT) spectrum (Table 1). 1 has a five-membered ketone conjugated with an exo-methylene group, judging from the following spectral data: UV_{max}^{EtOH}229 nm (logε 3.72); $IR_{max}^{KBr}cm^{-1}$: 1705 and 1640; ^1H NMR δ: 6.22, 5.72 (each 1H, ABd, J = 1.5 Hz); ^{13}C NMR δ: 154.9 (s), 112.3 (t) (double bond) and 207.3 (s) (ketone) (Xu *et al*, 1981). Its IR spectrum showed the characteristic absorption of hydroxyl groups at 3550 and 3500 $cm^{-1}$and ester group at 1735 and 1230 cm^{-1}. The presence of a secondary acetoxy group was suggested by its ^1H NMR data: δ1.97 (3H, s) and proton signal at δ5.50 (1H, d, J = 5.1 Hz) attached to the acetoxy-bearing carbon. Three hydroxyl signals at δ7.25, 6.48 and 5.64 (each 1H, 3 × OH) and a triple-doublet signal at 4.60 and AB signal at 3.90 and 3.69 (each 1H, ABdd, J = 10.4, 5.1 Hz) indicated the existence of a primary, a secondary and a tertiary hydroxyl. The above-mentioned data and two tertiary methyl signals at δ1.17 and 1.10 suggested that this compound has a typical 15-oxo-ent-kaurene nucleus as a basic skeleton (Fujita *et al*, 1976). The location of four oxygen functional groups were deduced as follows. The chemical shift value of C-4 (δ39.2) suggested that there is an oxygen functional substituent on the α position (C-3, 5, 18 or 19); The δ value of C-18 (δ28.0) and C-19 (64.4) suggested that a hydroxyl group was located at C-19 (Gonzalez *et al*, 1981). The chemical shift value of C-10 (δ38.9) was shown no oxygen functional substituent on its α position (C-1, 5, 9, 20). The downfield shift of C-6 and C-8 to δ 29.6 and 60.0, indicated that a hydroxyl group might be presented at the 7α position (Xu *et al*, 1981; Nomoto et al, 1976). The δ value of C-9 (δ59.2) and C-12 (47.4) are suggested that there is an acetoxy group at C-11 position; this acetoxy group is in β orientation by ^1H NMR data: 5.50 (1H, d, J = 5.1 Hz) (Matsuo *et al*, 1978). the tertiary hydroxyl group was located at 13α-position judging from the downfield shift of C-12 and C-16 to δ47.4 and 154.9, respectively (Kohda *et al*, 1976). Therefore, the chemical structure of rosthornin C(1) could be represented as *ent*-11α-acetoxy-7β,13β,19-trihydroxykaur-16-en-15-one (1). This presumption was supported by its COSY spectrum.

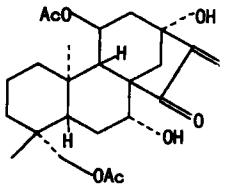
Rosthornin D (2), $C_{22}H_{32}O_6$, M 392, showed the presence of three methyl groups, four methylene groups, seven methine groups, three quaternary carbons, two olefinic carbons, one ketonic carbon and one acetoxy signal in the ^{13}C NMR (DEPT) spectrum (Table 1). **2** has a five-membered ketone conjugated with an exo-methylene group, judging from the following spectral data: $UV\lambda_{max}^{EtOH}$228.5 nm (logε 3.76); $IR_{max}^{KBr}cm^{-1}$: 1700 and 1630; ^1H NMR δ: 6.19, 5.44 (each 1H, br s); ^{13}C NMR δ: 144.2 (s), 119.4 (t) (double bond) and 206.9 (s) (ketone) (Xu *et al*, 1981). Its IR spectrum showed the characteristic absorption of hydroxyl groups at 3490 and 3450 cm^{-1} and ester group at 1728 and 1225 cm^{-1}. The presence of a secondary acetoxy group was suggested by its ^1H NMR data: δ1.86 (3H, s, OAc) and proton signal at δ 4.83 (1H, br s) attached to the acetoxy-bearing carbon. Three secondary hydroxyl signals at δ5.18 (1H, br s), 4.44 (1H, dd, J = 12.5, 4.8 Hz) and 3.87 (1H, d, J = 3.7 Hz). The above-mentioned data and three tertiary methyl signals at δ 1.24, 0.91 and 0.86 suggested that this compound has a typical 15-oxo-ent-kaurene nucleus as a basic skeleton (Fujita *et al*, 1976). The location of four oxygen functional groups were deduced as follows. The chemical shift value of C-4 (δ33.3) suggested no oxygen functional substituent on the α position (C-3, 5, 18 or 19); the chemical shift value of C-10 (δ39.1) suggested no oxygen functional substituent on its α position (C-1, 5, 9, 20). The downfield shift of C-6 and C-8 to δ27.8 and 59.6, indicated that a hydroxyl



