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Two new stilbenetetramers from the stem of *Vitis vinifera* 'Kyohou'

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Abstract—Two new stilbenetetramers named (+)-viniferol B and (+)-viniferol C having a bicyclo[5.3.0]decane ring system were isolated from the stem of *Vitis vinifera* 'Kyohou' and the structures were elucidated on the basis of the spectral evidence.

1. Introduction

In our previous paper, we reported the isolation and structure of (+)-viniferol A, a novel stilbenetetramer having a bicyclo[6.3.0]undecane ring system, from the stem of *Vitis vinifera* 'Kyohou' cultivated in Wakayama Prefecture, Japan.[1] Our further study of the constituents of the above plant led to the isolation of two new stilbenetetramers named (+)-viniferol B and (+)-viniferol C. In this paper, we describe the isolation and structural elucidation of the stilbenetetramers having a bicyclo[5.3.0]decane ring system from the stem of *V. vinifera* Kyohou.

2. Results and discussion

2.1. Isolation

The ethyl acetate soluble fraction described in the previous paper[1] of the stem of *V. vinifera* Kyohou was fractionated by medium-pressure column chromatography (MPCC) using silica-gel to give 13 fractions. The fraction (F11) including (+)-viniferol A (**1**)[1] was further separated by MPCC using reversed phase silica gel (C-8) followed by recycled HPLC to give (+)-viniferol B (**2**) together with (+)-viniferol A (**1**).[1] The previous fraction (F10) was successively separated by MPCC using reversed phase silica gel (C-8), by column chromatography using Sephadex LH-20 and preparative TLC to give (+)-viniferol C (**3**).

2.2. Structure of (+)-viniferol B

(+)-Viniferol B (**2**), $[\alpha]_D$=+43.2° (*c* 0.28, MeOH) was found to have the molecular formula $C_{56}H_{42}O_{12}$ determined by high-resolution FABMS. The ^{1}H NMR spectrum in methanol-d_4 of **2** exhibited signals for four sets of AA′XX′-type (1,4-disubstituted) aromatic hydrogens at δ 7.06 and 6.64 (each 2H, d, *J*=8.8 Hz); 6.41 and 6.06 (each 2H, d, *J*=8.8 Hz); 6.69 and 6.27 (each 2H, d, *J*=8.8 Hz); 7.07 and 6.74 (each 2H, d, *J*=8.4 Hz), two sets of *meta*-coupled aromatic hydrogens δ 6.23 and 5.90 (each 1H, d, *J*=2.2 Hz); 6.16 and 5.69 (each 1H, d, *J*=2.2 Hz), and one set of AX_2-type *meta*-coupled aromatic hydrogens δ 5.80 (2H, d, *J*=2.2 Hz) and 6.07 (1H, t, *J*=2.2 Hz), and an uncoupled aromatic hydrogen δ 6.12 (1H, s), as shown in Table 1. These were in good accordance with (+)-viniferol B being a tetramer of resveratrol (3,5,4′-trihydroxystilbene). By the comparison of the ^{1}H NMR data of (+)-ε-viniferin (**4**) and other oligostilbenes (**5**, **6**), the signals for two sets of aliphatic hydrogen at δ 5.65 and 4.25 (each 1H, d, *J*=12.1 Hz); 5.19 and 4.06 (each 1H, d, *J*=5.1 Hz) suggested the presence of two dihydrobenzofuran moieties bearing 4-oxyphenyl and 3,5-dioxyphenyl groups characteristic of oligostilbenes derived from the resveratrol molecule. The four aliphatic hydrogens coupled at δ 5.34 (1H, d, *J*=3.3 Hz, H-7b), 3.81 (1H, ddd, *J*=8.1, 3.3, 2.2 Hz, H-8b), 3.54 (1H, d, *J*=8.1 Hz, H-7c) and 4.57 (1H, s, H-8c), along with the biogenetic consideration, suggested the presence of a bicyclo[5.3.0]decane ring system. This was further confirmed by the following evidence. The correlations of the HMBC spectrum were observed between H-8a and C-9a, C-10b, between H-7b and C-10a, C-11a, C-2b (6b), C-9b, between H-8b and C-9b, between H-8c and C-13b, C-14b, C-9c, C-10c, respectively. The partial structure (C-9c to C-14d) was characterized by similarity of the ^{13}C NMR data of **2** with those of (+)-ε-viniferin (**4**). From the discussion above, (+)-viniferol B (**2**) seems to be a

Keywords: oligostilbene; *Vitis vinifera*; Kyohou; resveratrol tetramer.

