Pergamon

Tetrahedron Vol. 51, No. 44, pp. 11979-11986, 1995
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0040-4020/95 $9.50+0.00

0040-4020(95)00757-1

Novel Oligostilbenes from *Vitis coignetiae*[1]

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Abstract: Phytochemical investigation on oligostilbenes in a methanol extract of *Vitis coignetiae* (Japanese name: yama-budou) resulted in the isolation of a novel stilbene dimer, ε-viniferin diol, and two novel stilbene tetramers, vitisin B and its stereoisomer *cis*-vitisin B. The structures of the oligostilbenes were determined by spectroscopic evidence and chemical reactions.

INTRODUCTION

During our studies on the hepatoprotective compounds from the Vitaceaeous plants, we isolated not only the hepatoprotective principle, ε-viniferin, but also the strongly hepatotoxic oligostilbenes, ampelopsin C and the vitisin A–*cis*-vitisin A mixture from *Ampelopsis brevipedunculata* var. *hancei* and *Vitis coignetiae*.[2-5] Our further phytochemical investigation on the Vitaceaeous oligostilbenes, which have unique carbon skeletons obtained by oxidative condensation of two – four moles of resveratrol, resulted in the isolation of a new stilbene dimer, ε-viniferin diol (**1**) and two novel stilbene tetramers, vitisin B (**3**) and its stereoisomer, *cis*-vitisin B (**4**).

RESULTS AND DISCUSSION

The molecular formula $C_{28}H_{24}O_8$ indicated for ε-viniferin diol (**1**), $[\alpha]_D$ +136.0°, was established by its FAB mass spectrum (*m/z*: 489 [MH^+]) and an analysis of its ^1H and ^{13}C NMR spectra (Table 1). A comparative study of the ^1H and ^{13}C NMR spectra of ε-viniferin diol (**1**) and ε-viniferin (**2**), a representative stilbene dimer of the Vitaceaeous plants,[6] indicated that ε-viniferin diol (**1**) has a 4-hydroxyphenyl group and a dihydrobenzofuran moiety with 3,5-dihydroxyphenyl and 4-hydroxyphenyl substituents at C-8' and C-7', respectively. In addition to two methine hydrogen signals at δ 4.40 and 5.37 (each 1H, d, J=4.0 Hz), two oxymethine hydrogen signals were observed at δ 4.35 and 4.51 (each 1H, d, J=4.0 Hz) in the aliphatic hydrogen region of the ^1H NMR spectrum of ε-viniferin diol (**1**). Further, two olefinic carbon signals of ε-viniferin (**2**) were replaced by two oxymethine carbon signals at δ 75.1 and 75.9 (each d) in the ^{13}C NMR spectrum of ε-viniferin diol (**1**). On the basis of these spectral data, ε-viniferin diol (**1**) was regarded as a dihydroxy derivative of ε-viniferin (**2**).

The relative configuration of the C-7' and C-8' substituents in the dihydrobenzofuran moiety was determined to be *trans* by detection of NOEs between H-7'–H-10'(14') and H-8'–H-2'(6'). Oxidation of ε-viniferin (**2**) with osmium tetroxide afforded ε-viniferin diol (**1**) as a main product. The reaction demonstrated that the diol part in the molecule **1** is *threo*. Moreover, osmium tetroxide was assumed to predominantly approach from α-face of the double bond of ε-viniferin (**2**) because of steric effect of the 3,5-dihydroxyphenyl group at C-8', and therefore the stereochemical relation of the dihydrobenzofuran and diol parts was concluded to be that of the formula **1**.

