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Absolute Structures of New Hydroxystilbenoids, Vitisin C and Viniferal, from *Vitis vinifera* 'Kyohou'

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Abstract: Two new hydroxystilbenoids named vitisin C and viniferal were isolated from *Vitis vinifera* 'Kyohou' and the structures were characterized on the basis of spectroscopic and chemical evidence. Furthermore, the absolute configurations of (-)-vitisin B and (-)-*cis*- vitisin B as well as (+)-vitisin C and (-)-viniferal were determined by the synthetic evidence from (+)-ε-viniferin. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

In a previous paper, [1] we reported the isolation and structures of (-)-vitisin B (**1**) and (-)-*cis*-vitisin B (**2**) from the stem of *Vitis coignetiae* (Vitaceae). Continuous study on the constituents of the Vitaceaeous plants led to the isolation of two new hydroxystilbenes named (+)-vitisin C (**3**) and (-)-viniferal (**4**) along with (-)-vitisin B (**1**) and (+)-ε-viniferin (**5**) from the methanol extract of the corks of *Vitis vinifera* 'Kyohou' cultivated in Wakayama Prefecture. The structures of the two stilbenes (**3**, **4**) were elucidated by spectroscopic methods. On the basis of their biogenesis, furthermore, an oxidative coupling reaction of (+)-ε-viniferin (**5**) with horseradish peroxidase and hydroperoxide gave (-)-vitisin B (**1**) and (+)-vitisin C (**3**). This result showed the absolute configurations of the above oligostilbenes to be **1**, **2**, **3** and **4**, respectively. Both (-)-vitisin B and (+)-vitisin C showed inhibitory activity against tumor necrosis factor (TNF).[2]

RESULTS AND DISCUSSION

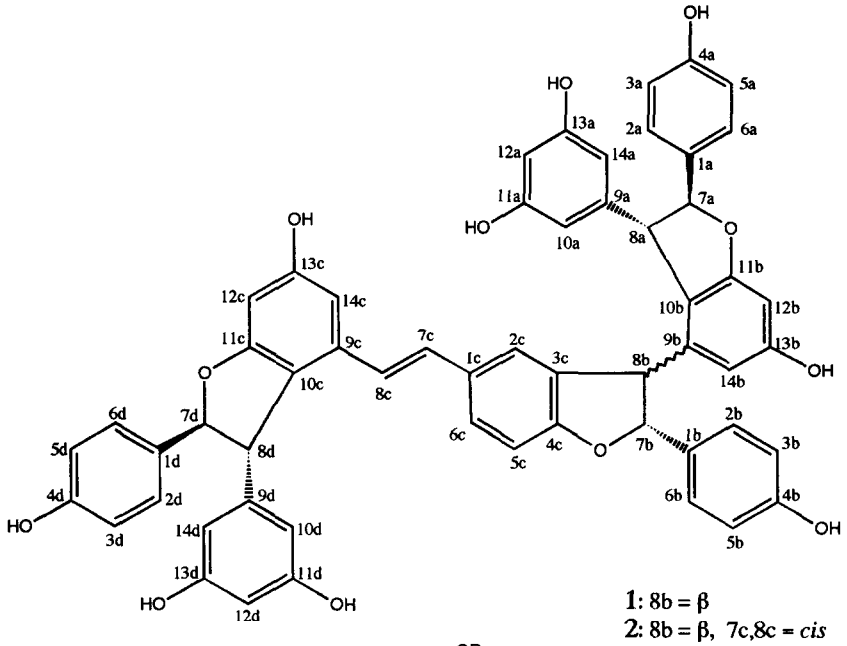
Structure of (+)-vitisin C (3) (+)-Vitisin C (**3**), $[\alpha]_D$ +239.9° (*c* 0.5, MeOH), showed a quasimolecular ion peak at *m/z* 907.2733 [MH^+] (*m/z* 907.2755 calcd. for $C_{56}H_{43}O_{12}$)) in the high resolution FAB mass spectrum. The ^1H NMR spectrum of vitisin C (**3**) exhibited signals for six sets of *ortho*-coupled aromatic hydrogens (δ 6.74, 6.94 (each 2H, d, J=8.8 Hz); 6.66, 6.98 (each 2H, d, J=8.8 Hz); 6.76, 7.14 (each 2H, d, J=8.8 Hz)), two sets of *meta*-coupled aromatic hydrogens (δ 6.13, 6.25 (each 1H, d, J=2.4 Hz); 6.25, 6.60 (each 1H, d, J=2.0 Hz)) and two sets of AX_2-type *meta*-coupled aromatic hydrogens (δ 5.87 (2H, d, J=2.4 Hz), 6.10 (1H, t, J=2.4 Hz); 6.14 (2H, d, J=2.4 Hz), 6.17 (1H, t, J=2.4 Hz)) (Table 1). The aliphatic hydrogen signals at δ 3.60, 5.19 (each 1H, d, J=4.9 Hz), 4.27, 5.18 (each 1H, d, J=9.76 Hz) and 4.36, 5.35 (each 1H, d, J=5.86 Hz)) suggested the presence of three dihydrobenzofuran moieties bearing 4-oxyphenyl and 3,5-dioxyphenyl groups characteristic of oligostilbenes biosynthesized from resveratrol molecules. In addition to these signals, the presence of an 1-oxy-2,4-disubstituted benzene ring and a *trans*-

