HETEROCYCLES, Vol. 65, No. 10, 2005, pp. 2461 - 2469
Received, 19th July, 2005, Accepted, 15th August, 2005, Published online, 23rd August, 2005

THREE NEW STILBENEOLIGOMERS FROM THE ROOTS OF *VITIS VINIFERA* 'KYOHOU'

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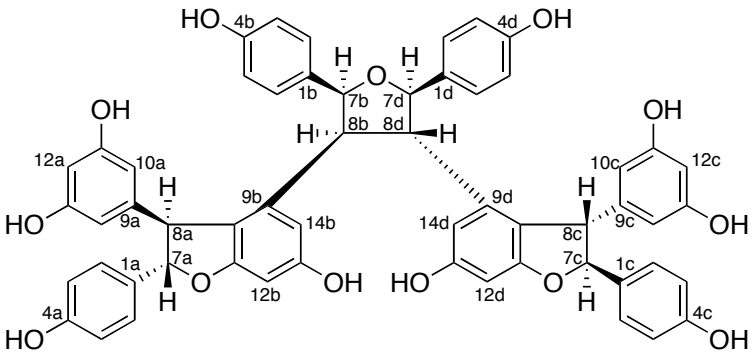
Abstract – Three new stilbeneoligomers named (+)-viniferol E, (+)-viniferether A and (+)-viniferether B were isolated from the roots of *Vitis vinifera* 'Kyohou' and the structures were elucidated on the basis of the spectral evidence

INTRODUCTION

Our continuous efforts for the study of the constituents of *Vitis vinifera* 'Kyohou' cultivated in Mie Prefecture led to the isolation of one new stilbenetetramer named (+)-viniferol E (**1**), and two new stilbenedimers named (+)-viniferether A (**2**) and (+)-viniferether B (**3**).[1] In this paper, we describe the isolation and structural elucidation of three new stilbeneoligomers together with nine known oligostilbenes from the roots of *V. vinifera* 'Kyohou'. Furthermore, we discuss the biogenesis of (+)-viniferether A (**2**) and (+)-viniferether B (**3**) because **2** and **3** correspond to the intermediate [**I**] of the biogenetic pathway of (–)-ampelopsin D (**4**) showed in the previous papers.[2]



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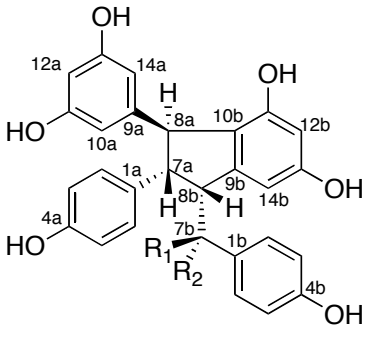

2 R_1=OMe, R_2=H
3 R_1=H, R_2=OMe

Figure 1 Structures of (+)-viniferol E (**1**), (+)-viniferether A (**2**) and (+)-viniferether B (**3**)

RESULTS AND DISCUSSION

Isolation

The methanol extract of the roots of *V. vinifera* 'Kyohou' cultivated in Mie Prefecture was successively partitioned between water and ethyl acetate and *n*-butanol to give the corresponding solubles. The ethyl acetate soluble was subjected to repeated chromatographic separation using normal and/or reversed phase silica-gel to give one new stilbenetetramer named (+)-viniferol E (**1**), and two new stilbenedimers named (+)-viniferether A (**2**) and (+)-viniferether B (**3**) in 0.00021%, 0.000081% and 0.00009% yields, respectively, based on the methanol extract, together with nine known stilbeneoligomers, (+)-vitisinol B,[3] (+)-hopeaphenol,[4] (+)-ampelopsin A,[5] (+)-ampelopsin C,[5] (–)-stenophyllol C,[6] and (+)-viniferol D,[1] (–)-*cis*-vitisin B,[7] ampelopsin E,[8] and *cis*-ampelopsin E.[8]