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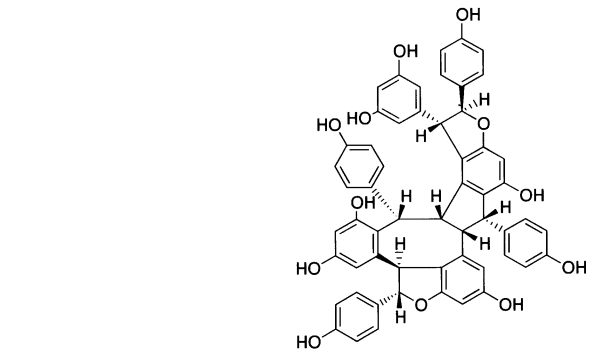
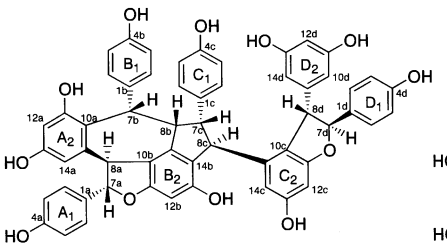


(+)-Viniferol A (**1**)



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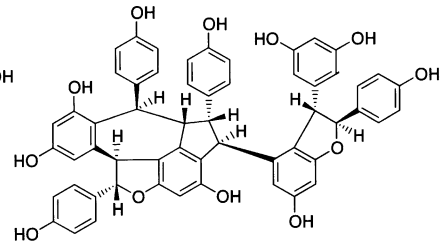

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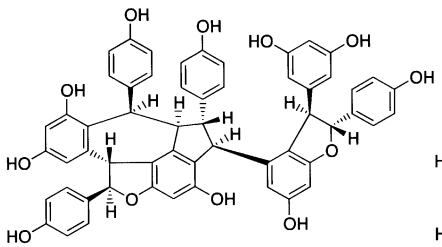
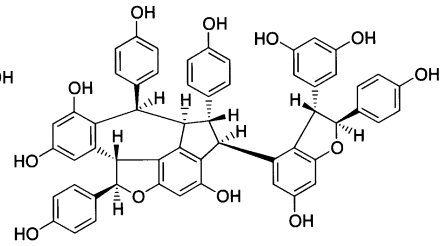


(–)-Vaticanol B (**5**)



(–)-Vaticaphenol A (**6**)