Table 1. ^{1}H NMR Data of (-)-Vitisin B (**1**), (+)-Vitisin C (**3**), (-)-Viniferal (**4**) and Their Derivatives (**8** and **9**).

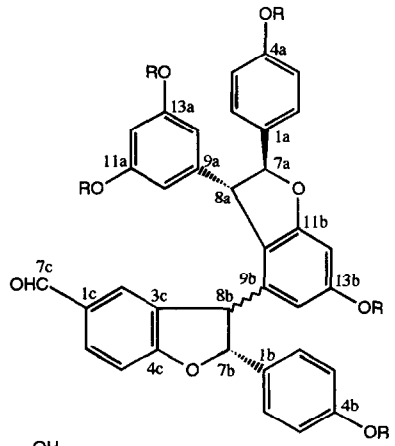
Position	1	3	4	8	9
1a					
2a,6a	7.13 (d, 8.4)	6.94 (d, 8.8)	7.15 (d, 8.4)	7.04 (d, 8.8)	7.21 (d, 8.4)
3a,5a	6.76 (d, 8.4)	6.74 (d, 8.8)	6.80 (d, 8.4)	6.84 (d, 8.8)	6.89 (d, 8.4)
4a					
7a	5.36 (d, 6.2)	5.19 (d, 4.9)	5.32 (d, 4.8)	5.32 (d, 5.2)	5.41 (d, 4.8)
8a	4.33 (d, 6.2)	3.60 (d, 4.9)	4.36 (d, 4.8)	3.57 (d, 5.1)	4.38 (d, 4.8)
9a					
10a,14a	6.14 (d, 1.5)	5.87 (d, 2.4)	5.94 (d, 2.2)	6.00 (d, 2.2)	6.01 (d, 2.4)
11a,13a					
12a	6.13 (t, 1.5)	6.10 (t, 2.4)	6.04 (t, 2.2)	6.26 (t, 2.2)	6.09 (t, 2.4)
1b					
2b,6b	6.58 (d, 8.8)	6.98 (d, 8.8)	6.66 (d, 8.8)	7.06 (d, 8.8)	6.74 (d, 8.4)
3b,5b	6.52 (d, 8.8)	6.66 (d, 8.8)	6.57 (d, 8.8)	6.71 (d, 8.8)	6.62 (d, 8.4)
4b					
7b	5.42 (d, 5.1)	5.18 (d, 9.8)	5.63 (d, 5.9)	5.38 (d, 9.5)	5.59 (d, 6.6)
8b	4.25 (d, 5.1)	4.27 (d, 9.8)	4.39 (d, 5.9)	4.33 (d, 9.5)	4.40 (d, 6.6)
9b					
10b					
11b					
12b	6.28 (d, 2.2)	6.25 (d, 2.4)	6.30 (d, 2.2)	6.47 (d, 2.2)	6.47 (d, 2.4)
13b					
14b	6.09 (d, 2.2)	6.13 (d, 2.4)	6.14 (d, 2.2)	6.23 (d, 2.2)	6.21 (d, 2.4)
1c					
2c	6.65 (d, 1.8)	6.60 (d, 2.0)	7.34 (d, 1.8)	7.24 (d, 1.8)	7.31 (d, 1.8)
3c					
4c					
5c	6.68 (d, 8.4)	6.64 (d, 8.3)	6.96 (d, 8.4)	6.91 (d, 8.4)	6.90 (d, 8.4)
6c	6.98 (dd, 8.4, 1.8)	6.99 (dd, 8.3, 2.0)	7.72 (dd, 8.4, 1.8)	7.71 (dd, 8.4, 1.8)	7.68 (dd, 8.4, 1.8)
7c	6.50 (d, 16.5)	6.55 (d, 16.1)	9.62 (s)	9.73 (s)	9.70 (s)
8c	6.68 (d, 16.5)	6.74 (d, 16.1)			
9c					
10c					
11c					
12c	6.24 (d, 1.8)	6.25 (d, 2.0)			
13c					
14c	6.58 (d, 1.8)	6.60 (d, 2.0)			
1d					
2d,6d	7.18 (d, 8.4)	7.14 (d, 8.8)			
3d,5d	6.52 (d, 8.4)	6.76 (d, 8.8)			
4d					
7d	5.33 (d, 4.8)	5.35 (d, 5.9)			
8d	4.36 (d, 4.8)	4.36 (d, 5.9)			
9d					
10d,14d	5.98 (d, 2.2)	6.14 (d, 2.4)			
11d,13d					
12d	6.06 (t, 2.2)	6.17 (t, 2.4)			
4a-OMe				3.81 (s)	3.80 (s)
11a,13a-OMe				3.68 (s)	3.60 (s)
4b-OMe				3.72 (s)	3.77 (s)
13b-OMe				3.75 (s)	3.75 (s)

