

⑮ 197-2000

云南植物研究 2000, 22 (2): 197~200
Acta Botanica Yunnanica

旱生香茶菜中三个新的对映-贝壳杉烷型二萜

Q949.777

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Q946.8

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摘要: 从旱生香茶菜 (*Isodon xerophilus*) 叶中分离得到 3 个新的对映-贝壳杉烷型二萜, 旱生香茶菜素 G, H 和 I。通过波谱方法鉴定了它们的结构。

关键词: 旱生香茶菜; 唇形科, 对映-贝壳杉烷型二萜; 旱生香茶菜素 G-I

中图分类号: Q 946

文献标识码: A

文章编号: 0253-2700(2000)02-0197-04

Three New *ent*-Kaurane Diterpenoides from *Isodon xerophilus*

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Abstract: Three new *ent*-kaurane diterpenoids, xerophilusins G, H and I, were isolated from the leaves of *Isodon xerophilus*. Their structures were identified by spectral methods.

Key words: *Isodon xerophilus*; Labiatae; *ent*-kaurane diterpenoid; Xerophilusins G-I

As part of our studies on biologically active compounds from *Isodon* species, we have examined the leaves of *Isodon xerophilus* (C. Y. Wu et H. W. Li) H. Hara (Labiatae) for its diterpene constituents and have previously isolated a series of *ent*-kauranoids (Hou *et al.*, 1999a; Hou *et al.*, 1999b; Hou *et al.*, 1999c; Hou *et al.*, 1999d). In our continuing chemical investigation on this plant, three new *ent*-kaurane diterpenoids, xerophilusins G-I (1~3), were obtained, which are three of a few of diterpenoids having 1 β substitutes. Herein we describe the structure elucidation of 1~3 by spectroscopic methods.

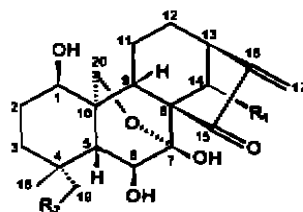
Xerophilusin G (1), colorless needles, mp: 216~218°C, $[\alpha]_D^{25} - 116.3^\circ$ (c 0.43, C₅H₅N), was isolated as colorless needles and has a molecular formula of C₂₂H₃₀O₈ established by positive HRFABMS (obsd 423.1955, calcd 423.2019). It contains an *exo*-methylene group conjugated with a carbonyl group on a five-membered ring [UV λ_{max}^{MeOH} nm (log ϵ): 237.5 (3.94); IR ν_{max}^{KBr} cm⁻¹: 1704 and 1642; ¹H NMR: δ 5.44 and 6.21 (each 1H, s); ¹³C NMR: δ 119.6 (t), 152.9 (s) and 209.3 (s)], an acetoxyl group [¹H NMR: δ 1.99 (3H, s); ¹³C NMR: δ 20.8 (q) and 170.9 (s)], and a ketalic group [¹³C NMR: δ 98.9 (s)]. In addition to the above-mentioned signals, the ¹³C NMR spectrum also showed signals due to one methyl, six methylenes (including two oxygenated ones), six methines (including three oxygen-bearing ones) and three quaternary carbons. These facts

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Received date: 1999-08-25, Accepted date: 1999-09-23

and the degree of unsaturation indicated the presence of pentacyclic ring system. With consideration of the types of diterpenoids in the *Isodon* genus (Takeda *et al.*, 1992; Wang *et al.*, 1998), the basic skeleton of **1** was presumed to be 7β -hydroxy- 7α , 20-epoxy-*ent*-kaur-16-en-15-one, which was substituted by three hydroxyls and one acetoxyl.