Structure of (+)-viniferol E

(+)-Viniferol E (**1**), $[\alpha]_D$ +285.3° (*c* 0.2, MeOH) was found to have the molecular formula $C_{56}H_{44}O_{13}$ determined by high-resolution FABMS spectrum. The ^{1}H NMR spectrum in methanol-d_4 of **1** exhibited signals for four sets of *ortho*-coupled aromatic hydrogens at δ_H 6.50, 6.66 (each 2H, d, *J*=8.0 Hz); 6.55, 6.77 (each 2H, d, *J*=8.0 Hz); 6.64, 6.83 (each 2H, d, *J*=8.0 Hz); 6.65, 6.76 (each 2H, d, *J*=8.0 Hz), for two sets of *meta*-coupled aromatic hydrogens at δ_H 5.56, 5.87 (each 2H, d, *J*=2.0 Hz); 6.16, 6.52 (each 2H, d, *J*=2.0 Hz), two sets of AX_2 type *meta*-coupled aromatic hydrogens at δ_H 6.14 (2H, d, *J*=2.0 Hz), 6.19 (1H, t, *J*=2.0 Hz); 6.14 (2H, d, *J*=2.0 Hz), 6.23 (1H, t, *J*=2.0 Hz), four sets of consecutive aliphatic hydrogens at δ_H 3.48, 3.86 (each 1H, dd, *J*=12.2, 9.8 Hz); 4.67, 4.99 (each 1H, d, *J*= 9.8 Hz); 3.72, 5.02 (each 1H, d, *J*=5.2 Hz); 3.93, 5.20 (each 1H, d, *J*= 5.2 Hz), as shown in Table 1. These data suggest the presence of a 4-hydroxyphenyl group, 3,5-dihydroxyphenyl group, dihydrobenzofuran moiety, and tetrahydrofuran moiety, which have their origins in resveratrol (3,5,4´-trihydroxystilbene). Furthermore, the correlations in the HMBC spectrum, which are shown in Table 1, suggested the structure of (+)-viniferol E to be **1** except for the stereochemistry. The stereochemistry was determined by the ROESY spectrum as follows. The correlations between H-7b and H-7d, H-8b and H-7d, H-14b and H-8d, H-7d and H-14d, H-8b and H-14d, H-14b and H-8c, and H-8d and H-14b were observed, respectively. These correlations suggested the configurations of H-7b, H-7c, H-7d, H-8b, H-8c, and H-8d to be α (or β), α (or β), α (or β), α (or β), β (or α), and β (or α), respectively. The following evidence supported these suggestions. The higher-field shift of H-14b (δ_H 5.56) than that of H-14d (δ_H 6.52) was observed because of the location on the C_1 benzene ring. Therefore, the structure of (+)-viniferol E should be **1**, although the absolute structure remains undetermined.

Table 1. NMR Spectral Data of (+)-Viniferol E (**1**)

Positions	^{13}C	^{1}H [a]	HMBC
1a	133.7		3a(5a), 8a
2a, 6a	129.1	6.83 (2H, d, *J*=8.0)	
3a, 5a	116.3	6.64 (2H, d, *J*=8.0)	
4a	158.6		2a
7a	94.4	5.20 (1H, d, *J*=5.2)	
8a	56.4	3.93 (1H, d, *J*=5.2)	10a (14a)
9a	148.4		7a
10a, 14a	107.5	6.14 (2H, d, *J*=2.0)	
11a, 13a	159.5		12a
12a	102.5	6.19 (1H, t, *J*=2.0)	
1b	133.1		3b (5b), 8b
2b, 6b	129.5	6.76 (2H, d, *J*=8.0)	
3b, 5b	115.6	6.65 (2H, d, *J*=8.0)	
4b	157.4		2b (6b)
7b	82.9	4.67 (1H, d, *J*=9.8)	2b (6b)
8b	59.1	3.86 (1H, dd, *J*=12.2, 9.8)	14b
9b	136.8		8b
10b	123.9		8a, 12b, 14b
11b	160.4		8a
12b	96.7	5.87 (1H, d, *J*=2.0)	
13b	158.1		12b
14b	111.0	5.56 (1H, d, *J*=2.0)	
1c	133.7		3c (5c), 8c
2c, 6c	128.5	6.66 (2H, d, *J*=8.0)	
3c, 5c	116.2	6.50 (2H, d, *J*=8.0)	
4c	158.1		2c
7c	95.4	5.02 (1H, d, *J*=5.2)	
8c	56.1	3.72 (1H, d, *J*=5.2)	10c (14c)
9c	148.7		7c
10c, 14c	107.5	6.14 (2H, d, *J*=2.0)	
11c, 13c	160.1		12c
12c	102.1	6.23 (1H, t, *J*=2.0)	
1d	129.8		3d (5d), 7d
2d, 6d	129.5	6.77 (2H, d, *J*=8.0)	
3d, 5d	116.3	6.55 (2H, d, *J*=8.0)	
4d	158.1		2d (6d)
7d	85.9	4.99 (1H, d, *J*=9.8)	2d (6d)
8d	54.3	3.48 (1H, dd, *J*=12.2, 9.8)	14d
9d	138.7		8d
10d	123.1		8c, 12d, 14d
11d	162.1		8c
12d	96.4	6.16 (1H, d, *J*=2.0)	
13d	159.8		12d
14d	105.9	6.52 (1H, d, *J*=2.0)	