Table 2. ^{13}C NMR Data of (-)-Vitisin B (**1**), (+)-Vitisin C (**3**), (-)-Viniferal (**4**) and Their Derivatives (**8** and **9**).

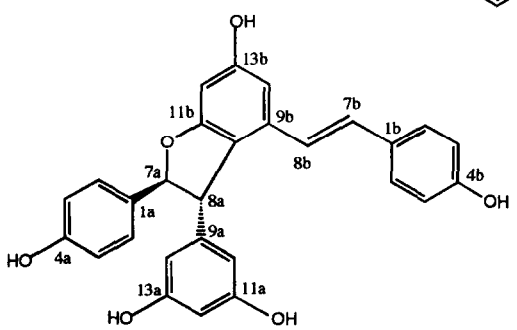
Position	1	3	4	8	9
1a	133.9 (s)	134.0 (s)	136.4 (s)	133.6 (s)	133.8 (s)
2a,6a	128.2 (d)	128.1 (d)	127.8 (d)	126.7 (d)	126.6 (d)
3a,5a	116.3 (d)	116.3 (d)	116.5 (d)	114.0 (d)	114.3 (d)
4a	158.5 (s)	158.4 (s)	158.6 (s)	159.5 (s)	159.8 (s)
7a	94.8 (d)	94.5 (d)	94.8 (d)	92.8 (d)	93.3 (d)
8a	58.2(d)	56.9 (d)	57.9 (d)	56.1 (d)	56.9 (d)
9a	147.2 (s)	147.7 (s)	147.5 (s)	145.5 (s)	145.9 (s)
10a,14a	107.5 (d)	107.2 (d)	106.9 (d)	105.7 (d)	105.4 (d)
11a,13a	160.0 (s)	159.9 (s)	160.1 (s)	161.2 (s)	161.2 (s)
12a	102.3 (d)	102.2 (d)	102.6 (d)	98.9 (d)	99.0 (d)
1b	132.7 (s)	132.2 (s)	134.0 (s)	131.2 (s)	131.6 (s)
2b,6b	127.8 (d)	128.7 (d)	127.8 (d)	127.5 (d)	126.9 (d)
3b,5b	116.0 (d)	116.4 (d)	116.3 (d)	114.1 (d)	114.0 (d)
4b	158.0 (s)	158.8 (s)	158.4 (s)	159.9 (s)	159.6 (s)
7b	92.2 (d)	95.0 (d)	93.7 (d)	94.2 (d)	92.7 (d)
8b	53.0 (d)	55.2 (d)	52.8 (d)	53.2 (d)	55.2 (d)
9b	142.5 (s)	140.7 (s)	141.6 (s)	138.4 (s)	139.9 (s)
10b	120.0 (s)	121.9 (s)	120.2 (s)	121.2 (s)	120.5 (s)
11b	162.7 (s)	162.6 (s)	163.1 (s)	161.5 (s)	161.8 (s)
12b	96.7 (d)	96.9 (d)	97.0 (d)	94.8 (d)	94.7 (d)