The signals at $\delta 3.63$ (1H, br s), $\delta 64.6$ (d) and the downfield shift of C-10 in NMR spectra suggested one hydroxyl group at C-1. The peak form of H-1, a broad singlet, resulted from the β -orientation of 1-OH (Wang *et al.*, 1997). On the basis of $^1\text{H}-^1\text{H}$ COSY spectrum, the other two hydroxyls were assigned to C-6 and C-14, which was further confirmed by HMQC experiment. The acetoxyl was presumed to be at C-19 because only one methyl at $\delta 27.6$ (Me-18) was observed. The methylene at $\delta 67.2$ (C-19) and the correlation between Ha, b-19 and the ester carbonyl at $\delta 170.9$ in HMBC spectrum proved the presumption. According to the NOE effects (H-6 α with M-18 and Ha-19; H-14 α with H-11 α and H-20 α), the two hydroxyls at C-6 and C-14 both had β -orientation. In conclusion, xerophilusin G (**1**) was elucidated as 1β , 6β , 7β , 14β -tetrahydroxy-19-acetoxy- 7α , 20-epoxy-*ent*-kaur-16-en-15-one.



- 1: $R_1 = \text{OH}$, $R_2 = \text{OAc}$
 2: $R_1 = \text{H}$, $R_2 = \text{OAc}$
 3: $R_1 = \text{H}$, $R_2 = \text{H}$

Xerophilusin H (**2**), colorless needles, mp: $238 \sim 240^\circ\text{C}$, $[\alpha]_D^{25} - 149.4^\circ$ (c 0.31, $\text{C}_5\text{H}_5\text{N}$); $\text{UV}\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 240.5 (3.98); $\text{IR}\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3498, 3201, 2955, 2888, 1734, 1705, 1641, 1403, 1369, 1297, 1250, 1064. It has the molecular formula of $\text{C}_{22}\text{H}_{30}\text{O}_7$ established by positive HRFABMS (obsd 407.1992, calcd 407.2070). Most of the proton and carbon signals were in agreement with those of **1** except for several (Tables 1 and 2). The singlet at $\delta 5.21$ (H-14 α) in **1** shifted upfield and changed into a doublet at $\delta 2.34$ (H-14 α) and a doublet of doublet at $\delta 2.51$ (H-14 β) in **2**. At the same time, the signal of H-13 α also varied from a doublet at $\delta 3.17$ in **1** into a doublet of doublet at $\delta 2.89$ in **2**. The absence of a hydroxyl at C-14 in **2** was the reasonable explanation for these differences, which was further verified by the alternations of C-8, C-14 and C-13 between **1** and **2** in the ^{13}C NMR spectra (Table 2). Thus, xerophilusin H (**2**) was identified as 1β , 6β , 7β -trihydroxy-19-acetoxy- 7α , 20-epoxy-*ent*-kaur-16-en-15-one.

Xerophilusin I (**3**), white amorphous powders, $[\alpha]_D^{25} - 146.3^\circ$ (c 0.41, $\text{C}_5\text{H}_5\text{N}$); $\text{UV}\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 240.5 (3.98); $\text{IR}\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3464, 3359, 3233, 2930, 1707, 1642, 1453, 1333, 1274, 1193, 1061. It has a molecular weight of 349.2039 (positive HRFABMS) corresponding to $\text{C}_{20}\text{H}_{29}\text{O}_5$.

The difference between **2** and **3** was that Me-19 in **3** was not occupied by any group, which was proved by the following facts. In the ^{13}C NMR spectrum of **3**, no signals attributable to an acetoxy were observed while a methyl signal at $\delta 23.1$ replaced the signal at $\delta 67.1$ (t, C-19) in **2**. Furthermore, the signals of C-3 and Me-18 in **3** shifted downfield without the γ -steric compression effect of OAc. A comparison of the ^1H NMR data showed that the disappearance of two AB-type doublets and a 3H singlet of OAc, and the emergence of a methyl signal at $\delta 1.14$ (Me-19) were notable characteristics of **3**. Therefore, xerophilusin I (**3**) was determined to be 1β , 6β , 7β -trihydroxy- 7α , 20 -epoxy-*ent*-kaur-16-en-15-one.