[a] Coupling constants (*J*) were expressed in Hz.

Structure of (+)-viniferether A

(+)-Viniferether A (**2**), $[\alpha]_D$ +58.4° (*c* 0.14, MeOH) was found to have the molecular formula $C_{29}H_{26}O_7$ determined by high-resolution FABMS spectrum. The ^{1}H NMR spectrum in methanol-d_4 of 2 exhibited signals for two sets of AA´XX´-type (1,4-disubstituted) aromatic hydrogens at δ 6.95 and 6.69 (each 2H, d, *J*= 8.4 Hz), 7.08 and 6.82 (each 2H, d, *J*= 8.4 Hz), one set of *meta*-coupled aromatic hydrogens δ 6.20 and 5.36 (each 1H, d, *J* = 2.0 Hz), one set of AX_2-type *meta*-coupled aromatic hydrogens δ 6.03 (2H, d, *J*= 2.0 Hz) and 6.08 (1H, t, *J* = 2.0 Hz), four consecutive aliphatic hydrogens [3.47 (1H, d, *J*= 10.3 Hz), 3.95 (1H, dd, *J*= 10.3, 7.4 Hz), 3.68 (1H, br d, *J*= 7.4 Hz), 4.24 (1H, br s)], and a methoxyl group (2.58, 3H, s) as shown in Table 2. The high-field shifts of an aromatic hydrogen of H-14b (δ 5.36, δ-C-14b 105.6) and of three hydrogens of a methoxyl group (δ 2.58, δ-C-OMe 54.8) are due to a magnetic anisotropy effect by the benzene rings A and C, respectively, as described later. The ^{1}H-^{13}C correlations

Table 2. NMR Spectral Data of (+)-Viniferether A (**2**) and (+)-Viniferether B (**3**)

	2			**3**		
Positions	^{13}C	^{1}H [a]	HMBC	^{13}C	^{1}H [a]	HMBC
1a	136.6		3a(5a), 8a, 8b	135.9		7a
2a,6a	130.5	6.95 (2H, d, *J*=8.4)		130.5	6.50 (2H, s)	
3a,5a	115.5	6.69 (2H, d, *J*=8.4)		115.4	6.50 (2H, s)	
4a	156.7		2a(6a)	156.8		2a(6a)
7a	59.8	3.68 (1H, br d, *J*=7.4)	2a(6a)	59.8	2.94 (1H, dd, *J*=7.4, 2.2)	2a(6a)
8a	55.0	4.24 (1H, br s)	10a(14a)	56.0	4.13 (1H, d, *J*=2.2)	10a(14a)
9a	148.5		7a	148.2		8a
10a,14a	107.0	6.02 (1H, d, *J*=2.0)		107.1	6.03 (1H, d, *J*=2.0)	
11a,13a	159.3		10a(14a)	159.3		10a(14a)
12a	101.3	6.08 (1H, t, *J*=2.0)	10a(14a)	101.4	6.07 (1H, t, *J*=2.0)	
1b	132.3		3b(5b)	131.5		7b
2b,6b	131.1	7.08 (2H, d, *J*=8.4)		130.1	6.57 (2H, s)	
3b,5b	116.3	6.82 (2H, d, *J*=8.4)		115.4	6.57 (2H, s)	
4b	158.7		2b (6b)	158.0		2b(6b)
7b	84.2	3.47 (1H, d, *J*=10.3)	2b(6b), OMe	86.5	3.95 (1H, d, *J*=9.3)	2b(6b), OMe
8b	54.2	3.95 (1H, dd, *J*=10.3, 7.4)		54.2	3.85 (1H, dd, *J*=9.3, 7.4)	
9b	147.0		7a, 8a, 8b	149.9		7a, 8a
10b	125.0		14b	123.7		8a, 12b, 14b
11b	155.4		8a, 12b	155.3		12b
12b	102.3	6.20 (1H, d, *J*=2.0)	14b	102.3	6.21 (1H, d, *J*=2.0)	
13b	158.7		12b, 14b	158.0		14b
14b	105.6	5.36 (1H, br s)		105.1	6.65 (1H, d, *J*=2.0)	
OMe–	54.8	2.58 (3H, s)		55.5	3.02 (3H, s)	

[a] Coupling constants (*J*) were expressed in Hz.