13b	160.5 (s)	160.4 (s)	160.7 (s)	161.8 (s)	162.0 (s)
14b	107.5 (d)	108.2 (d)	107.6 (d)	106.6 (d)	106.6 (d)
1c	132.7(s)	132.3 (s)	132.2 (s)	131.0 (s)	132.4 (s)
2c	125.5 (d)	125.8 (d)	127.6 (d)	126.8 (d)	126.2 (d)
3c	132.3 (s)	131.6 (s)	131.9 (s)	131.3 (s)	128.4 (s)
4c	160.2 (s)	161.1 (s)	165.8 (s)	165.1 (s)	164.2 (s)
5c	110.7 (d)	110.4 (d)	111.0 (d)	110.0 (d)	110.3 (d)
6c	126.8 (d)	126.6 (d)	133.9 (d)	132.7 (d)	133.2 (d)
7c	124.2 (d)	124.3 (d)	192.5 (d)	190.5 (d)	190.5 (d)
8c	130.5 (d)	130.7 (d)			
9c	136.8 (s)	137.0 (s)			
10c	120.1(s)	119.9 (s)			
11c	162.8 (s)	162.8 (s)			
12c	96.9(d)	96.9 (d)			
13c	159.6 (s)	159.7 (s)			
14c	104.6 (d)	105.0 (d)			
1d	134.6(s)	134.0 (s)			
2d,6d	127.8 (d)	128.2 (d)			
3d,5d	116.5 (d)	116.3 (d)			
4d	158.3 (s)	158.5 (s)			
7d	94.7 (d)	94.8(d)			
8d	57.9 (d)	58.2 (d)			
9d	147.7 (s)	147.5 (s)			
10d,14d	107.0 (d)	107.4 (d)			
11d,13d	160.1 (s)	160.0 (s)			
12d	102.5 (d)	102.2 (d)			
4a-OMe				55.3 (q)	55.3 (q)
11a,13a-OMe				55.3 (q)	55.2 (q)
4b-OMe				55.2 (q)	55.5 (q)
13b-OMe				55.5 (q)	55.6 (q)



1: 8b = β
2: 8b = β, 7c,8c = *cis*
3: 8b = α



4: 8b = β, R = H
8: 8b = α, R = Me
9: 8b = β, R = Me



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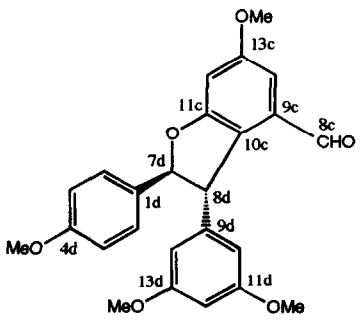

