Pergamon

Tetrahedron 55 (1999) 2529–2544

TETRAHEDRON

New Oligostilbenes Having a Benzofuran from *Vitis vinifera* 'Kyohou'

Junko Ito,[a] Yoshiaki Takaya,[b] Yoshiteru Oshima[b] and Masatake Niwa*[a]

[a]Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 4688503, Japan

[b]Faculty of Pharmaceutical Sciences, Tohoku University, Aoba, Sendai 9808578, Japan

Received 24 November 1998; accepted 7 January 1999

Abstract: Three new oligostilbenes having a benzofuran moiety, viniferifuran, (+)-vitisifuran A and (-)-vitisifuran B, were isolated from *Vitis vinifera* 'Kyohou'. The structures of these oligostilbenes including the absolute configuration were elucidated by spectroscopic and chemical methods. Furthermore, these were chemically transformed from (+)-ε-viniferin, (+)-vitisin A and (-)-vitisin B, respectively, whose absolute configurations are known.

Keywords: Benzofurans; Natural products; Oligomers; Dehydrogenation.

INTRODUCTION

In previous papers,[1-4] we reported the isolation and structures of oligostilbenes having dihydrobenzofuran moieties isolated from the corks of *Vitis vinifera* 'Kyohou' cultivated in Wakayama Prefecture. Continuous study of the constituents of the above plant led to the isolation of three novel oligostilbenes, viniferifuran (**1**), (+)-vitisifuran A (**2**) and (-)-vitisifuran B (**3**) having a benzofuran moiety, respectively. These compounds **1**, **2** and **3** fluoresce a light-blue color when exposed to ultraviolet light. The structures, including their absolute configurations, were determined on the basis of the spectroscopic and chemical evidence. Furthermore, viniferifuran (**1**), (+)-vitisifuran A (**2**) and (-)-vitisifuran B (**3**) were successfully transformed from (+)-ε-viniferin (**4**), (+)-vitisin A (**5**) and (-)-vitisin B (**6**), respectively.

RESULTS AND DISCUSSION

Structure of viniferifuran (1) Viniferifuran (**1**) showed a quasimolecular ion peak at *m/z* 453.1341 [MH$^+$] (*m/z* 453.1338 calcd. for $C_{28}H_{21}O_6$) in the high resolution FAB-MS. As shown in Tables 1 and 2, the ^{1}H- and ^{13}C-NMR spectral data of viniferifuran (**1**) resembled very closely those of (+)-ε-viniferin (**4**)[5] except for the olefinic signals (**1**; δ_C 150.6 (C-7a), 117.4 (C-8a), **4**; δ_H 5.36 (d, *J*=6.6 Hz, H-7a), 4.34 (d, *J*=6.6 Hz, H-8a), δ_C 94.8 (C-7a), 58.3 (C-8a)). In the HMBC spectrum of **1**, cross peaks between C-7a and H-2a (6a) and between C-8a and H-10a (14a) were observed. These indicated viniferifuran (**1**) to be a dehydro-ε-viniferin and this was unambiguously substantiated by the following evidence. The methylation of **1** with methyl iodide and potassium carbonate in acetone gave a pentamethyl ether (**7**) (*m/z* 523 [MH$^+$]). The ether **7** was oxidized with ozone followed by treatment with dimethyl sulfide to give three degradative products **8**, **9** and **10** in 40.9, 39.1