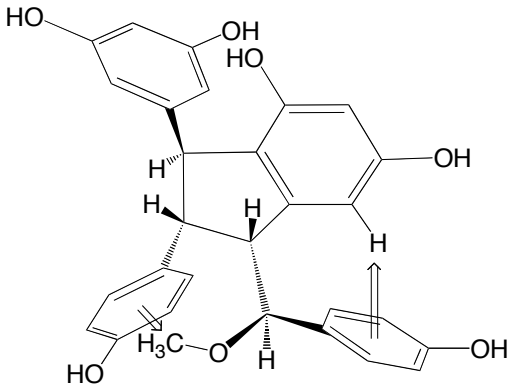

Figure 2. Stereostructure of (+)-viniferether A (**2**)

were observed in the HMBC spectrum of **2** as shown in Table 2. The position of the methoxyl group was particularly assigned to C-7b by the correlation between C-7b (δ_C 84.2) and H-OMe (δ_H 2.58). From the above spectral evidence, the plane structure of **2** was clarified to be 7b-methoxy-7b,8b-dihydroampelopsin D.[4] The relative stereostructure of **2** was determined by the difference NOE experiments, as follows. The NOEs were observed between H-8a and H-2a(6a) (8.6%), H-7a and H-10a(14a) (4.8%), H-8b and H-10a(14a) (5.6%), H-7b and H-2a(6a) (4.5%), and H-7b and H-14b (5.7%), respectively. Furthermore, the NOE was observed between H-OMe and H-2a(6a) (1.8%). A study using the dreiding stereomodels on the basis of these spectral evidence explained reasonably the relative stereostrucutre to be 2. As shown in Figure 2, the methoxyl group is located on the benzene ring A and H-14b is located on the benzene ring C. This evidence, along with the ^{1}H-^{13}C correlations between C-7a and H-2a(6a) in the HMBC spectrum and the vicinal coupling between H-7a and H-8b, also revealed that **2** does not possess the quadrangularin A-type structure[9] but the ampelopsin D-type structure.

Structure of (+)-viniferether B

(+)-Viniferether B (**3**), $[\alpha]_D$ +53.8° (*c* 0.21, MeOH) was found to have the molecular formula $C_{29}H_{26}O_7$ determined by high-resolution FABMS spectrum. The ^{1}H NMR spectrum in methanol-d_4 of **3** exhibited signals for four aromatic hydrogens at δ 6.50 (4H, s), four aromatic hydrogens at 6.57 (4H, s), one set of *meta*-coupled aromatic hydrogens δ 6.21 and 6.65 (each 1H, d, *J*= 2.0 Hz), one set of AX_2-type *meta*-coupled aromatic hydrogens δ 6.03 (2H, d, *J*= 2.0 Hz) and 6.07 (1H, t, *J*= 2.0 Hz), four consecutive aliphatic hydrogens [3.95 (1H, d, *J*= 9.3 Hz, 3.85 (1H, dd, *J*= 9.3, 7.4 Hz, 2.94 (1H, dd, *J*= 7.4, 2.2 Hz), 4.13 (1H, *J*= 2.2 Hz)), and a methoxyl group (3.02, 3H, s) as shown in Table 2. Two singlet signals at δ 6.50 (4H, s)[9] and 6.57 (4H, s)[9] correspond to two sets of AA´XX´-type (1,4-disubstituted) aromatic hydrogens, which are assigned by the HSQC spectrum. The ^{1}H NMR spectral data of **3** are somewhat different from those of **2**, although the ^{13}C NMR spectral data of **3** are very similar to those of **2**. The correlations in the HSQC spectrum are observed between C-2a(6a) at δ 130.5 and H-2a(6a) at δ 6.57,