7

double bond was implied by hydrogen signals at δ 6.60 (1H, d, J=2.0 Hz), 6.64 (1H, d, J=8.3 Hz), 6.99 (1H, dd, J=8.3, 2.0 Hz) and 6.55, 6.74 (each 1H, d, J=16.1 Hz), respectively. These data resembled very closely those of vitisin B (**1**), except for the coupling constant values at H-7b and H-8b (**1**; $J_{7b\text{-}8b}$=5.1 Hz, **3**; $J_{7b\text{-}8b}$=9.8 Hz).[1] Vitisin C (**3**) was methylated with methyl iodide and potassium carbonate in acetone to afford a nonamethyl ether (**6**) (FAB MS: *m/z* 1033 [MH$^+$]), which was oxidized with ozone to give two degradative products (**7** and **8**). The compound **7** was shown to be identical in all respects with the aldehyde previously obtained from vitisin B (**1**) by the same reactions.[1] The other degradative product **8** (EI MS: *m/z* 644 [M$^+$]) was an aldehyde similar to the aldehyde (**9**) derived from vitisin B (**1**) except for the coupling constant values at H-7b and H-8b (**8**; $J_{7b\text{-}8b}$=9.5 Hz, **9**; $J_{7b\text{-}8b}$=6.2 Hz), as shown in Table 1.[3] In the aldehyde **8**, the coupling constant values, $J_{7a\text{-}8a}$=5.1 Hz and $J_{7b\text{-}8b}$=9.5 Hz indicated the stereochemistries between H-7a and H-8a to be *trans* and between H-7b and H-8b to be *cis*, respectively. The relative stereostructure of the aldehyde including two dihydrobenzofuran groups was concluded to be **8** from NOEs between H-8a and H-8b (3.9 %) and between MeO-11a (13a) and H-7c (0.8 %) together with the study using Dreiding stereomodel. This evidence led to the relative structure of (+)-vitisin C to be represented as **3**, which was a stereoisomer of (-)-vitisin B (**1**) at the position of C-8b.

Structure of (-)-viniferal (4) (-)-Viniferal (**4**), $[\alpha]_D$ -131.7° (*c* 1.6, MeOH), showed a quasimolecular ion peak at *m/z* 575.1664 [MH$^+$] (*m/z* 575.1706 calcd. for $C_{35}H_{27}O_8$)) in the high resolution FAB mass spectrum. The IR and ^{1}H NMR spectra of (-)-viniferal (**4**) exhibited the presence of an aldehyde group (ν 1605 cm^{-1} and δ 9.62 (1H, s). The aliphatic hydrogen signals at δ 4.36, 5.32 (each 1H, d, J=4.8 Hz) and 4.39, 5.63 (each 1H, d, J=5.9 Hz)) suggested the presence of two dihydrobenzofuran moieties having *trans* configuration, respectively. (-)-Viniferal (**4**) was methylated with methyl iodide and potassium carbonate in acetone to afford a pentamethyl ether (EIMS: *m/z* 644 [M$^+$]), which was completely identified with the aldehyde (**9**) derived from (-)-vitisin B (**1**) including the value of the optical rotation.[1] This evidence led to the relative structure of (-)-viniferal to be represented as **4**.