Table 1. ^{1}H NMR data of compounds **2**–**6**

Positions	**2**	**3**	**5**	**6**	**4**
2a, 6a	7.06 (2H, d, 8.8)	7.54 (2H, d, 8.8)	7.23 (2H, d, 8.8)	7.22 (2H, d, 8.5)	
3a, 5a	6.64 (2H, d, 8.8)	6.88 (2H, d, 8.8)	6.79 (2H, d, 8.8)	6.78 (2H, d, 8.5)	
7a	5.65 (1H, d, 12.1)	5.84 (1H, d, 11.4)	5.77 (1H, d, 11.7)	5.76 (1H, d, 11.0)	
8a	4.25 (1H, dd, 12.1, 2.2)	5.01 (1H, dd, 11.4, 2.2)	4.44 (1H, d, 11.7)	4.43 (1H, d, 11.0)	
12a	6.23 (1H, d, 2.2)	5.94 (1H, d, 2.2)	6.29 (1H, d, 2.0)	6.27 (1H, d, 1.8)	
14a	5.90 (1H, d, 2.2)	6.16 (1H, d, 2.2)	6.12 (1H, d, 2.0)	6.11 (1H, d, 1.8)	
2b, 6b	6.41 (2H, d, 8.8)	6.81 (2H, brs)	7.17 (2H, d, 8.8)	7.16 (2H, d, 8.3)	
3b, 5b	6.06 (2H, d, 8.8)	6.44 (2H, brd, 8.4)	6.70 (2H, d, 8.8)	6.69 (2H, d, 8.3)	
7b	5.34 (1H, d, 3.3)	4.11 (1H, d, 11.7)	5.21 (1H, d, 3.9)	5.20 (1H, d, 3.0)	
8b	3.81 (1H, ddd, 8.1, 3.3, 2.2)	3.95 (1H, ddd, 11.7, 6.6, 2.2)	3.13 (1H, dd, 11.3, 3.9)	3.10 (1H, brd, 11.5)	
12b	6.12 (1H, s)	6.13 (1H, s)	6.05 (1H, s)	6.04 (1H, s)	
2c, 6c	6.69 (2H, d, 8.8)	6.03 (2H, d, 8.8)	6.42 (2H, d, 8.8)	6.40 (2H, d, 8.5)	7.17 (2H, d, 8.4)
3c, 5c	6.27 (2H, d, 8.8)	6.19 (2H, d, 8.8)	6.52 (2H, d, 8.8)	6.50 (2H, d, 8.5)	6.73 (2H, d, 8.4)
7c	3.54 (1H, d, 8.1)	3.63 (1H, d, 6.6)	4.10 (1H, dd, 11.3,10.7)	4.09 (1H, t, 11.5)	6.90 (1H, d, 16.5)
8c	4.57 (1H, s)	3.92 (1H, s)	4.55 (1H, d, 10.7)	4.55 (1H, d, 11.5)	6.71 (1H, d, 16.5)
12c	6.16 (1H, d, 2.2)	6.28 (1H, d, 2.2)	6.21 (1H, d, 2.0)	6.19 (1H, d, 2.0)	6.32 (1H, d, 2.2)
14c	5.69 (1H, d, 2.2)	6.05 (1H, d, 2.2)	6.49 (1H, d, 2.0)	6.47 (1H, d, 2.0)	6.72 (1H, d, 2.2)
2d, 6d	7.07 (2H, d, 8.4)	7.27 (2H, d, 8.8)	7.19 (2H, d, 8.8)	7.19 (2H, d, 8.8)	7.20 (2H, d, 8.4)
3d, 5d	6.74 (2H, d, 8.4)	6.94 (2H, d, 8.8)	6.78 (2H, d, 8.8)	6.77 (2H, d, 8.8)	6.82 (2H, d, 8.4)
7d	5.19 (1H, d, 5.1)	5.31 (1H, d, 3.3)	5.38 (1H, d, 4.7)	5.37 (1H, d, 5.5)	5.42 (1H, d, 5.5)
8d	4.06 (1H, d, 5.1)	4.38 (1H, d, 3.3)	4.68 (1H, d, 4.7)	4.68 (1H, d, 5.5)	4.47 (1H, d, 5.5)
10d, 14d	5.80 (1H, d, 2.2)	5.90 (1H, d, 2.2)	6.10 (1H, d, 2.4)	6.10 (1H, brs)	6.23 (2H, s)
12d	6.07 (1H, t, 2.2)	5.99 (1H, t, 2.2)	6.30 (1H, t, 2.4)	6.28 (1H, t, 2.5)	6.23 (1H, s)

The data of **2** and **3** were measured in methanol-d_4, and the data of **4**, **5** and **6** were taken in acetone-d_6.