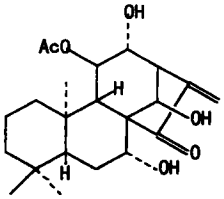
Rosthornin C(1)



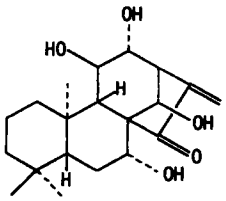
Rosthornin A(3)



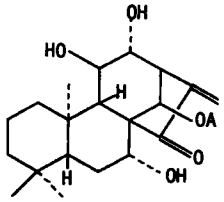
Rosthornin B(4)



Rosthornin D(2)



Rabdoloxin B(5)



Rabdokumin A(6)

Table 1　^{13}C NMR data of rosthornin C (1), A (3), B (4), D (2)*, rabdoloxin B (5) and rabdokumin A (6) in C_5D_5N.

Carbons	1	3	4	2*	5	6
1	37.0 t	35.9 t	36.2 t	39.0 t	39.5 t	39.4 t
2	18.5 t	18.3 t	18.1 t	18.2 t	18.7 t	18.8 t
3	36.0 t	33.9	36.9 t	41.4 t	41.8 t	41.9 t
4	39.2 s	39.1 s	37.2 s	33.3 s	33.3 s	33.4 s
5	53.0 d	56.0 d	52.6 d	52.9 d	53.2 d	52.5 d
6	29.6 t	19.0 t	29.2 t	27.8 t	29.6 t	29.0 t
7	70.3 d	39.7 t	69.8 d	75.0 d	74.8 d	73.3 d
8	60.0 s	53.5 s	59.7 s	59.6 s	60.1 s	61.4 s
9	59.2 d	59.3 d	58.9 d	62.3 d	67.6 d	68.9 d
10	38.9 s	39.0 s	38.6 s	39.1 s	39.0 s	39.2 s
11	69.9 d	69.4 d	69.6 d	72.0 d	70.9 d	70.8 d
12	47.4 t	46.5 t	47.2 t	76.0 d	79.1 d	79.8 d
13	75.3 s	74.9 s	75.1 s	52.0 d	54.6 d	53.9 d
14	39.7 t	45.0 t	39.3 t	70.1 d	71.6 d	72.9 d
15	207.3 s	207.3 s	206.8 s	206.9 s	208.0 s	206.7 s
16	154.9 s	154.1 s	154.7 s	144.2 s	147.6 s	146.3 s
17	112.3 t	112.7 t	112.3 t	119.4 t	116.0 t	115.4 t
18	28.0 q	27.9 q	27.4 q	33.5 q	33.4 q	33.6 q
19	64.4 t	64.2 t	66.8 t	21.6 q	21.8 q	21.9 q
20	18.5 q	18.2 q	18.1 q	16.9 q	17.4 q	17.2 q
OAc	169.2 s	169.0 s	170.7 s	169.5 s		171.4 s
	21.3 q	21.3 q	169.0 s	21.3 q		21.9 q
			21.2 q			
			20.6 q			

* in $CDCl_3$

group might bepresented at the 7α position (Xu *et al*, 1981; Nomoto *et al*, 1976). The δ value of C-9 (δ62.3), C-8 (59.6) and C-13 (52.0) suggested that there are oxygen functional substituents at C-11, C-12 and C-14 positions (Nomoto *et al*, 1976). Rosthornin D (2), its UV, IR, ^{1}H and ^{13}C NMR were very similar to those of rabdoloxin B (5) (Sun *et al*, 1991) and rabdokunmin A (6) (Zhang *et al*, 1989). The only differences in the ^{13}C NMR spectra of **2** and **5** are the presence of an extra acetoxy signal (δ169.5 s and 21.3 q) and the upfield shift of the signals for C-9 and C-12 from 67.6 and 79.1 in **5** to 62.3 and 76.0 in **2**. Therefore, the chemical structure of rosthornin D (2) could be established as 11-Acetylrabdoloxin B i.e. *ent*-11α-acetoxy-7β,12β,14α-trihydroxykaur-16-en-15-one (2) (Fujita *et al*, 1981). This presumption was supported by its COSY spectrum.