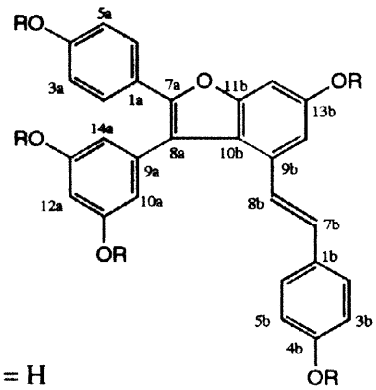
E-mail address: *[a] masa@meijo-u.ac.jp

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00039-3

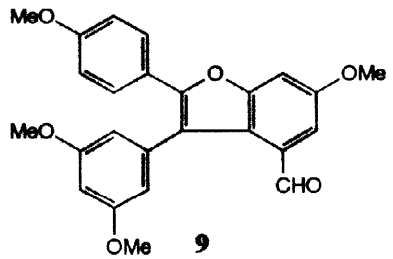
and 9.7 % yields, respectively. The product **8** was identical with 4-methoxybenzaldehyde by comparison with an authentic sample. The product **9** (*m/z* 419 [MH$^+$], δ_H 3.78 (3H, s, MeO-4a), 3.77 (6H, s, MeO-11a,13a), 3.90 (3H, s, MeO-13b), 9.75 (1H, s, H-8b), δ_C 152.2 (C-7a), 114.9 (C-8a), 189.7 (C-8b)) was characterized as 2-(4-methoxyphenyl)-3-(3,5-dimethoxyphenyl)-4-formyl-6-methoxybenzofuran. The product **10** (*m/z* 451 [MH$^+$], δ_H 3.82 (3H, s, MeO-4a), 3.71 (6H, s, MeO-11a,13a), 3.93 (3H, s, MeO-13b), 9.88 (1H, s, H-8b), δ_C 163.7 (C-7a), 193.5 (C-8a), 189.4 (C-8b)) was characterized as 2-(3,5-dimethoxybenzoyl)-3-(4-methoxybenzoyloxy)-5-methoxybenzaldehyde, which was apparently produced by further oxidation of **9** with ozone. Thus, the structure of viniferifuran is represented as **1**. Finally, (+)-ε-viniferin (**4**) was successfully converted into viniferifuran (**1**), as follows. (+)-ε-Viniferin (**4**) was acetylated with acetic anhydride and pyridine to give (+)-ε-viniferin pentaacetate (**11**) (*m/z* 665 [MH$^+$], δ_C 92.7 (C-7a), 56.6 (C-8a)). The acetate (**11**) was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene to give a dehydrogenated ester (**12**) (*m/z* 663 [MH$^+$], δ_C 151.1 (C-7a), 116.0 (C-8a)). The ester (**12**) was treated with potassium hydroxide in methanol to give a phenol, which was completely identical with natural viniferifuran (**1**).

Structure of (+)-vitisifuran A (2) (+)-Vitisifuran A (**2**), $[\alpha]_D$ +236.1° (*c* 0.44, MeOH), showed a quasimolecular ion peak at *m/z* 905.2593 [MH$^+$] (*m/z* 905.2598 calcd. for $C_{56}H_{41}O_{12}$) in the high resolution FAB-MS. As shown in Tables 1 and 2, the ^{1}H- and ^{13}C-NMR spectral data of (+)-vitisifuran A (**2**) resembled very closely those of (+)-vitisin A (**5**)[4] except for the olefinic signals (**2**; δ_C 150.5 (C-7a), 117.4 (C-8a), **5**; δ_H 5.31 (d, *J*=6.3 Hz, H-7a), 4.26 (d, *J*=6.3 Hz, H-8a), δ_C 94.7 (C-7a), 58.2 (C-8a)). Furthermore, the NMR data of the partial structure corresponding to viniferifuran (**1**) in (+)-vitisifuran A (**2**) were very similar to those of **1**. In the HMBC spectrum of **2**, cross peaks between C-7a and H-2a (6a), between C-8a and H-10a (14a), between C-7d and H-2d (6d) and between C-8d and H-14d were observed. These indicated (+)-vitisifuran A (**2**) to be a structure dehydrogenated between H-7a and H-8a of (+)-vitisin A (**5**). This was further supported by the following chemical evidence. The methylation of **2** with methyl iodide and potassium carbonate in acetone gave a decamethyl ether (**13**) (*m/z* 1045 [MH$^+$]). The ether (**13**) was oxidized with ozone followed by treatment with dimethyl sulfide to give three degradative products **9**, **10** and **14** in 47.5, 15.1 and 53.2 % yields, respectively. The product **14** was identical with an aldehyde derived from (+)-vitisin A (**5**),[4] including the sign of the optical rotation. Finally, (+)-vitisifuran A (**2**) was successfully converted from (+)-vitisin A (**5**) as follows. (+)-Vitisin A (**5**) was acetylated with acetic anhydride and pyridine to give decaacetyl (+)-vitisin A (**15**) (*m/z* 1327 [MH$^+$], δ_C 92.6 (C-7a), 56.5 (C-8a)). The acetate (**15**) was oxidized with DDQ in toluene to give a dehydrogenated ester (**16**) (*m/z* 1325 [MH$^+$], δ_C 150.7 (C-7a), 116.0 (C-8a)). The ester (**16**) was treated with potassium hydroxide in methanol to give a phenol, which was completely identical with natural (+)-vitisifuran A (**2**), including the sign of the optical rotation. Thus, the absolute structure of (+)-vitisifuran A is represented as **2**.