Table 2. ^{13}C NMR data of compounds **2**–**6** in methanol-d_4

Positions	2	3	5	6	4
1a	130.2 (s)	130.4 (s)	130.8 (s)	130.7 (s)	
2a, 6a	130.4 (d)	130.5 (d)	130.2 (d)	130.1 (d)	
3a, 5a	116.5 (d)	116.8 (d)	116.04 (d)	115.8 (d)	
4a	159.0 (s)	159.8 (s)	158.5 (s)	158.5 (s)	
7a	91.6 (d)	91.2 (d)	90.4 (d)	90.3 (d)	
8a	48.8 (d)	48.8 (d)	48.8 (d)	48.8 (d)	
9a	141.8 (s)	142.4 (s)	141.8 (s)	141.7 (s)	
10a	126.8 (s)	122.5 (s)	124.5 (s)	124.4 (s)	
11a	155.1 (s)	158.3 (s)	155.7 (s)	155.6 (s)	
12a	102.0 (d)	103.9 (d)	101.6 (d)	101.5 (d)	
13a	156.9 (s)	156.7 (s)	156.7 (s)	156.6 (s)	
14a	106.1 (d)	105.3 (d)	105.8 (d)	105.6 (d)	
1b	133.9 (s)	133.3 (s)	133.5 (s)	133.4 (s)	
2b, 6b	130.8 (d)	132.9 (d)	130.7 (d)	130.6 (d)	
3b, 5b	114.1 (d)	115.1 (d)	115.5 (d)	115.9 (d)	
4b	154.0 (s)	157.5 (s)	155.9 (s)	155.8 (s)	
7b	39.6 (d)	46.3 (d)	37.1 (d)	36.9 (d)	
8b	48.6 (d)	47.8 (d)	53.1 (d)	53.1 (d)	
9b	145.0 (s)	147.6 (s)	143.2 (s)	143.1 (s)	
10b	117.0 (s)	118.5 (s)	115.78 (s)	115.6 (s)	
11b	160.0 (s)	160.2 (s)	158.8 (s)	158.7 (s)	
12b	96.0 (d)	96.3 (d)	96.5 (d)	96.4 (d)	
13b	155.1 (s)	155.8 (s)	154.9 (s)	154.8 (s)	
14b	122.1 (s)	123.0 (s)	122.1 (s)	122.1 (s)	
1c	135.0 (s)	134.8 (s)	131.4 (s)	131.3 (s)	130.0 (s)
2c, 6c	130.5 (d)	129.4 (d)	129.2 (d)	129.2 (d)	127.9 (d)
3c, 5c	115.4 (d)	115.1 (d)	115.84 (d)	115.3 (d)	116.1 (d)
4c	156.3 (s)	156.0 (s)	156.3 (s)	156.2 (s)	158.1 (s)
7c	59.8 (d)	62.0 (d)	57.6 (d)	57.5 (d)	123.4 (d)
8c	50.6 (d)	53.3 (d)	49.3 (d)	49.1 (d)	129.8 (d)
9c	144.5 (s)	143.5 (s)	141.6 (s)	141.6 (s)	136.3 (s)
10c	119.8 (s)	119.6 (s)	123.3 (s)	123.3 (s)	119.8 (s)
11c	162.8 (s)	163.1 (s)	161.7 (s)	161.5 (s)	162.4 (s)
12c	95.9 (d)	96.2 (d)	95.6 (d)	95.5 (d)	96.7 (d)
13c	159.6 (s)	160.0 (s)	159.4 (s)	159.3 (s)	159.5 (s)
14c	106.7 (d)	107.8 (d)	107.0 (d)	106.9 (d)	104.1 (d)
1d	134.1 (s)	134.6 (s)	134.7 (s)	134.5 (s)	133.8 (s)
2d, 6d	128.0 (d)	127.7 (d)	128.2 (d)	128.2 (d)	128.7 (d)
3d, 5d	116.5 (d)	117.1 (d)	115.98 (d)	116.0 (d)	116.2 (d)
4d	157.6 (s)	159.8 (s)	157.9 (s)	157.9 (s)	158.1 (s)
7d	95.0 (d)	94.7 (d)	94.6 (d)	94.5 (d)	93.8 (d)
8d	57.8 (d)	57.8 (d)	57.5 (d)	57.4 (d)	57.0 (d)
9d	146.4 (s)	146.9 (s)	147.9 (s)	147.9 (s)	147.4 (s)
10d, 14d	107.5 (d)	106.9 (d)	107.5 (d)	107.3 (d)	106.9 (d)
11d, 13d	159.6 (s)	159.7 (s)	159.8 (s)	159.7 (s)	159.8 (s)
12d	102.1 (d)	102.2 (d)	102.2 (d)	102.1 (d)	102.0 (d)