EXPERIMENTAL SECTION

General. Kofler melting points were uncorrected; Optical rotations were taken on a Jasco-20C digital polarimeter. IR were recorded on KBr discs with a Perkin-Elmer 577 spectrometer. UV was obtained in EtOH on a UV-210A spectrometer. EIMS (positive) were measured on a VG Auto Spec-3000 spectrometer with direct inlet 70 or 20 eV. FABMS negative used the 3-NBA as the matrix. NMR were run on a Brucker AM-400 spectrometer using TMS as internal standard; chemical shift values are reported in δ(ppm) units (C_5D_5N and $CDCl_3$). Coupling constants (J) were expressed in Hz.

Plant material The same plant material was used as in previous report (Xu *et al*, 1989).

Extraction and isolation of constituents The residue (3.0 g) from previous report was further submitted to CC (silica gel), eluting with EtOAc-Hexane and increasing proportions of EtOAc. Fractions were monitored by TLC. All components were further purified by a combination of prep. TLC (silica gel) and recrystallization yielding in order of increasing polarities: Rosthornin D (2, 14.0 mg), Rosthornin A (3, 146.5 mg), Rosthornin B (4, 188.4 mg), and Rosthornin C (1, 40.0 mg). The physical properties of the isolated compounds were as follows.

Rosthornin C (1), $C_{22}H_{32}O_6$, M 392, colorless needles, mp 174~ 176 ℃ ; $[\alpha]_D^{25.7}$-172.16 ° (c 0.44, MeOH), UVλ_{max}^{EtOH}229 nm(logε 3.72): IRν_{KBr}^{max}cm^{-1}: 3550, 3500, 1735, 1705, 1640, 1230, 1110, 1092, 1045, 972, 950; FABMS negative m / z: 391[M-H]$^+$; ^{1}H NMR(400MHz, C_5D_5N δ: 7.25 (1H, br s, OH-13α), 6.48 (1H, d, J = 4.8 Hz, OH-7α), 6.22, 5.72 (each 1H, ABd, J = 1.5 Hz, H-17), 5.64 (1H, t, J = 5.1 Hz, OH-19), 5.50 (1H, d, J = 5.1 Hz, H-11α), 4.60 (1H, ddd, J = 12.5, 4.8, 4.0 Hz, H-7β), 3.90, 3.69 (each 1H, ABdd, J = 10.4, 5.1 Hz, H-19), 2.97 (1H, dd, J = 11.4, 2.2 Hz, H-14β), 2.64 (1H, dd, J = 14.3, 5.1 Hz, H-12β), 2.51 (1H, d, J = 11.4 Hz, H-14α), 2.47 (1H, dd, J = 14.3, 1.5 Hz, H-12α), 2.32 (1H, dd, 12.5, 4.0 Hz, H-6β), 2.06 (1H, br d, J = 13.2 Hz, H-3α), 1.97 (3H, s, OAc), 1.96(1H, br d, J = 14.4 Hz, H-1α), 1.86 (1H, q, J = 12.5 Hz, H-6α), 1.62 (1H, br s, H-9β), 1.61 (1H, br q, 14.3 Hz, H-2α), 1.36 (1H, br dd, J = 14.3, 3.3 Hz, H-2β), 1.18 (1H, d, 12.5 Hz, H-5β), 1.17 (3H, s, Me-18), 1.10 (3H, s, Me-20), 0.98 (2H, m, H-1β and H-3β). ^{13}C NMR (100MHz, C_5D_5N) δ: See Table 1.

Rosthornin D (2), $C_{22}H_{32}O_6$, M 392, colorless needles, mp 152~ 154℃ ; $[\alpha]_D^{25.7}$ ° -111.23 ° (c 0.39, MeOH), UVλ_{max}^{EtOH}228.5 nm (logε 3.76): IRν_{max}^{KBr}cm^{-1}: 3490, 3450, 1728, 1700, 1630, 1225, 1105, 1085, 1042, 970, 945; FABMS negative m / z: 391[M-H]$^+$; ^{1}H NMR(400MHz, $CDCl_3$) δ: 6.19, 5.44 (each 1H, br s, H-17), 5.18 (1H, br s, H-14α), 4.83 (1H, br s, H-11α), 4.44 (1H, dd, J = 12.5, 4.8 Hz, H-7β), 3.87 (1H, d, J = 3.7 Hz, H-12β), 3.13 (1H, m, H-13α), 1.98 (1H, ddd, J = 12.5, 5.1, 4.8 Hz, H-6β), 1.86 (3H, s, OAc),