Table 1 ^1H NMR Data for Compounds **1**–**3** in $\text{C}_5\text{D}_5\text{N}$ (400 MHz, δ in ppm, mult. J in Hz)

proton	1	2	3
1 α	3.63 (br s)	3.66 (br s)	3.66 (br s)
2 α , β	1.77 (overlap)	1.78 (m)	1.74 (m)
3 α	2.05 (dd, 5.4, 13.6)	2.15 (overlap)	2.21 (m)
3 β	1.67 (d, 13.6)	1.69 (dd, 2.9, 13.5)	1.22 (d, 13.2)
5 β	2.34 (d, 5.9)	2.38 (d, 5.5)	2.13 (d, 5.1)
6 α	4.44 (d, 5.9)	4.44 (d, 5.5)	4.31 (d, 5.1)
9 β	2.66 (dd, 5.9, 12.5)	2.51 (dd, 4.6, 12.3)	2.51 (dd, 5.3, 12.5)
11 α	1.90 (m)	1.83 (m)	1.86 (m)
11 β	2.11 (m)	2.07 (m)	2.11 (overlap)
12 α	2.37 (overlap)	2.13 (overlap)	2.12 (overlap)
12 β	1.53 (m)	1.33 (m)	1.36 (m)
13 α	3.17 (d, 9.4)	2.89 (dd, 4.0, 9.5)	2.92 (dd, 3.8, 9.2)
14 α	5.21 (s)	2.34 (d, 12.3)	2.38 (d, 12.2)
14 β	—	2.51 (dd, 4.6, 12.3)	2.53 (dd, 4.2, 12.2)
17a	6.21 (s)	5.94 (s)	5.94 (s)
17b	5.44 (s)	5.23 (s)	5.24 (s)
Me-18	1.43 (s)	1.42 (s)	1.30 (s)
Me-19	—	—	1.14 (s)
19a	4.78 (ABd, 11.2)	4.77 (ABd, 12.0)	—
19b	4.47 (ABd, 11.2)	4.46 (ABd, 12.0)	—
20a	4.22 (ABd, 10.1)	4.19 (ABd, 10.1)	4.12 (ABd, 9.8)
20b	4.14 (ABd, 10.1)	4.06 (ABd, 10.1)	4.08 (ABd, 9.8)
OAc	1.99 (s)	1.96 (s)	—

Table 2. ^{13}C NMR data for compounds **1**–**3** in $\text{C}_5\text{D}_5\text{N}$ (100 MHz, δ in ppm)

carbon	1	2	3
1	64.6 (d)	64.3 (d)	64.8 (d)
2	27.4 (t)	27.3 (t)	27.6 (t)
3	28.6 (t)	28.5 (t)	34.5 (t)
4	37.8 (s)	37.9 (s)	34.2 (s)
5	56.6 (d)	57.3 (d)	56.4 (d)
6	73.6 (d)	73.7 (d)	74.7 (d)
7	98.9 (s)	96.5 (s)	96.4 (s)
8	62.3 (s)	59.6 (s)	59.9 (s)

续表 2

carbon	1	2	3
9	48.0 (d)	45.8 (d)	46.0 (d)
10	41.3 (s)	41.4 (s)	41.4 (s)
11	16.3 (t)	16.4 (t)	16.3 (t)
12	30.3 (t)	29.9 (t)	30.0 (t)
13	44.0 (d)	35.2 (d)	35.3 (d)
14	74.0 (d)	27.0 (t)	27.0 (t)
15	209.3 (s)	212.2 (s)	211.0 (s)
16	152.9 (s)	154.0 (s)	154.2 (s)
17	119.6 (t)	116.3 (t)	116.2 (t)
18	27.6 (q)	27.4 (q)	33.7 (q)
19	67.2 (t)	67.1 (t)	23.1 (q)
20	66.7 (t)	66.5 (t)	66.0 (t)
OAc	170.9 (s)	170.8 (s)	—
	20.8 (q)	20.7 (q)	—

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