The data of **2** and **3** were taken in methanol-d_4, and the data of **4**, **5** and **6** were taken in acetone-d_6.

stereoisomer of vaticanol B (**5**)[2,3] and vaticaphenol A (**6**),[4] which have the same molecular skeleton. The ^{13}C NMR data of **2** are certainly very close to those of **5** and **6**, as shown in Table 2. The stereochemistry of **2** was determined on the basis of ^1H NMR spectral data, as follows. The coupling constant (J=12.1 Hz) of H-7a and H-8a suggested the stereochemistry between H-7a and H-8a to be *trans*, as shown in the cases of (+)-viniferol A (**1**) (J=12.8 Hz),[1] vaticanol B (**5**) (J=11.7 Hz)[2,3] and vaticaphenol A (**6**) (J=11.0 Hz).[4] The chemical shift value of H-8a (δ 4.25) indicated the stereochemistry between H-8a and H-7b to be *anti*, as shown in the cases of (+)-viniferol A (**1**) (δ 4.30),[1] vaticanol B (**5**) (δ 4.44)[2,3] and vaticaphenol A (**6**) (δ 4.43).[4] It caused such an upfield shift that H-8a is held in the shielding region of the aromatic group (B_1) at C-7b.[6,7] The stereochemistry between H-7b and H-8b was assigned to *cis* by the comparison of the coupling constant (J=3.3 Hz) with that of vaticanol B (**5**) (J=3.9 Hz)[2,3] and vaticaphenol A (**6**) (J=3.0 Hz).[4] Furthermore, the stereochemistries of **2** were, respectively, confirmed by the NOESY and difference NOE experiments. The cross peaks observed between H-7b and H-7c, between H-7c and H-8d, between H-8b and H-14c, and between H-8c and H-2c (6c) suggested the stereochemistry between H-7b and H-8b, between H-8b and H-7c, between H-7c and H-8c and between H-8c and H-8d to be *syn*, *syn*, *anti* and *anti* configuration, respectively. Irradiation of H-8a showed enhancement of the signal of H-2a (H-6a) (7.2%). Irradiation of H-7c showed enhancement of the signal of H-8d (2.2%). Irradiation of H-2b (6b) showed enhancement of the signal of H-8a (1.4%). Irradiation of H-7c showed enhancement of the signal of H-8d (2.2%). Irradiation of H-8c showed enhancement of the signals of H-2c (6c) (5.3%) and H-10d (14d) (1.5%). Irradiation of H-8b showed enhancement of the signal of H-14c (2.3%). The stereostructure of **2** was also supported by the comparison of the observed J-values with the calculated J-values based on the dihedral angles, as shown in Table 3. From the evidence mentioned above, the structure of (+)-viniferol B should be represented as **2** including the stereochemistry. Finally, (+)-viniferol B (**2**) seems to be biogenetically synthesized from (+)-ε-viniferin (**4**) as shown in Fig. 1. This biogenetic consideration supported the stereostructure of (+)-viniferol B (**2**).

2.3. Structure of (+)-viniferol C

(+)-Viniferol C (**3**), $[\alpha]_D$=+2.8° (c 0.15, MeOH) was found to have the molecular formula $C_{56}H_{42}O_{12}$ determined by high-resolution FABMS. The molecular formula and the NMR data in Tables 1 and 2 suggested (+)-viniferol C also to be a tetramer of resveratrol. The correlations of the HMBC spectrum were observed between H-8a and C-14a, C-10b, between H-7b and C-9a, C-11a, C-2b (6b), C-9b, between H-8b and C-9b, between H-7c and C-14b, C-9c, C-10c, and between H-8c and C-14b, C-9c, respectively. Furthermore, the correlations of the HH-COSY spectrum were observed between H-7b and H-8b, and between H-8b and H-7c. These data suggested the presence of the same

