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OLIGOSTILBENES FROM *VITIS HEYNEANA*

WEN-WU LI,* LI-SHENG DING,† BO-GANG LI† and YAO-ZU CHEN*‡

*Department of Chemistry, Zhejiang University, Hangzhou 310027, China; †Chengdu Institute of Biology, Academia Sinica, Chengdu 610041, China

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Key Word Index—*Vitis heyneana*; Vitaceae; stems; stereochemistry; oligostilbenes; heyneanol A; ampelopin C; ampelopsin A; (+)-ε-viniferin; structural elucidation.

Abstract—A novel tetrastilbene, heyneanol A, was isolated from stems of *Vitis heyneana* together with the previously known ampelopsin C, ampelopsin A and (+)-ε-viniferin. Its complex polycyclic structure was elucidated by 1D and 2D NMR analyses.

INTRODUCTION

Vitis heyneana Roem. & Schult (*V. quinquangularis* Rehd.) is a traditional drug used for the treatment of arthritis, fever, carbuncles and inflammatory conditions [1]. So far, the chemical composition of this genus has never been reported. We now report on the isolation and structural determination of a tetrastilbene, heyneanol A (**1**), along with a tristilbene, ampelopsin C (**2**) [2] and two distilbenes, amelopsin A (**3**) [2] and (+)-ε-viniferin (**4**) [3] from the stems of *V. heyneana*.

RESULTS AND DISCUSSION

Compound **1** was isolated as a brown solid {$[\alpha]_D$ −53° (methanol; *c* 0.31)}, together with the previously known compounds **2**–**4**. Compound **1** showed a $[M+1]^+$ ion at *m/z* 907 (FAB mass spectrum) in agreement with the molecular formular $C_{56}H_{42}O_{12}$. This was supported by the ^{13}C and ^1H NMR spectra. This formula corresponds to a tetrastilbene. The UV and IR spectra showed similar patterns to those of other vitis oligostilbenes [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 aryls on ring A_3 was deduced from the NOEs between H-7a/H-10(14)a and H-8a/H-2(6)a. Two similar relationships were observed for the protons on ring B and D. The spatial relationship between rings A_3 and B_3 was determined by NOESY. The presence of NOEs between H-8a and H-8b indicated the spatial vicinity of these protons. Furthermore, the fact that the ^1H NMR signals of H-10(14)a and H-2(6)b appear at relatively higher field is accounted for by the overlapping of rings A_2 and B_1. Hence, we determined that the relative configuration between rings A_3 and B_3 was rel-(8a*S*, 8b*R*). (+)-ε-Viniferin {**4**, $[\alpha]_D$ +39° (circular dichroism: $\Delta\varepsilon_{322}$ −2.06, $\Delta\varepsilon_{287}$ −1.72, $\Delta\varepsilon_{260}$ +2.41, $\Delta\varepsilon_{235}$ +17.71)} was identified by ^1H and ^{13}C NMR and its absolute configuration was determined to be 7a*S*, 8a*S* in comparison with (−)-ε-viniferin [3]. On biogenetic grounds, we deduce that **1** was formed by the coupling of two (+)-ε-viniferin molecules and that its absolute configuration may be deduced as 7a*S*, 8a*S*, 7b*R*, 8b*R*, 7d*S*, 8d*S*. The stereostructure of **1** was thus concluded to be as shown in Fig. 1.

EXPERIMENTAL

^1H and ^{13}C NMR; Me_2CO-d_6 using TMS as int. standard.

Isolation. Stems of *V. heyneana* were collected from Junlian, Sichuan Province, China, in October, 1994, and identified by Prof. Chao-Luan Li, Chengdu Institute of Biology. A voucher specimen is deposited in Chengdu Institute of Biology. The dried stems (2.5 kg) were extracted with EtOH. The EtOH extracts were concd under red. pres. and fractionated by a series of solvent partitions into an EtOAc-soluble phenolic fr. The residue (50 g) of this fr. was fractionated first by CC and finally by TLC (silica gel) giving **1** (200 mg), **2** (650 mg), **3** (27 mg) and **4** (25 mg).