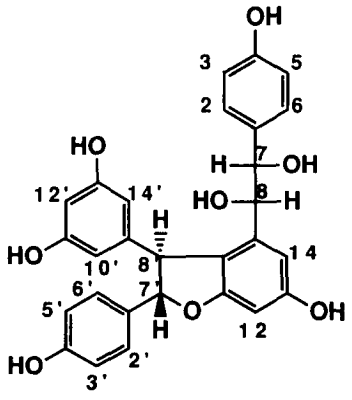
Vitisin B (**3**), $[\alpha]_D$ -90.0°, showed a quasimolecular ion peak at *m/z* 907.2723 [MH^+] (*m/z* 907.2755 calcd. for $C_{56}H_{43}O_{12}$)) in the high resolution FAB mass spectrum. The ^1H NMR spectrum of vitisin B (**3**) exhibited signals for six sets of *ortho*-coupled aromatic hydrogens (δ 6.76, 7.13 (each 2H, d, J=8.4 Hz); 6.58, 6.82 (each 2H, d, J=8.8 Hz); 6.52, 7.18 (each 2H, d, J=8.4 Hz)), two sets of *meta*-coupled aromatic hydrogens (δ 6.09, 6.28 (each 1H, d, J=2.2 Hz); 6.24 (1H, d, J=1.8 Hz), 6.58 (1H, brs)) and two sets of AX_2-type *meta*-coupled aromatic hydrogens (δ 6.14 (2H, d, J=1.5 Hz), 6.13 (1H, t, J=1.5 Hz); 5.98 (2H, d, J=2.2 Hz), 6.06 (1H, t, J=2.2 Hz)) (Table 2). The presence of aliphatic hydrogen signals at δ 4.33, 5.36 (each 1H, d, J=6.2 Hz), 4.25, 5.42 (each 1H, d, J=5.1 Hz) and 4.36, 5.33 (each 1H, d, J=4.8 Hz)) suggested the presence of three dihydrobenzofuran moieties bearing 4-oxyphenyl and 3,5-dioxyphenyl groups characteristic for oligostilbenes biosynthesized from resveratrol molecules. In addition to these signals, like vitisin A,[4] the presence of an 1-oxy-2,4-disubstituted benzene ring and a *trans*-double bond was implied by hydrogen signals at δ 6.65 (1H, d, J=1.8 Hz), 6.68 (1H, d, J=8.4 Hz), 6.98 (1H, dd, J=8.4, 1.8 Hz) and 6.50, 6.68 (each 1H, d, J=16.5 Hz), respectively.

Vitisin B (**3**) was methylated with dimethyl sulfate and potassium carbonate in acetone to afford a nonamethyl ether (**5**) (FAB MS: *m/z* 1033 [MH^+]), which was oxidized with ozone to give two degradative products (**6** and **7**). The compound **6** was shown to be identical in all respect with the aldehyde which was previously obtained from the vitisin A–*cis* vitisin A mixture by the same reactions.[4] The degradative product **7** (EI MS: *m/z* 644 [M^+]) showed an aldehyde hydrogen signal (δ 9.70 (1H, s)) and those for four sets of *ortho*-coupled aromatic hydrogens (δ 6.89, 7.21 (each 2H, d, J=8.4 Hz); 6.62, 6.74 (each 2H, d, J=8.4 Hz)), a set of *meta*-coupled aromatic hydrogens (δ 6.21, 6.47 (each 1H, d, J=2.4 Hz)), a set of AX_2-type *meta*-coupled aromatic hydrogens (δ 6.01 (2H, d, J=2.4 Hz), 6.09 (1H, t, J=2.4 Hz)) and a set of 1-oxy-2,4-disubstituted

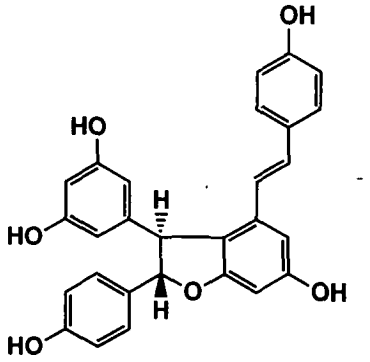
Table 1. ^{1}H and ^{13}C NMR Data of ε-viniferin diol (**1**) and ε-viniferin (**2**)[1]

