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OLIGOSTILBENES FROM *VITIS BETULIFOLIA*

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Key Word Index—*Vitis betulifolia*; Vitaceae; stems; oligostilbenes; betulifol A; betulifol B; resveratrol; (+)-ε-viniferin; ampelopsin A; ampelopsin C; heyneanol A; hopeaphenol; vitisin A; structure elucidation.

Abstract—Two novel distilbenes, betulifol A and betulifol B, were isolated from stems of *Vitis betulifolia* together with the previously known resveratrol, (+)-ε-viniferin; ampelopsin A; ampelopsin C; heyneanol A; hopeaphenol and vitisin A. Their structures were elucidated by 1D and 2D NMR analyses. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Vitis betulifolia Diels et Gilg is distributed in the southeast of Tibet, east of Yunnan, Sichuan and Hubei, and south of Shanxi province in China [1]. So far, the chemical composition of this plant has never been reported. We now report on the isolation and structure determination of two new distilbenes, betulifol A(**1**) and betulifol B(**2**), along with resveratrol [2], two distilbenes, (+)-ε-viniferin [3] and ampelopsin A [3,4], a tristilbene, ampelopsin C [3,4] and three tetrastilbenes, heyeanol A [3], hopeaphenol [5–8] and vitisin A [9] from the stems of *V. betulifolia*.

RESULTS AND DISCUSSION

Betulifol A(**1**) gave a $[M+1]^+$ ion at *m/z* 453 (FAB mass spectrum) and high resolution positive FAB mass spectrometry established the molecular formula of **1** as $C_{28}H_{20}O_6$. This was supported by the ^1H and ^{13}C NMR spectra. This formula corresponded to a distilbene. The UV and IR spectra showed similar patterns to those of other *Vitis* oligostilbenes such as ampelopsin A [3,4]. The 2D NMR spectra, including HH-, CH-, and long range C-H COSY of **1**, allowed assignment of all proton and carbon signals (Tables 1 and 2). The planar structure was deduced mainly from the long range C-H COSY results.

The relative configuration of **1** was established by NOESY. The *trans*-orientation of the two hydrogens of the furan nucleus was deduced from the NOEs between H-7a(b)/H-14a(b) and H-8a(b)/H-2(6)a(b).

Table 1. ^1H NMR data for compounds **1**(pyridine-d_5) and **2**(acetone-d_6)

H	1	2
2(6)a	7.73 (*d*, *J* = 8.3 Hz)	7.15 (*d*, *J* = 8.4Hz)
3(5)a	7.25 (*d*, *J* = 8.3 Hz)	6.83 (*d*, *J* = 8.4 Hz)
7a	5.79 (*d*, *J* = 10.3 Hz)	5.35 (*d*, *J* = 5.1 Hz)
8a	4.81 (*d*, *J* = 10.3 Hz)	4.40 (*d*, *J* = 5.1 Hz)
10a		6.04 (*d*, *J* = 2.1 Hz)
12a	6.83 (*brs*)	6.04 (*d*, *J* = 2.1 Hz)
14a	6.76 (*brs*)	6.04 (*d*, *J* = 2.1 Hz)
2(6)b	7.73 (*d*, *J* = 8.3 Hz)	6.93 (*d*, *J* = 8.4 Hz)
3(5)b	7.25 (*d*, *J* = 8.3 Hz)	6.65 (*d*, *J* = 8.4 Hz)
7b	5.79 (*d*, *J* = 10.3 Hz)	4.93 (*d*, *J* = 8.7 Hz)
8b	4.81 (*d*, *J* = 10.3 Hz)	4.58 (*d*, *J* = 8.7 Hz)
12b	6.83 (*brs*)	6.37 (*d*, *J* = 2.0 Hz)
14b	6.76 (*brs*)	6.67 (*d*, *J* = 2.0 Hz)

Considering the torsion of ring A, its conformation must be a boat form with H-8a and H-8b in the same orientation. Therefore, the structure of **1** was concluded to be as shown in formula **1**.