Table 3. J-values estimation of (+)-viniferol B (**2**) and (+)-viniferol C (**3**)

		H-7b and H-8b	H-8b and H-7c	H-7c and H-8c
(+)-Viniferol B (**2**)	Dihedral angle (°)	73.6	−40.1	−84.0
	Calculated J-value (Hz)	0.4	5.2	0.2
	Observed J-value (Hz)	3.3	8.1	0
(+)-Viniferol C (**3**)	Dihedral angle (°)	−169.9	−40.1	−84.0
	Calculated J-value (Hz)	8.8	5.2	0.2
	Observed J-value (Hz)	11.7	6.6	0

Calculation was performed using the CAChe Work System 4.1.1 molecular modeling programs. The initial minimization was carried out by Conjugate Gradient method, the MM2 force incorporated in CAChe.

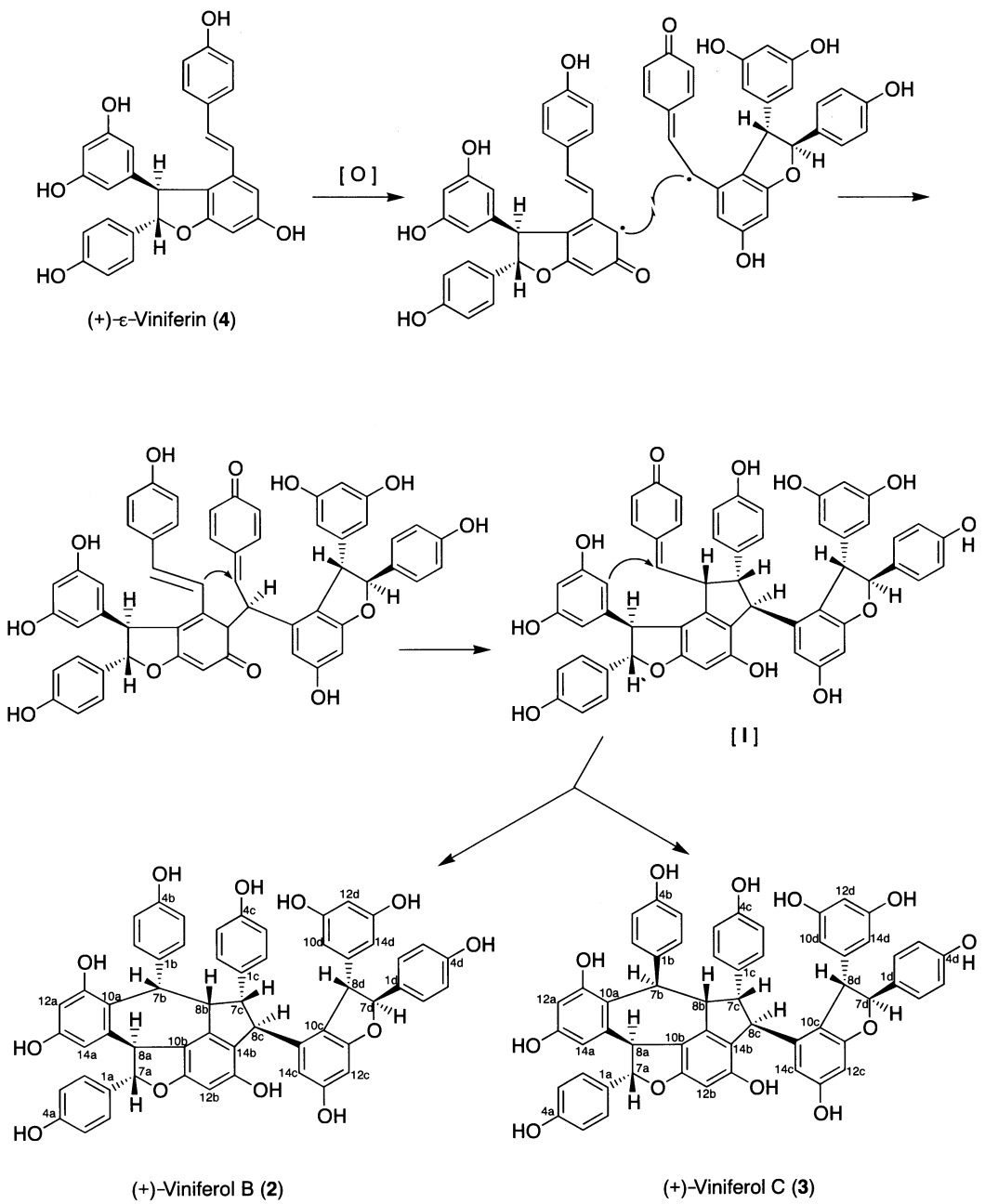


Figure 1. Plausible biogenetic pathways of (+)-viniferols B (**2**) and C (**3**) from (+)-ε-viniferin (**4**).

bicyclo[5.3.0]decane ring system in **3** as in **2**. The partial structure (C-9c to C-14d) was also characterized by the comparison of the ^{13}C NMR data of **3** with those of (+)-viniferol B (**2**) and (+)-ε-viniferin (**4**), as shown in Table 2.

The chemical shift value of H-8a (δ 5.01) indicated the stereochemistry between H-8a and H-7b to be *syn*, as shown in the case of (−)-isohopeaphenol (**7**) (δ 5.37).[5–7] The coupling constant value of H-7b and H-8b (11.7 Hz) indicated the stereochemistry between H-7b and H-8b to be *trans*, because the corresponding value of viniferol B (3.3 Hz), vaticanol B (3.9 Hz) and vaticaphenol A (3.0 Hz) having the same ring system, indicated the stereochemistry between H-7b and H-8b to be *cis*. Furthermore, the difference NOE experiments confirmed the stereochemistries including H-8b, H-7c, H-8c, H-8d and H-7d as follows. Irradiation