Position No.	1		2	
1		135.0 (s)		130.0 (s)
2,6	6.77 (d, 8.6)	129.2 (d)	7.15 (d, 8.0)	128.6 (d)
3,5	6.62 (d, 8.6)	116.7 (d)	6.71 (d, 8.0)	116.1 (d)
4		157.5 (s)		158.0 (s)
7	4.35 (d, 4.0)	75.1 (d)[2]	6.91 (d, 16.0)	123.3 (d)
8	4.51 (d, 4.0)	75.9 (d)[2]	6.65 (d, 16.0)	130.1 (d)
9		142.3 (s)		136.3 (s)
10		119.8 (s)		119.7 (s)
11		162.4 (s)		162.3 (s)
12	6.34 (d, 2.0)	97.2 (d)	6.30 (d, 2.0)	96.7 (d)
13		159.7 (s)		159.4 (s)
14	6.68 (d, 2.0)	108.8 (d)	6.70 (d, 2.0)	104.1 (d)
1'		134.7 (s)		133.8 (s)
2',6'	7.17 (d, 8.5)	128.1 (d)	7.19 (d, 8.0)	127.8 (d)
3',5'	6.83 (d, 8.5)	115.8 (d)	6.80 (d, 8.0)	116.0 (d)
4'		158.6 (s)		158.0 (s)
7'	5.37 (d, 4.0)	94.3 (d)	5.40 (d, 5.0)	93.8 (d)
8'	4.40 (d, 4.0)	57.5 (d)	4.44 (d, 5.0)	57.0 (d)
9'		148.5 (s)		147.3 (s)
10',14'	6.18 (d, 2.5)	107.5 (d)	6.22 (s)	106.9 (d)
11',13'		160.5 (s)		159.7 (s)
12'	6.32 (t, 2.5)	102.6 (d)	6.22 (s)	101.9 (d)

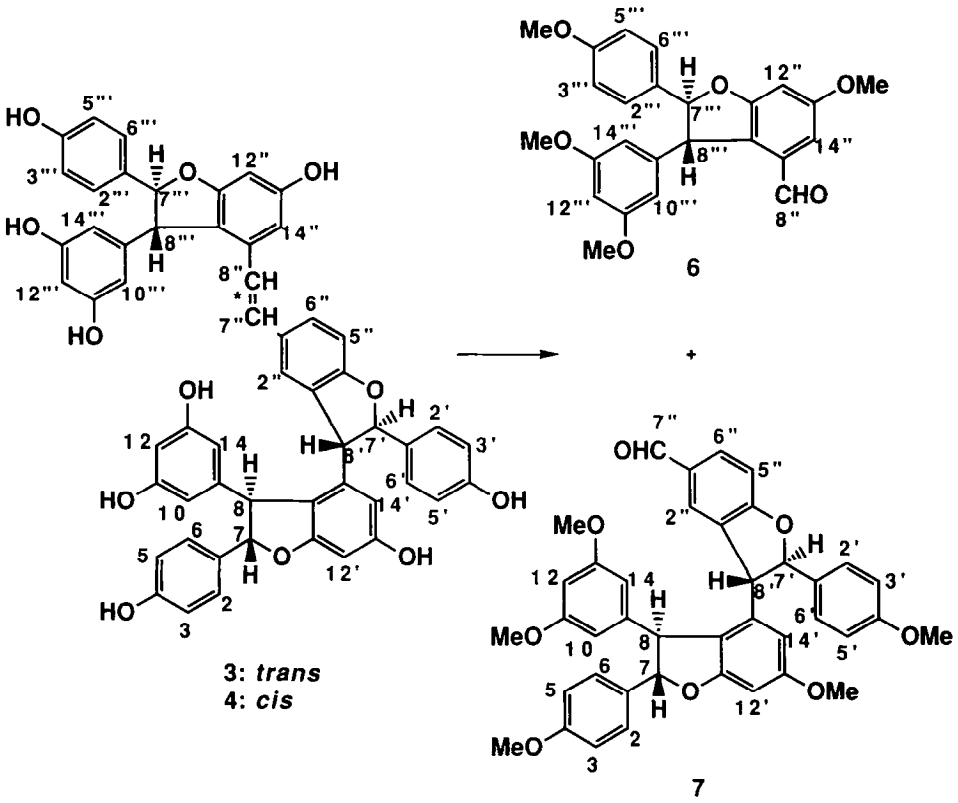
[1]Spectra were measured in acetone-d_6 at 500 and 125 MHz for ^{1}H and ^{13}C NMR. Assignments of the ^{1}H NMR signals were confirmed by decoupling experiments. [2]Assignment may be reversed.