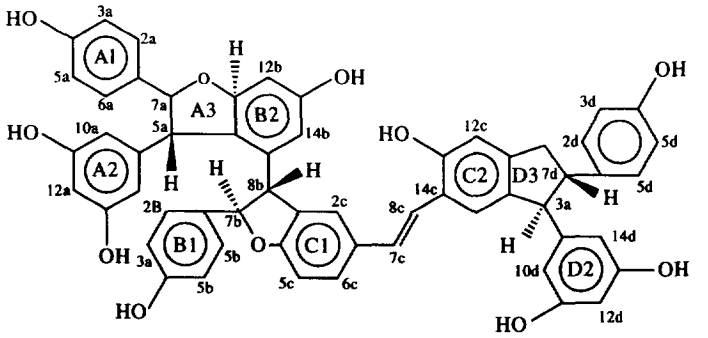
‡Author to whom correspondence should be addressed.

Table 1. ^{1}H NMR data for compounds **1–4** (400 MHz)

H	1	2	3	4
2(6)a	7.25*d*(8.6)	7.18*d*(8.4)	6.91*d*(8.4)	7.21*d*(7.0)
3(5)a	6.92*d*(8.6)	6.68*d*(8.4)	6.66*d*(8.4)	6.83*d*(7.0)
7a	5.42*d*(5.0)	5.26*d*(2.9)	5.46*d*(5.1)	5.44*d*(5.4)
8a	4.52*d*(5.0)	3.62*dd*(11.7, 2.9)	5.41*br s*	4.46*d*(5.4)
10a	6.11*d*(2.2)			6.24*br s*
12a	6.23*t*(2.2)	6.17*s*	6.16*d*(2.0)	6.24*br s*
14a	6.11*d*(2.0)		6.63*d*(2.0)	6.24*br s*
2(6)b	6.59*d*(8.6)	7.25*d*(8.4)	7.11*d*(8.4)	7.19*d*(7.0)
3(5)b	6.63*d*(8.6)	6.80*d*(8.4)	6.77*d*(8.4)	6.74*d*(7.0)
7b	5.55*d*(5.0)	5.83*d*(11.7)	5.76*d*(11.7)	6.91*d*(16.2)
8b	4.32*d*(5.0)	4.45*d*(11.7)	4.17*d*(11.7)	6.71*d*(16.2)
12b	6.33*d*(2.0)	6.33*d*(2.0)	6.42*d*(2.0)	6.33*d*(2.0)
14b	6.25*d*(2.0)	6.18*d*(2.0)	6.23*d*(2.0)	6.77*d*(2.0)
2c	6.83*d*(2.0)	7.01*d*(8.4)		
3c		6.72*d*(8.4)		
5c	6.77*d*(8.6)	6.72*d*(8.4)		
6c	7.17*dd*(8.6, 2.0)	7.01*d*(8.4)		
7c	6.77*d*(15.6)	4.23*d*(9.4)		
8c	6.65*d*(15.6)	3.79*dd*(11.7, 9.4)		
10c		6.24*d*(2.0)		
12c	6.33*d*(2.0)	6.18*t*(2.0)		
14c	6.67*d*(2.0)	6.24*d*(2.0)		
2(6)d	7.19*d*(8.6)			
3(5)d	6.83*d*(8.6)			
7d	5.39*d*(5.5)			
8d	4.44*d*(5.5)			
10(14)d	6.21*d*(2.0)			
12d	6.24*d*(2.0)			

Table 2. ^{13}C NMR data for compounds **1–4** (100 MHz)