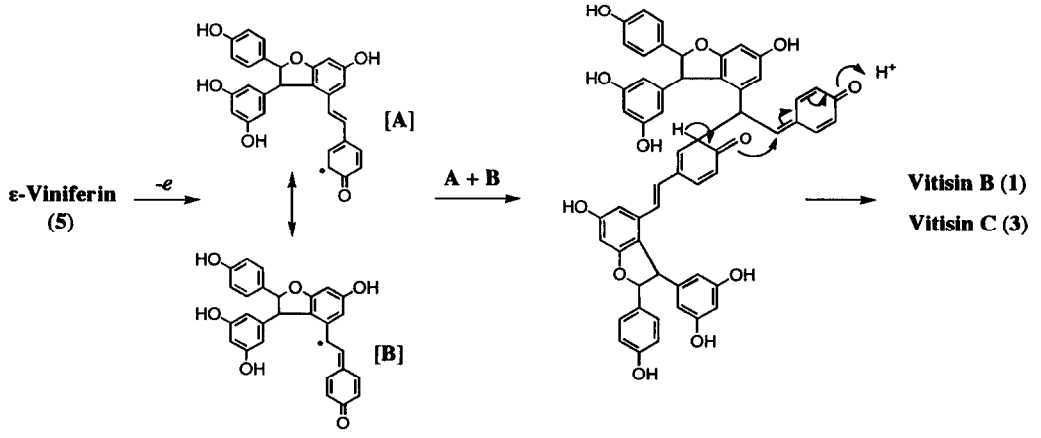

Fig. 1. Biogenetic Pathways of Vitisins B and C

Oxidation of (+)-ε-viniferin (5) The plausible biosynthetic pathways of (-)-vitisin B (**1**) and (+)-vitisin C (**3**) are shown in Fig. 1. (+)-ε-Viniferin (**5**) ([α]D +49.1 °), whose absolute configuration is known, was treated with horseradish peroxidase and hydrogen peroxide in aqueous acetone at 25 °C for 15 min to give (-)-vitisin B (**1**) and (+)-vitisin C (**3**) in 5 % and 4 % yields, respectively.[4,5,6] These results indicated that the absolute configurations of not only (+)-vitisin C but also (-)-vitisin B, (-)-*cis*-vitisin B and (-)-viniferal should be represented as **3**, **1**, **2** and **4**, respectively.

EXPERIMENTAL

General procedure. IR spectra were recorded as KBr disk on a JASCO FT/IR-5000 infrared spectrophotometer. UV spectra were recorded on a JASCO UVIDEC-610 spectrophotometer in MeOH. Optical rotations were determined on a JASCO DIP-370 digital polarimeter (cell length 100 mm, unless otherwise indicated). Circular dichroism (CD) spectra were taken on a JASCO J-600 spectropolarimeter (cell length 10 mm, unless otherwise indicated). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL A-600 spectrometer.

Isolation of vitisin C and viniferal. Dried corks of Vitis vinifera 'Kyohou' (3.8 kg) cultivated in Wakayama Prefecture, Japan, were extracted with MeOH (30 l x 2) at room temperature to yield an extract (409 g). A part of the extract (205 g) was partitioned between hexane, chloroform and ethyl acetate, and water to give hexane (4.9 g), chloroform (30.7 g) and ethyl acetate (62.2 g) solubles, respectively. A part of the ethyl acetate soluble fraction (15.5 g) was subjected to medium pressure column chromatography over silica gel using a gradient solvent system of chloroform and methanol (20 : 1 to 4 : 1). The chloroform and methanol (6 : 1) eluting fraction (256 mg) was subjected to column chromatography over silica gel (chloroform and methanol (20 : 1)), followed by preparative TLC (chloroform and methanol (5 : 1) and hexane and acetone (1 : 1)) to give viniferal (**4**) 12 mg. The chloroform and methanol (4 : 1) eluting fraction (709 mg) was subjected to medium pressure column chromatography over silica gel (chloroform and methanol (20 : 1 to 10 : 1)) to give (+)-ε-viniferin (**5**) 279 mg. The chloroform and methanol (3 : 1) eluting fraction (5.18 g) was subjected to medium pressure column chromatography over silica gel (chloroform and methanol (20 : 1 to 10 : 1)) to give vitisin C (**3**) 40 mg and vitisin B (**1**) 3.96 g. **1**; [α]D -90 ° (*c* 2.3, MeOH), CD (MeOH) Δε (nm); -12 (309), +24 (237), -8.2 (221), +23 (207). **3**; [α]D +239.9 ° (*c* 0.5, MeOH), CD (MeOH) Δε (nm); +6.4 (307), +60 (237), -50 (216), +23 (204). IR ν_{max} (film) 3300 br, 1605 cm^{-1}, EIMS *m/z* 644 [M^+], ^{1}H NMR given in Table 1, ^{13}C NMR given in Table 2. **4**; [α]D -131.7 ° (*c* 1.6, MeOH), IR ν_{max} (film) 3460 br, 1675, 1605 cm^{-1}, HR-FABMS *m/z* 575.1664 [MH^+], ^{1}H NMR given in Table 1, ^{13}C NMR given in Table 2. **5**; [α]D +49.1 ° (*c* 1.9, MeOH), FABMS *m/z* 455 [M^+], ^{1}H NMR given in Table 1, ^{13}C NMR given in Table 2.