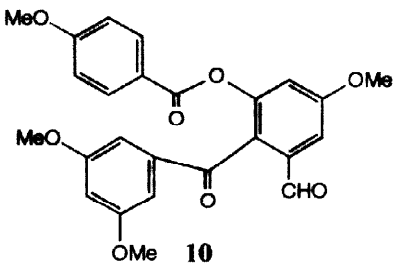
Structure of (-)-vitisifuran B (3) (-)-Vitisifuran B (**3**), $[\alpha]_D$ -133.7° (*c* 0.12, MeOH), showed a quasimolecular ion peak at *m/z* 905.2618 [MH$^+$] (*m/z* 905.2598 calcd. for $C_{56}H_{41}O_{12}$) in the high resolution FAB-MS. As shown in Tables 1 and 2, the ^{1}H- and ^{13}C-NMR spectral data of (-)-vitisifuran B (**3**) resembled very closely those of (-)-vitisin B (**6**)[6] except for the olefinic signals (**3**; δ_C 150.6 (C-7a), 117.4 (C-8a), **6**; δ_H 5.33 (d, *J*=4.8 Hz, H-7a), 4.36 (d, *J*=4.8 Hz, H-8a), δ_C 94.7 (C-7a), 57.9 (C-8a)). Furthermore, the NMR data of the partial structure corresponding to viniferifuran (**1**) in (-)-vitisifuran B (**3**) were very similar to those of **3**. In the HMBC spectrum of **3**, cross peaks between C-7a and H-2a (6a), between C-8a and H-10a (14a), between C-7d



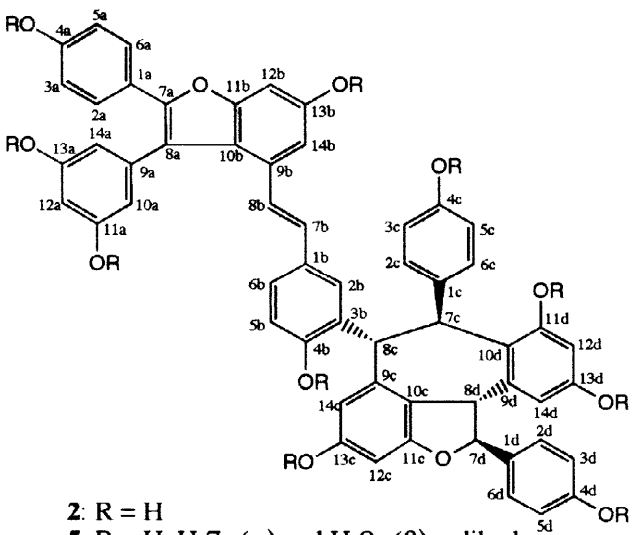
1: R = H
4: R = H, H-7a (α) and H-8a (β) = dihydro
7: R = Me
11: R = Ac, H-7a (α) and H-8a (β) = dihydro
12: R = Ac