1



2



benzene ring hydrogens (δ 6.90 (1H, d, J=8.4 Hz), 7.31 (1H, brd, J=1.8 Hz), 7.68 (1H, dd, J=8.4, 1.8 Hz)) in its ^{1}H NMR spectrum. Moreover, the ^{1}H NMR spectrum of the compound **7** exhibited the presence of two dihydrobenzofuran moieties in the molecule (δ 4.38, 5.41 (each 1H, d, J=4.8 Hz); 4.40, 5.59 (each 1H, d, J=6.6 Hz)). From detailed decoupling experiments of the ^{1}H NMR spectrum, three benzylic hydrogens at δ 4.38, 5.41 and 5.59 were found to long-range couple with the aromatic hydrogens at δ 6.01, 7.21 and 6.74, respectively, while the long-range coupling of the remaining benzylic hydrogen at δ 4.40 was not clearly observed. After the assignment of the ^{13}C NMR signals of the compound **7** by HMQC spectrum (Table 2), the HMBC spectrum was analyzed, which showed the following long range ^{13}C–^{1}H correlations: δ 56.9 (C-8)–6.01 (H-10, 14), 105.4 (C-10, 14)–4.38 (H-8), 126.6 (C-2, 6)–5.41 (H-7), 126.9 (C-2', 6')–5.59 (H-7'). These ^{13}C–^{1}H long-range couplings supported the benzylic couplings obtained by the decoupling experiments described above. Furthermore, the HMBC spectrum showed the cross peak between the C-14' signal at δ 106.6 and the H-8' benzyl hydrogen signal at δ 4.40, demonstrating the connectivity of C-8' and C-9' in the compound **7**.

The relative configurations of three dihydrobenzofuran groups of vitisin B (**3**) were concluded to be *trans* from NOEs between H-7–H-10(14), H-8–H-2(6); H-7'–H-14', H-8'–H-2'(6'); H-7'''–H-10'''(14'''), H-8'''–H-2'''(6''') in the ^{1}H NMR spectrum of a catalytic hydrogenation product (**8**) of the nonamethyl ether (**5**).

Table 2. ^{1}H and ^{13}C NMR Data of Vitisin B (**3**), *cis*-Vitisin B (**4**) and Their Derivative (**7**)[1]

Position No.	**3**[2]		**4**[2]		**7**[3]	
1		133.9 (s)		133.9 (s)		133.8 (s)
2,6	7.13 (d, 8.4)	128.2 (d)	7.01 (d, 8.8)	128.5 (d)	7.21 (d, 8.4)	126.6 (d)
3,5	6.76 (d, 8.4)	116.3 (d)	6.73 (d, 8.8)	116.3 (d)	6.89 (d, 8.4)	114.3 (d)
4		158.5 (s)		158.4 (s)		159.8 (s)
7	5.36 (d, 6.2)	94.8 (d)	5.21 (d, 5.9)	94.9 (d)	5.41 (d, 4.8)	93.3 (d)
8	4.33 (d, 6.2)	58.2 (d)	3.85 (d, 5.9)	57.8 (d)	4.38 (d, 4.8)	56.9 (d)
9		147.2 (s)		147.2 (s)		145.9 (s)
10,14	6.14 (d, 1.5)	107.5 (d)	5.93 (d, 2.2)	107.3 (d)	6.01 (d, 2.4)	105.4 (d)
11,13		160.0 (s)		159.6 (s)		161.2 (s)
12	6.13 (t, 1.5)	102.3 (d)	6.09 (t, 2.2)	101.9 (d)	6.09 (t, 2.4)	99.0 (d)
1'		132.7 (s)		132.5 (s)		131.6 (s)
2',6'	6.58 (d, 8.8)	127.8 (d)	6.60 (d, 8.8)	127.8 (d)	6.74 (d, 8.4)	126.9 (d)
3',5'	6.52 (d, 8.8)	116.0 (d)	6.54 (d, 8.8)	116.2 (d)	6.62 (d, 8.4)	114.0 (d)
4'		158.0 (s)		158.0 (s)		159.6 (s)
7'	5.42 (d, 5.1)	92.2 (d)	5.44 (d, 5.9)	92.3 (d)	5.59 (d, 6.6)	92.7 (d)
8'	4.25 (d, 5.1)	53.0 (d)	4.22 (d, 5.9)	52.9 (d)	4.40 (d, 6.6)	55.2 (d)
9'		142.5 (s)		142.3 (s)		139.9 (s)
10'		120.0 (s)		120.3 (s)		120.5 (s)
11'		162.7 (s)		162.8 (s)		161.8 (s)
12'	6.28 (d, 2.2)	96.7 (d)	6.28 (d, 2.2)	96.7 (d)	6.47 (d, 2.4)	94.7 (d)
13'		160.5 (s)		160.4 (s)		162.0 (s)
14'	6.09 (d, 2.2)	107.5 (d)	6.11 (d, 2.2)	107.3 (d)	6.21 (d, 2.4)	106.6 (d)
1"		132.7 (s)		131.7 (s)		132.4 (s)
2"	6.65 (d, 1.8)	125.5 (d)	6.54 (brs)	127.0 (d)	7.31 (brd, 1.8)	126.2 (d)
3"		132.3(s)		132.7 (s)		128.4 (s)
4"		160.2 (s)		160.0 (s)		164.2 (s)
5"	6.68 (d, 8.4)	110.7 (d)	6.56 (d, 8.4)	110.0 (d)	6.90 (d, 8.4)	110.3 (d)
6"	6.98 (dd, 8.4, 1.8)	126.8 (d)	6.91 (dd, 8.4, 1.8)	130.0 (d)	7.68 (dd, 8.4, 1.8)	133.2 (d)
7"	6.50 (d, 16.5)	124.2 (d)	5.96 (d, 13.2)	126.7 (d)	9.70 (s)	190.5 (d)
8"	6.68 (d, 16.5)	130.5 (d)	6.06 (d, 13.2)	131.5 (d)		
9"		136.8 (s)		137.5 (s)		
10"		120.1 (s)		120.3 (s)		
11"		162.8 (s)		162.7 (s)		
12"	6.24 (d, 1.8)	96.9 (d)	6.17 (d, 2.2)	96.8 (d)		
13"		159.6 (s)		159.4 (s)		
14"	6.58 (brs)	104.6 (d)	6.20 (d, 2.2)	108.8 (d)		
1"'		134.6 (s)		134.2 (s)		
2"',6"'	7.18 (d, 8.8)	127.8 (d)	7.12 (d, 8.8)	128.0 (d)		
3"',5"'	6.82 (d, 8.8)	116.5 (d)	6.76 (d, 8.8)	116.4 (d)		
4"'		158.3 (s)		158.5 (s)		
7"'	5.33 (d, 4.8)	94.7 (d)	5.30 (d, 4.8)	94.9 (d)		
8"'	4.36 (d, 4.8)	57.9 (d)	4.27 (d, 4.8)	57.9 (d)		
9"'		147.7 (s)		147.6 (s)		
10"',14"'	5.98 (d, 2.2)	107.0 (d)	5.97 (d, 2.2)	107.2 (d)		
11"',13"'		160.1 (s)		160.0 (s)		
12"'	6.06 (t, 2.2)	102.5 (d)	6.06 (t, 2.2)	102.5 (d)		