Methylation of vitisin C. A mixture of vitisin C (**3**) (40 mg), methyl iodide (0.6 ml) and anhydrous potassium carbonate (1.39 g) in acetone (10 ml) was refluxed for 5 hr under nitrogen atmosphere. After evaporation of the solvent, the residue was chromatographed over silica gel (benzene - ethyl acetate (20 : 1)) to give a nonamethyl ether (**6**) (28 mg); FABMS: *m/z* 1033 [MH^+]; ^{1}H NMR ($CDCl_3$, 600MHz) δ 7.04 (2H, d, J=8.8 Hz, H-2a,6a), 6.82 (2H, d, J=8.8 Hz, H-3a,5a), 5.31 (1H, d, J=4.4 Hz, H-7a), 3.55 (1H, d, J=4.4 Hz, H-8a), 5.98 (2H, d, J=2.2 Hz, H-10a,14a), 6.24 (1H, t, J=2.2 Hz, H-12a), 7.05 (2H, d, J=8.8 Hz, H-2b,6b), 6.68 (2H, d, J=8.8 Hz, H-3b,5b), 5.21 (1H, d, J=9.5 Hz, H-7b), 4.26 (1H, d, J=9.5 Hz, H-8b), 6.46 (1H, d, J=2.2 Hz, H-12b), 6.26 (1H, d, J=2.2 Hz, H-14b), 6.61 (1H, d, J=2.2 Hz, H-2c), 6.69 (1H,

J=8.1 Hz, H-5c), 6.98 (1H, dd, J=8.1, 2.20 Hz, H-6c), 6.50 (1H, d, J=16.1 Hz, H-7c), 6.74 (1H, d, J=16.1 Hz, H-8c), 6.45 (1H, d, J=2.2 Hz, H-12c), 6.66 (1H, d, J=2.2 Hz, H-14c), 7.25 (2H, d, J=8.8 Hz, H-2d,6d), 6.86 (2H, d, J=8.8 Hz, H-3d,5d), 5.51 (1H, d, J=5.9 Hz, H-7d), 4.48 (1H, d, J=5.9 Hz, H-8d), 6.32 (2H, d, J=2.2 Hz, H-10d,14d), 6.33 (1H, t, J=2.2 Hz, H-12d), 3.77 (3H, s, MeO-4a), 3.62 (6H, s, MeO-11a,13a), 3.71 (3H, s, MeO-4b), 3.74 (3H, s, MeO-13b), 3.85 (3H, s, MeO-13c), 3.78 (3H, s, MeO-4d), 3.68 (6H, s, MeO-11d,13d). ^{13}C NMR ($CDCl_3$, 150MHz) δ 133.6 (s, C-1a), 126.7 (d, C-2a,6a), 113.9 (d, C-3a,5a), 159.4 (s, C-4a), 92.7 (d, C-7a), 55.9 (d, C-8a), 145.62 (s, C-9a), 105.7 (d, C-10a,14a), 161.1 (s, C-11a,13a), 98.8 (d, C-12a), 131.9 (s, C-3b,5b), 159.9 (s, C-4b), 93.1 (d, C-7b), 54.1 (d, C-8b), 129.9 (s, C-9b), 121.1 (s, C-10b), 161.6 (s, C-11b), 94.7 (d, C-12b), 161.3 (s, C-13b), 106.5 (d, C-14b), 130.7 (s, C-1c), 124.2 (d, C-2c), 139.0 (s, C-3c), 159.7 (s, C-4c), 109.7 (s, C-5c), 126.2 (d, C-6c), 123.0 (d, C-7c), 130.0 (d, C-8c), 135.5 (s, C-9c), 119.6 (s, C-10c), 161.4 (s, C-11c), 95.1 (d, C-12c), 161.2 (s, C-13c), 102.5 (d, C-14c), 133.8 (s, C-1d), 126.9 (d, C-2d,6d), 114.0 (d, C-3d,5d), 159.5 (s, C-4d), 93.0 (d, C-7d), 56.8 (d, C-8d), 145.8 (s, C-9d), 105.8 (d, C-10d,14d), 161.2 (s, C-11d,13d), 98.9 (d, 12d), 55.17 (OMe), 55.22 (OMe x 3), 55.28 (OMe x 3), 55.51 (OMe), 55.53 (OMe).