between C-3a(5a) at δ 115.4 and H-3a(5a) at δ 6.57, between C-2b(6b) at δ 130.1 and H-2b(6b) at δ 6.50, and between C-3b(5b) at δ 115.4 and H-3b(5b) at δ 6.57, respectively. The ^{1}H-^{13}C long-range correlations were observed in the HMBC spectrum of **3** as shown in Table 2. The position of the methoxyl group was determined by a similar correlation between C-7b (δ_C 86.5) and H-OMe (δ_H 3.02) to that of compound (**2**). From the above spectral evidence, the plane structure of **3** was clarified to be a stereoisomer of **2** at the position of C-7b. The relative stereostructure of **3** was determined by the difference NOE experiments, as follows. The NOEs were observed between H-2a(6a) and H-8a (1.3%), H-2b(6b) and H-8b (2.1%), H-7b and H-2a(6a) (5.5%), respectively. Furthermore, the NOE was observed between H-OMe and H-14b (2.1%). The high-field shift of H-7a (δ_H 2.94) was observed in **3** instead of those of H-14b and MeO observed in **2** because of the location on the benzene ring C. A study using the dreiding stereomodels on the basis of these spectral evidence explained reasonably the relative stereostructure to be **3**.

Biogenesis

In the previous paper, we presented a plausible reaction pathway of (+)-ε-viniferin (**5**) to (–)-ampelopsin D (**4**).[4] The isolation of (+)-viniferether A (**2**) and (+)-viniferether B (**3**) proved the biogenetic pathway of (–)-ampelopsin D (**4**) from (+)-ε-viniferin (**5**) by way of the intermediate cation [**I**] as shown Figure 3. So we tried the transformation of (+)-ε-viniferin (**5**) to (+)-viniferether A (**2**) and/or (+)-viniferether B (**3**) under various conditions, but have not yet found **1** and/or **2** in the reaction mixture. The transformation of (–)-ampelopsin D (**4**) to (+)-viniferether A (**2**) and/or (+)-viniferether B (**3**) under the extract condition of the plant materials was also not observed even after 4 weeks.

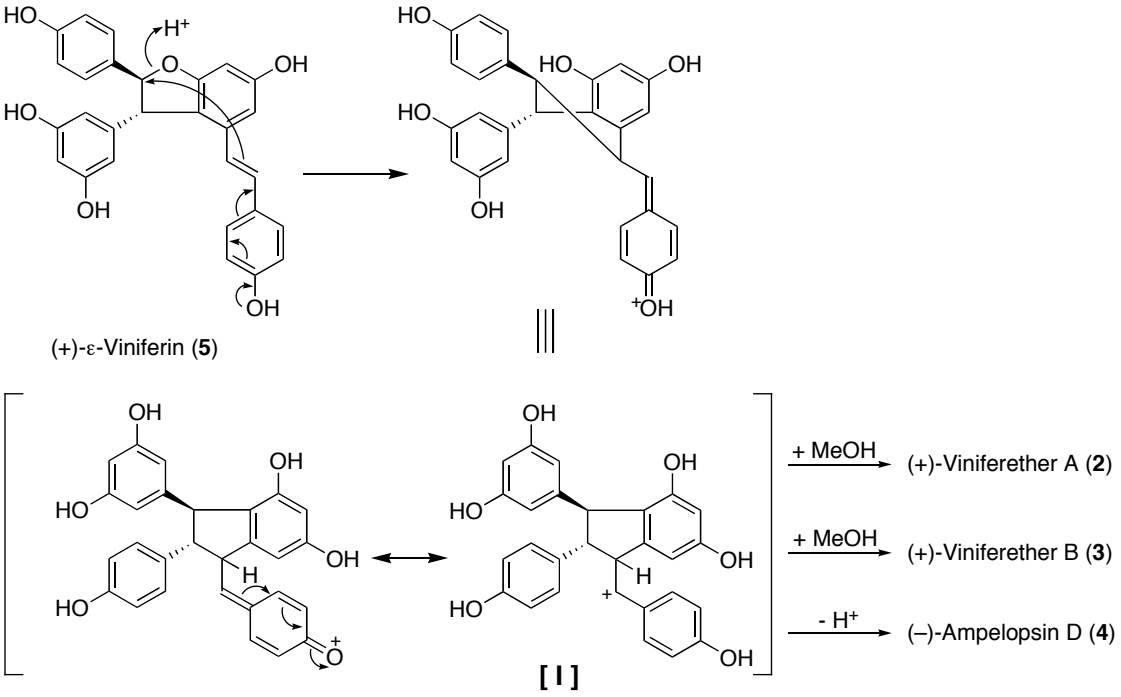

Figure 3. Biogenetic Pathways of (+)-Viniferethers A (**1**) and B (**2**), and (–)–Ampelopsin D (**4**)