of H-2b (6b) showed enhancement of the signals of H-8b (2.3%) and H-7c (2.7%), respectively. Irradiation of H-8b showed enhancement of the signals of H-14c (3.9%). Irradiation of H-2c (6c) showed enhancement of the signal of H-8c (1.9%). Irradiation of H-7c showed enhancement of the signal of H-8d (2.1%). Irradiation of H-8c showed enhancement of the signal of H-14d (2.4%). These results indicated the stereochemistry between H-7a and H-8a to be *anti*, between H-8a and H-7b to be *syn*, between H-7b and H-8b to be *anti*, between H-8b and H-7c to be *syn*, between H-7c and H-8c to be *anti*, between H-8c and H-8d to be *anti*, and between H-8d and H-7d to be *anti*. These were further supported by the upfield shift of H-7b (δ 4.11) held in the shielding region of the aromatic group (C_1) at C-7c. In the case of (+)-viniferol B, such upfield shift of H-7b (δ 5.34) was not observed. Consequently,

(+)-viniferol C (**3**) is an epimer of (+)-viniferol B (**2**) at the position of C-7b. This result was supported by the observation of a long-range coupling between H-8a and H-8b (J=2.2 Hz) in both (+)-viniferol B (**2**)[10] and (+)-viniferol C (**3**).[10] This was also supported by the comparison of the observed J-values with the calculated J-values based on the dihedral angles, as shown in Table 3. (+)-Viniferol C (**3**) seems to be biogenetically synthesized from the intermediate [I] common to (+)-viniferol B (**2**) as shown in Fig. 1. As (+)-ε-viniferin (**4**) was isolated from the same plant, the absolute configurations of (+)-viniferol B and (+)-viniferol C may be represented as **2** and **3**, respectively.