C	1	2	3	4	C	1	2
1a	134.1	133.1	129.7	133.6	1c	131.7	133.1
2(6)a	127.7	130.5	128.7	127.9	2c	125.4	129.6
3(5)a	116.1	115.9	115.6	116.0	3c	132.5	116.2
4a	158.1	155.7	159.0	157.9	4c	159.7	155.7
7a	94.0	61.7	44.1	93.6	5c	110.5	116.2
8a	57.1	48.3	71.3	57.0	6c	126.4	129.6
9a	147.1	144.7	140.8	147.1	7c	130.9	52.6
10a	106.9	125.0	118.7	106.8	8c	124.0	37.7
11a	160.2	159.2	160.0	159.5	9c	136.2	141.5
12a	102.1	102.3	97.4	101.9	10c	119.7	121.6
13a	160.2	157.6	159.6	159.5	11c	162.4	159.9
14a	106.9	107.2	110.9	106.8	12c	96.6	97.1
1b	132.1	132.7	132.4	129.9	13c	159.7	159.1
2(6)b	127.5	130.5	129.8	128.4	14c	104.5	106.0
3(5)b	115.9	115.9	116.1	116.1	1d	133.7	
4b	157.9	155.7	158.0	157.9	2(6)d	127.8	
7b	91.3	90.6	88.5	129.9	3(5)d	116.3	
8b	52.0	58.0	49.5	123.2	4d	157.7	
9b	141.9	147.9	142.7	136.1	7d	94.0	
10b	119.8	129.9	118.8	119.5	8d	57.0	
11b	162.3	159.1	156.5	162.2	9d	147.2	
12b	96.5	102.3	101.9	96.6	10(14)d	106.9	
13b	159.4	156.7	156.5	159.2	11(13)d	159.9	
14b	106.9	107.2	105.4	104.0	12d	102.4	



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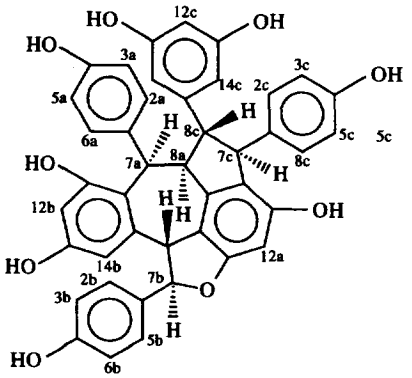

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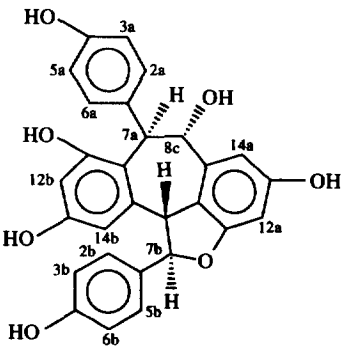

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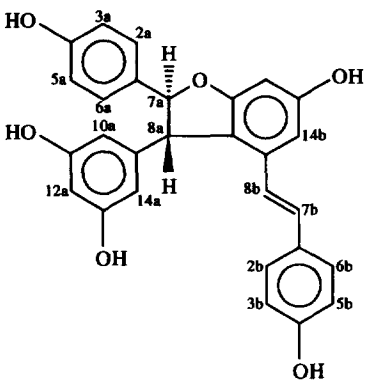

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Fig. 1. Structures of compounds **1–4**.

Heyneanol A (**1**). Brown solid. $[\alpha]_D$ −53° (MeOH; *c* 0.30). FABMS *m/z*: 907 $[M+1]^+$; IR ν_{max} cm^{-1}: 3388, 1612, 1516, 1448, 1296, 961, 832, 758; UV (nm, MeOH): 284, 320. ^1H and 13C NMR: Tables 1 and 2.

Apelopsin C (**2**). Brown solid. FABMS *m/z*: 681 $[M+1]^+$. ^1H and ^{13}C NMR: Tables 1 and 2.

Ampelopsin A (**3**). Brown solid. FABMS *m/z*: 471 $[M+1]^+$. ^1H and ^{13}C NMR; Tables 1 and 2. (+)-ε-Viniferin (**4**), Brown solid $[\alpha]_D$ +39° (MeOH; *c* 0.40), CD: $\Delta\varepsilon_{322}$ −2.06, $\Delta\varepsilon_{287}$ −1.72, $\Delta\varepsilon_{260}$ +2.41, $\Delta\varepsilon_{235}$ +17.71. ^1H and ^{13}C NMR: Tables 1 and 2.

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