Betulifol B(**2**) was assigned the molecular formula $C_{28}H_{24}O_8$ by high resolution positive FAB mass spectrometry. This was also supported by the ^1H and ^{13}C NMR spectra. This formula corresponded to an oxidized distilbene. The UV and IR spectra showed similar patterns to **1** and ampelopsin A [3,4]. Comparing the ^1H and ^{13}C NMR data of **2** to those of (+)-ε-viniferin [3], compound **2** had signals at δ 74.5 (*d*) and 75.3 (*d*) and δ 4.93 (*d*, *J* = 8.7 Hz) and 4.58 (*d*, *J* = 8.7 Hz), but the signals for olefinic carbons found in (+)-

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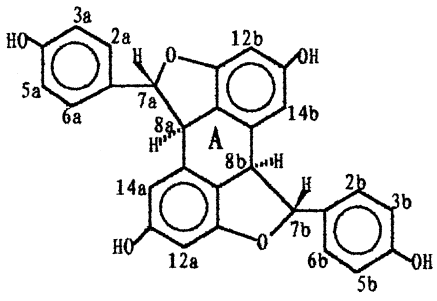
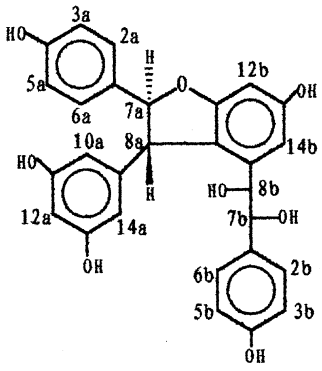


1



2

Table 2. ^{13}C NMR data of compounds **1**(pyridine-d_5) and **2**(acetone-d_6)

C	1	2	C	1	2
1a	130.5 *s*	134.2 *s*	1b	130.5 *s*	131.2 *s*
2(6)a	130.3 *d*	128.7 *d*	2(6)b	130.3 *d*	127.5 *d*
3(5)a	116.7 *d*	116.5 *d*	3(5)b	116.7 *d*	115.4 *d*
4a	159.7 *s*	159.1 *s*	4b	159.7 *s*	158.0 *s*
7a	92.8 *d*	93.7 *d*	7b	92.8 *d*	74.5 *d*
8a	48.3 *d*	56.9 *d*	8b	48.3 *d*	75.3 *d*
9a	136.8 *s*	148.0 *s*	9b	136.8 *s*	134.6 *s*
10a	121.8 *d*	106.9 *d*	10b	121.8 *s*	119.2 *s*
11a	160.8 *s*	160.0 *s*	11b	160.8 *s*	161.9 *s*
12a	97.3 *d*	102.0 *d*	12b	97.3 *d*	96.7 *d*
13a	159.7 *s*	160.0 *s*	13b	159.7 *s*	159.1 *s*
14a	104.5 *d*	106.9 *d*	14b	104.5 *d*	108.2 *d*

ε-viniferin were absent; the other signals were very similar. Thus, we established that **2** was the oxidized form of (+)-ε-viniferin with the structure shown in formula **2**.

EXPERIMENTAL

^1H and ^{13}C NMR: 400 and 100 MHz, respectively. EIMS and FABMS: VG Auto Spec 3000 instrument.

Extraction and isolation

Dried and finely powdered stems of *V. betulifolia* (2.8 kg), collected in 1996 at Maoxian, Sichuan Province, China, were extracted with Me_2CO at room temp. Me_2CO extracts were concd under red. pres. and fractionated by a series of solvent partitions into an EtOAc-soluble fr. The residue (40 g) of this fr. was subjected to CC over silica gel, the column was eluted successively with $CHCl_3$-MeOH(10:0–10:1), followed by PTLC to yield 120 mg **1** and 3 mg **2**.

Betulifol A (**1**). White solid, $[\alpha]_D$ +28.9(MeOH, c 0.28). IR ν_{max}^{KBr} (cm^{-1}): 3500, 3400, 1629, 1618, 1593, 1519, 1451, 1174, 1125, 979, 828; UV λ_{max}^{MeOH}nm: 282; EIMS *m/z*: 434[M−H_2O]$^+$, 416, 398, 374, 356, 338, 414, 296, 278, 263, 241, 225, 167, 121, 107, 91, 71; FAB(positive) MS *m/z*: 453[M+1]$^+$; HR FAB-(positive)MS *m/z*: 453.1407($C_{28}H_{21}O_6$, M+1, cald. 453.1338); ^1H and ^{13}C NMR: Tables 1 and 2.

Betulifol B(**2**). Brown solid, $[\alpha]_D$+81.6(MeOH; c 0.19). IR ν_{max}^{KBr} (cm^{-1}): 3409, 1613, 1601, 1514, 1451, 1336, 1241, 1172, 1158, 1125, 833; UV λ_{max}^{MeOH}nm: 282; HRFAB-MS(positive) *m/z*: 489.1513 ($C_{28}H_{25}O_8$)[M+1]$^+$, cald. 489.1548); ^1H and ^{13}C NMR: Tables 1 and 2.

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