[1]Assinments were confirmed by 2D ^{1}H-^{1}H COSY, 2D ^{1}H-^{13}C COSY, HMQC, COLOC and HMBC spectra. [2]Spectra were measured in CD_3OD at 600 and 150 MHz for ^{1}H and ^{13}C NMR. [3]Spectra were measured in $CDCl_3$ at 600 and 150 MHz for ^{1}H and ^{13}C NMR. Methoxyl signals: 3.80 (4-OMe), 3.60 (11, 13-OMe), 3.77 (4'-OMe), 3.75 (13'-OMe); 55.2 (OMe x 2), 55.3, 55.5, 55.6.

In addition to the strong NOE between H-7' and H-14', NOEs were also detected between H-8–H-8', H-8–H-2" and H-8'–H-14'. Moreover, the following NOEs were unambiguously observed: H-8–H-7', H-8–H-2", H-7'–H-14', H-8'–H-14' and 11(13)-OMe–H-3'(5') in the NOE experiments of the degradative product (**7**). These results, together with the study using Dreiding stereomodel, implied the spatial relationship of C-7, 8 and C-7', 8'. Biogenetic consideration that vitisin B (**3**) is biosynthesized by oxidative coupling of two molecules of ε-viniferin (**2**) at C-7', 8' and C-3", 4", suggested the relative stereochemistry of C-7"' and C-8"' as described in the structure **3**.

The ^1H and ^{13}C NMR spectra of *cis*-Vitisin B (**4**), $[\alpha]_D$ -41.9°, FAB MS: *m/z* 907 [MH$^+$], resembled those of vitisin B (**3**) (Table 2). In the ^1H NMR spectrum, the former (**4**) clearly differs from the latter (**3**) in that the former (**4**) has *cis*-olefinic hydrogen signals at δ 5.96 and 6.06 (each 1H, d, J=13.2 Hz). The fact indicated that they are geometrical isomers of the double bond, and this was unambiguously substantiated by photochemical transformation from vitisin B (**3**) to *cis*-vitisin B (**4**). The H-8 signal in the *cis*-isomer (**4**) appeared at higher field relative to that of the *trans*-isomer (**3**), and the shift in the signal may be due to the shielding effect of the upper left stilbene part in the formula **4**.