3. Experimental

3.1. General

UV and IR spectra were recorded on JASCO Ubest V-560 (cell length 10 mm) and FT/IR-410 spectrometers, respectively. Optical rotations were measured with a JASCO P-1020 polarimeter (cell length 100 mm). ^{1}H and ^{13}C NMR spectra were recorded on JEOL ALPHA-600 (^{1}H: 600 MHz and ^{13}C: 150 MHz) and JEOL ALPHA-400 (^{1}H: 400 MHz and ^{13}C: 100 MHz) spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR are given in parts per million (δ) relative to the solvent signal (methanol-d_4: δ_H 3.30 and δ_C 49.0) as an internal standard. LR and HR FAB-MS were obtained with JEOL JMS HX-110 using *m*-nitrobenzyl-alcohol as matrix. Analytical TLC was performed on silica gel 60 F254 (Merck). Column chromatography was carried out on silica gel BW-820 MH (Fuji Silysia Chemicals, Co. Ltd).

3.1.1. Isolation of (+)-viniferol B (2) and (+)-viniferol C (3). A part of the ethyl acetate fraction (29.5 g) described in the previous paper[1] of the stem of *V. vinifera* Kyohou was fractionated by MPCC (45×450 mm) over silica gel (265 g) using a gradient solvent system of chloroform and methanol (20:1–0:1) to give 13 fractions (F-1–F-13). F-10 (2.4 g, chloroform–methanol=5:1) was subjected to reversed-phase MPCC (Develosil Lop C8-45S (45×450 mm), Nomura Chemical Co. Ltd) using a mixed solvent of methanol–water (55:45) (flow rate: 5.0 ml/min) give 6 fractions (F-101–F-106). A Sephadex LH-20 column chromatography of F-102 (585 mg) using methanol, followed by preparative TLC on silica gel (Merck, 05744, 0.5 mm, 20×20 cm, $CHCl_3$–CH_3OH–H_2O (100:20:1)) gave (+)-viniferol C (**3**) (14.3 mg).

F-11 (4.1 g, chloroform–methanol=4:1) was chromatographed (35×400 mm) over silica gel (110 g) eluting with increasing polarity of chloroform–methanol mixtures to give six fractions (F-111–F-116). A reversed-phase MPCC (Develosil Lop C8-45S (45×450 mm), Nomura Chemical Co. Ltd) of F-112 (785 mg) using a mixed solvent of methanol–water (55:45) (flow rate: 5.0 ml/min), followed by recycled HPLC (YMC-Pack C8-5 (20×250 mm), YMC Co. Ltd) using the same solvent system (flow rate: 3.0 ml/min) afforded two compounds. The first eluted compound was corresponding to (+)-viniferol A[1] (7.4 mg) and the last one was corresponding to (+)-viniferol B (**2**) (14.4 mg).

3.1.2. (+)-Viniferol B (2). $[\alpha]_D$=+43.2° (*c* 0.28, MeOH); a colorless amorphous solid; UV λ_{max} (MeOH) (nm (log ε)) 283 (4.14), 227 (sh, 4.81); IR ν_{max} (KBr) 3413, 1610, 1511, 1452 cm^{-1}; ^{1}H and ^{13}C NMR data are shown in Tables 1 and 2; HRFAB-MS: *m/z* 907.2802 $[M+H]^+$ (907.2755 calculated for $C_{56}H_{43}O_{12}$).

3.1.3. (+)-Viniferol C (3). $[\alpha]_D$=+2.8° (*c* 0.15, MeOH); a colorless amorphous solid; UV λ_{max} (MeOH) (nm (log ε)) 284 (4.04), 228 (sh, 4.86); IR ν_{max} (KBr) 3398, 1607, 1507, 1451 cm^{-1}; ^{1}H and ^{13}C NMR data are shown in Tables 1 and 2; HRFAB-MS: *m/z* 907.2748 $[M+H]^+$ (907.2755 calculated for $C_{56}H_{43}O_{12}$).

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6. In the case of *anti*-configuration between H-8a and H-7b, such an upfield shift was observed (ampelopsin A (δ 4.02)[8] and hopeaphenol (δ 4.12)[5]).
7. In the case of *syn*-configuration between H-7c and H-8a, such an upfield shift was not observed (balanocarpol (δ 5.14)[9] and isohopeaphenol (δ 5.37)[5]).
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10. Irradiation of H-8a caused a change from ddd to dd at H-8b.