EXPERIMENTAL

General

UV and IR spectra were recorded on JASCO Ubest V-560 (cell length 10 mm) and FT/IR-410 spectrophotometers, 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). Chemical shifts for ^{1}H and ^{13}C NMR spectra are given in parts per million (δ) relative to 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 and preparative TLC were performed on silica gel 5715, 5744 and 13895 (Merck), respectively. Column chromatography was carried out on silica gel BW-820MH (Fuji Silysia Chemicals, Co. Ltd.).

Extraction and Isolation

Roots of *V. vinifera* 'Kyohou' (2 kg) cultivated in Mie Prefecture were extracted with MeOH (20 L) at rt for 8 days to yield the extract (138 g). A part of the methanol extract (30 g) was partitioned between water and ethyl acetate, and between water and *n*-butanol to give an ethyl acetate soluble (24.8 g), a *n*-butanol soluble (1.4 g) and a water soluble (3.7 g), respectively.

Separation of the ethyl acetate soluble

The ethyl acetate soluble (24.8 g) was subjected to column chromatography over silica gel (300 g) eluting with increasing polarity of chloroform–methanol (19:1 to 7:3) to give three fractions [F-1 (561 mg), F-2 (21.4 g), F-3 (119 mg)]. F-2 (21.4 g) was further subjected to column chromatography over silica gel (400 g) eluting with increasing polarity of chloroform–methanol (19:1 to 7:3) to give four fractions [F-21 (874 mg), F-22 (8.3 g), F-23 (8.8 g), F-24 (2.9 g)]. F-23 (8.8 g) was again subjected to column chromatography over silica gel (200 g) using the same gradient solvent system of chloroform and methanol (19:1 to 7:3) to give six fractions [(F-231 (40 mg), F-232 (887 mg), F-233 (559 mg), F-234 (5.38 g), F-235 (964 mg), F-236 (247 mg)). A part of F-233 (250 mg) was separated by a reversed-phase HPLC (Develosil ODS-HG-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (40:60) (flow rate; 3.0 mL/min) to give seven fractions [F-2331 (5.5 mg), F-2332 (2.2 mg), F-2333 (7.1 mg), F-2334 (7.4 mg), F-2335 (21 mg), F-2336 (3.3 mg), F-2337 (5.1 mg)]. F-2333 (7.1 mg) was further separated by recycled HPLC (Develosil ODS-HG-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (60:40) (flow rate; 2.0 mL/min) to give (+)-viniferol E (**2**) (2.8 mg). F-2334 (7.4 mg) gave (+)-viniferol D (1.1 mg)[1] by recycled HPLC (Develosil ODS-HG-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of

methanol–water (60:40) (flow rate; 2.0 mL/min). F-2331 (5.5 mg), F-2332 (2.2 mg), F-2336 (21 mg) and F-2337 (5.1 mg) were respectively identified as (+)-hopeaphenol,[4] (+)-ampelopsin A,[5] (+)-ampelopsin C[5] and (–)-stenophyllol[6] by comparison with the reported spectral data. A part of F-234 (2.0 g) was subjected to column chromatography over silica gel (100 g) eluting with increasing polarity of chloroform–methanol (9:1 to 7:3) to give six fractions [F-2341 (9.1 mg), F-2342 (26 mg), F-2343 (253 mg), F-2344 (1.2 g), F-2345 (382 mg), F-2346 (160 mg)]. F-2343 (253 mg) was separated by preparative TLC [Merck 13895, chloroform–methanol (4:1)] to give three fractions [F-23431 (27 mg), F-23432 (168 mg), F-23433 (16 mg)]. F-23432 (168 mg) was further separated by reversed-phase HPLC (Develosil ODS-HG-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (40:60) (flow rate; 3.0 mL/min) to give seven fractions [F-234321 (13 mg), F-234322 (0.6 mg), F-234323 (0.8 mg), F-234324 (1.8 mg), F-234325 (2.8 mg), F-234326 (1.9 mg), F-234327 (0.9 mg)]. The fraction F-234327 (0.9 mg) was characterized as (+)-viniferether A (**2**). F-234325 (2.8 mg) was subjected to recycled HPLC (Develosil C8-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (60:40) (flow rate; 3.0 mL/min) to give (+)-viniferether B (**3**) (1.0 mg) and (+)-vitisinol B (0.8 mg).[3]