Like vitisin A and *cis*-vitisin A,[4] these compounds (**3** and **4**) have characteristic feature that the C-3 atom of resveratrol molecule involves in the bond formation in resveratrol oligomers.

EXPERIMENTAL

General Procedure. IR spectra were recorded as KBr on a SHIMADZU IR-408 spectrometer. UV spectra were recorded on a SHIMADZU UV-260 spectrometer in MeOH. FAB and FD MS were measured on JEOL JMS-DX 303 mass spectrometer. Optical rotations were determined on a JASCO DIP-360 digital polarimeter. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM FX-500 and A-600 spectrometers using tetramethylsilane as an internal standard. Coupling constants are in hertz. Multiplicity: s, singlet; d, doublet; brd, broad doublet; t, triplet; dd, double doublet; m, multiplet.

Isolation of ε-Viniferin Diol, Vitisin B and cis-Vitisin B. Dried stems of *Vitis coignetiae* (25.5 kg) (collected in Miyagi Prefecture, Japan) were extracted with MeOH (75 l x 3) at room temperature to yield the extract (850 g). The MeOH extract (850 g) was partitioned with AcOEt (3 l) and water (3 l) to give AcOEt (730 g) and water solubles. The AcOEt solubles (210 g) were chromatographed over silica gel (1 kg), and the column was eluted with *n*-hexane–AcOEt mixtures. The *n*-hexane–AcOEt (2:8)-eluting fraction (25 g) was chromatographed over silica gel (150 g), and the column was eluted with the increasing polarity of $CHCl_3$–MeOH mixtures. A silica gel chromatography of the $CHCl_3$–MeOH (9:1)-eluting fraction followed by repeated HPLC work ((1) column: Tosoh TSK gel ODS-120A: 30 x 2.15 cm i.d.; solvent: CH_3CN–water (27.5:72.5); flow rate: 3 ml/min, (2) column: YMC-Pack C_8: 25 x 2 cm i.d.; solvent: MeOH–water (6:4); flow rate: 2 ml/min) afforded vitisin B (**3**) and *cis*-vitisin B (**4**) (80 and 25 mg, respectively). The *n*-hexane-AcOEt (2:8) and AcOEt-eluting fraction of the AcOEt solubles (9 g) was chromatographed over silica gel (eluting solvent: $CHCl_3$-MeOH). The $CHCl_3$-MeOH (87:13)-eluting fraction was separated by HPLC (column: Tosoh TSK gel ODS-120A: 30 x 2.15 cm i.d.; solvent: CH_3CN–water (20:80 and 25:75); flow rate: 3 ml/min) yielded ε-viniferin diol (**1**) (16 mg).

ε-Viniferin diol (**1**): an amorphous powder, $[\alpha]_D$ +136.0° (*c* 0.19, MeOH), FAB MS *m/z*: 489 [MH$^+$]; UV λ_{max} nm (log ε): 284 (3.34); IR ν_{max} cm^{-1}: 3270, 1600, 1515, 1450; ^{1}H and ^{13}C NMR (see Table 1).

Vitisin B (**3**): an amorphous powder, $[\alpha]_D$ -90.0° (*c* 2.28, MeOH); high-resolution FAB-MS *m/z* 907.2723 [MH$^+$]; UV λ_{max} nm (log ε): 285 (4.10), 320 (4.04); IR ν_{max} cm^{-1}: 3180, 1600, 1510, 1450; ^{1}H and ^{13}C NMR (see Table 2).

cis-Vitisin B (**4**): $[\alpha]_D$ -41.9° (*c* 0.72, MeOH), FAB-MS *m/z* 907 [MH$^+$]; ^{1}H and ^{13}C NMR (see Table 2).

Osmium Tetroxide Oxidation of ε-Viniferin. To a AcOEt solution (10 ml) of ε-viniferin (**2**) (50 mg) was added *t*-BuOH solution (0.2 ml) of osmium tetroxide (0.5% w/v) and 4-methylmorphiline water solution (60% w/v) (0.2 ml), and the mixture was stirred for 1 hr at room temperature. The reaction mixture was chromatographed over aluminum to give ε-viniferin diol (**1**) (34 mg) which was identified with the natural ε-viniferin diol (**1**) by direct comparison of their $[\alpha]_D$, FAB MS, ^{1}H and ^{13}C NMR.