Ozonolysis of the nonamethyl ether. A solution of the nonamethyl ether (**6**) (13 mg) in ethyl acetate (15 ml) was cooled at -78 °C, treated with ozone for 5 min, and then worked up with dimethyl sufide to give the resulting mixture. The mixture was separated by preparative TLC (silica gel, benzene - ethyl acetate (20 : 1)) to give two compounds (**7** and **8**) (0.2 mg and 2.0 mg, respectively). The spectral data of **7** were identical with those of the aldehyde derived from vitisin B (**1**).[1] **8**; $[\alpha]_D$ +197.0 ° (*c* 0.1, $CHCl_3$, cell length; 100 mm), IR ν_{max} (film) 3010, 2925, 2835, 1690, 1595 cm^{-1}, EIMS *m/z* 644 [M^+], ^{1}H NMR given in Table 1, ^{13}C NMR given in Table 2.

Methylation of viniferal. A mixture of viniferal (**4**) (10 mg), methyl iodide (0.2 ml) and anhydrous potassium carbonate (240 mg) in acetone (10 ml) was refluxed for 3 hr under nitrogen atmosphere. After evaporation of the solvent, the residue was separated by preprative TLC (silica gel, chloroform - ethyl acetate (20 : 1)) to give a pentamethyl ether (**9**) (6 mg); $[\alpha]_D$ -120 ° (*c* 0.4, $CHCl_3$). The physicochemical data of the compound were identical to those of the aldehyde obtained from the nona methyl ether (**9**) of vitisin B (**1**).[1]

Reaction of of (+)-ε-viniferin with peroxidase and hydrogen peroxide. A mixture of (+)-ε-viniferin (**5**) (10 mg), horseradish peroxidase (0.04 mg) in 50% aqueous acetone (1 ml) was stirred at 25 °C for 5 min and then 30% hydrogen peroxide (2.5 μl) was added to the reaction mixture. After 15 min, the mixture was extracted with ethyl acetate. The extract was washed by brine, dried over sodium sulfate, concentrated, and separated by HPLC (YMC-C8 (ϕ20 x 250 mm), methanol - water (6 : 4) to give vitisin B (**1**) (0.5 mg) and vitisin C (**3**) (0.4 mg). The physicochemical data of the compounds were respectively identical to those of natural vitisins B (**1**)[1] and C (**3**). Synthetic vitisin B (**1**); CD (MeOH) Δε (nm): -4.9 (302), +22 (236), -21 (220), +37 (206). Synthetic vitisin C (**3**); CD (MeOH) Δε (nm): +6.2 (307), +67 (238), -46 (217), +24 (205).

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REFERENCES AND NOTES

1. Oshima, Y.; Kamijo, A.; Ohizumi, Y.; Niwa, M.; Ito, J.; Hisamichi, K.; Takeshita, M. *Tetrahedron* **1995**, 51, 11979 - 11986.
2. The details including those of the related compounds will be reported elsewhere.
3. The HMBC spectrum of **8** showed the long range ^{1}H-^{13}C correlations between H-7a and C-2a (6a), H-7a and C-9a, H-8a and C-10a (14a), H-8a and C-1a, H-8a and C-11b, H-7b and C-2b (6b), H- 8b and C-1b, H-14b and C-8b, H-14b and C-10b, and H-14b and C-12b, respectively.
4. Kurihara, H.; Kawabata, J.; Ichikawa, S; Mizutani, J. *Agric. Biol. Chem.* **1990**, 54, 1097 - 1099.
5. Langcake, P.; Pryce, R. J. *J. Chem. Soc. Chem. Commun.* 1977, 208 - 210.
6. Horseradish peroxidase was available from Wako Pure Chemical Industries. Ltd. (Osaka, Japan).

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