Separation of the *n*-butanol solubles

The *n*-butanol soluble (1.4 g) was subjected to column chromatography over silica gel (60 g) eluting with increasing polarity of chloroform–methanol (4:1 to 7:3) to give three fractions [BF-1 (75 mg), BF-2 (730 mg), BF-3 (422 mg)]. A part of BF-2 (292 mg) was subjected to preparative TLC (chloroform and methanol (4 : 1) to give four fractions [BF-21 (14.4 mg), BF-22 (28.0 mg), BF-23 (5.2 mg), BF-24 (48.2 mg)]. BF-21 (14.4 mg) was further separated by reversed-phase HPLC (Develosil C8-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (60:40) (flow rate; 3.0 mL/min) to give four fractions [BF-211 (2.4 mg), BF-212 (2.3 mg), BF-213 (4.2 mg), BF-214 (1.8 mg)]. BF-211 (2.4 mg) gave (+)-ampelopsin A (0.7 mg)[5] by separation with HPLC (Develosil C8-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (40:60) (flow rate; 3.0 mL/min). BF-212 (2.3 mg) gave (–)-*cis*-vitisin B[7] (0.6 mg) by separation with recycled HPLC (Develosil ODS-HG-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (60:40) (flow rate; 1.5 mL/min). BF-214 (1.8 mg) gave ampelopsin E (0.5 mg)[8] and *cis*-ampelopsin E (0.5 mg)[8] by separation with recycled HPLC (Develosil C8-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (40:60) (flow rate; 1.5 mL/min). BF-23 (5.2 mg) was subjected to recycled HPLC (Develosil C8-5 (ϕ20 x 250 mm), Nomura Chemical Co. Ltd.) using a mixed solvent of methanol–water (40:60) (flow rate; 1.5 mL/min) to give (+)-hopeaphenol (0.7 mg).[4]

(+)-Viniferol E (**1**). $[\alpha]_D$ +285.3° (*c* 0.2, MeOH); a colorless liquid; UV (MeOH) λ_{max} [nm (log ε)] 284 (4.13), 231 (4.83); IR ν_{max} (film) 3360 (br) cm^{-1}; ^1H NMR and ^{13}C NMR spectral data are shown in Table 1; HRFAB-MS: *m/z* 925.2881 $[M+H]^+$ (925.2860 calculated for $C_{56}H_{45}O_{13}$).

(+)-Viniferether A (2). $[\alpha]_D$ +58.4° (*c* 0.14, MeOH); a colorless liquid; UV λ_{max} (MeOH) [nm (log ε)] 280 (3.69), 229 (4.39); IR ν_{max} (film) 3400 cm^{-1}; ^1H NMR and ^{13}C NMR spectral data are shown in Table 2; HRFAB-MS: *m/z* 487.1784 $[M+H]^+$ (487.1757 calculated for $C_{29}H_{27}O_7$).

(+)-Viniferether B (**3**). $[\alpha]_D$ +53.8° (*c* 0.21, MeOH); a colorless liquid; UV λ_{max} (MeOH) [nm (log ε)] 280 (3.66), 231 (4.34); IR ν_{max} (film) 3400 cm^{-1}; ^1H NMR and ^{13}C NMR spectral data are shown in Table 2; HRFAB-MS: *m/z* 487.1748 $[M+H]^+$ (487.1757 calculated for $C_{29}H_{27}O_7$).

ACKNOWLEDGEMENTS

This research was financially supported by a Grant-in-Aid for High-Tech Research Center Project from the Ministry of Education, Culture, Sports, Science and Technology of Japan, which are gratefully acknowledged. The authors express sincere thanks to Mr. Hiroya Kondo and Mr. Yutaka Nishikawa of Agricultural Research Division, Mie Prefectural Science & Technology Promotion Center for collection of the plant material.

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