Methylation followed by Ozonolysis of Vitisin B. To a solution of vitisin B (**3**) (80 mg) in acetone (10 ml) were added dimethyl sulfate (1 ml) and anhydrous potassium carbonate (200 mg). The reaction mixture was refluxed at 80°C for 12 hr, and after evaporation of solvent, it was chromatographed over silica gel to yield a nonamethyl ether (**5**) (76 mg) (FAB MS *m/z*: 1033 [MH$^+$]). The solution of the ether (**5**) (40 mg) in methylene chloride (10 ml) at 0°C was treated with an ozone-saturated methylene chloride solution (10 ml), and excess dimethyl sulfide was added to the resulting mixture. After evaporation of the solvent, the residue was chromatographed over silica gel to afford two compounds (**6** and **7**) (12 and 18 mg, respectively). The physicochemical data of the compound **6** were identical to those of the aldehyde obtained from the vitisin A–*cis*-vitisin A mixture.[4] **7**: EI MS *m/z*: 644 [M$^+$]; ^{1}H and ^{13}C NMR (Table 2).

Catalytic Hydrogenation of Vitisin B Nonamethyl Ether. A mixture of vitisin B nonamethyl ether (**5**) (30 mg) and PtO_2 (10 mg) in MeOH (10 ml) was shaken under H_2 for 24 hr at room temperature, and the reaction mixture, after filtration, was chromatographed over silica gel to yield a dihydro derivative (**8**) (28 mg); an amorphous powder, FAB MS: *m/z* 1035 [MH$^+$]; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 2.26 (1H, m, H-7"), 2.36 (2H, t, J=7.3 Hz, H-8"), 2.44 (1H, m, H-7"), 3.60 (6H, s, 11,13-OMe), 3.61 (6H, 11"',13"'-OMe), 3.71 (3H, s, 13'-OMe), 3.745 (3H, 4'-OMe), 3.747 (3H, s, 13"-OMe), 3.751 (3H, s, 4-OMe), 3.76 (3H, s, 4"'-OMe), 4.18 (1H, d, J=6.6 Hz, H-8"'), 4.27 (1H, d, J=6.6 Hz, H-8'), 4.40 (1H, d, J=4.4 Hz, H-8), 5.42 (1H, d, J=4.4 Hz, H-7), 5.42 (1H, d, J=6.6 Hz, H-7'), 5.43 (1H, d, J=6.6 Hz, H-7"'), 6.07 (2H, brs, H-10,14), 6.13 (1H, brs, H-12), 6.21 (1H, brs, H-14"), 6.23 (1H, d, J=1.8 Hz, H-14'), 6.25 (2H, d, J=1.8 Hz, H-10"',14"'), 6.27 (1H, t, J=1.8 Hz, H-12"'), 6.36 (1H, brs, H-12"), 6.37 (1H, brs, H-2"), 6.44 (1H, d, J=1.8 Hz, H-12'), 6.53 (1H, brd, J=8.1 Hz, H-6"), 6.55 (2H, d, J=8.1 Hz, H-3',5'), 6.62 (1H, d, J=8.1 Hz, H-5"), 6.67 (2H, d, J=8.1 Hz, H-2',6'), 6.85 (2H, d, J=8.1 Hz, H-3"',5"'), 6.86 (2H, d, J=8.1 Hz, H-3,5), 7.17 (2H, d, J=8.1 Hz, H-2"',6"'), 7.22 (2H, d, J=8.1 Hz, H-2,6).

Photochemical Transformation of Vitisin B to cis-Vitisin B. A solution of vitisin B (**3**) (10 mg) in MeOH (10 ml) was irradiated with a commertial fluorescent lamp (15 W) at room temperatrure for 4 hr. After removal of solvent, the residue wa separated by HPLC (column: YMC-Pack C_8: 25 x 2 cm i.d.; solvent: MeOH–water

(6:4); flow rate: 2 ml/min) to afford *cis*-vitisin B (**4**) (6 mg). The spectral data of the synthetic *cis*-vitisin B were identified with those of natural *cis*-vitisin B (**4**).

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(*Received in Japan* 2 *August* 1995; *accepted* 6 *September* 1995)