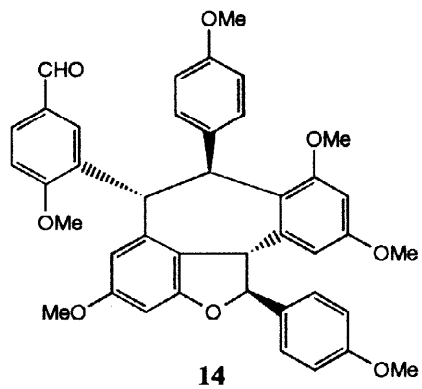
9



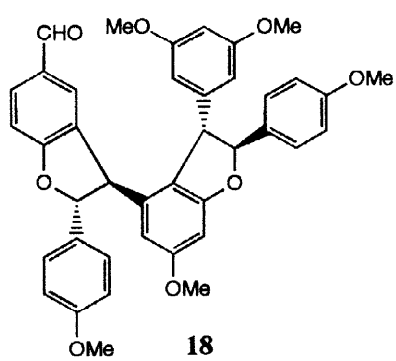
10



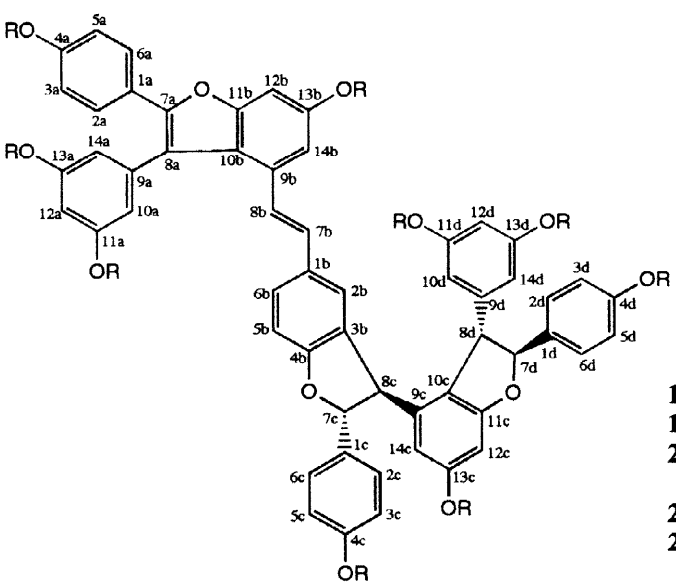
2: R = H
5: R = H, H-7a (α) and H-8a (β) = dihydro
13: R = Me
15: R = Ac, H-7a (α) and H-8a (β) = dihydro
16: R = Ac



14



18



3: R = H
6: R = H, H-7a (α) and H-8a (β) = dihydro
17: R = Me
19: R = Ac, H-7a (α) and H-8a (β) = dihydro
20: R = Ac, H-7a (α) and H-8a (β) = dihydro, H-7c and H-8c = dehydro
21: R = Ac
22: R = Ac, H-7c and H-8c = dehydro

Table 1. ^{1}H-NMR Data of Some Oligostilbenes (**1** - **6**)

	Viniferifuran (1)	ε-Viniferin (4)	Vitisifuran A (2)	Vitisin A (5)	Vitisifuran B (3)	Vitisin B (6)
1a						
2a	7.42 (d, 8.8)	7.13 (d, 8.8)	7.38 (d, 8.8)	7.07 (d, 8.5)	7.41 (d, 8.8)	7.18 (d, 8.4)
3a	6.69 (d, 8.8)	6.76 (d, 8.8)	6.68 (d, 8.8)	6.77 (d, 8.5)	6.69 (d, 8.8)	6.82 (d, 8.4)
4a						
5a	6.69 (d, 8.8)	6.76 (d, 8.8)	6.68 (d, 8.8)	6.77 (d, 8.5)	6.69 (d, 8.8)	6.82 (d, 8.4)
6a	7.42 (d, 8.8)	7.13 (d, 8.8)	7.38 (d, 8.8)	7.07 (d, 8.5)	7.41 (d, 8.8)	7.18 (d, 8.4)
7a		5.36 (d, 6.6)		5.31 (d, 6.3)		5.33 (d, 4.8)
8a		4.34 (d, 6.6)		4.26 (d, 6.3)		4.36 (d, 4.8)
9a						
10a	6.40 (d, 2.2)	6.15 (d, 2.2)	6.36 (d, 2.2)	6.10 (d, 2.2)	6.37 (d, 2.2)	5.98 (d, 2.2)
11a						
12a	6.47 (t, 2.2)	6.17 (t, 2.2)	6.46 (t, 2.2)	6.19 (t, 2.2)	6.42 (t, 2.2)	6.06 (t, 2.2)
13a						
14a	6.40 (d, 2.2)	6.15 (d, 2.2)	6.36 (d, 2.2)	6.10 (d, 2.2)	6.37 (d, 2.2)	5.98 (d, 2.2)
1b						
2b	6.98 (d, 8.8)	7.03 (d, 8.8)	5.85 (d, 1.8)	5.92 (d, 2.0)	6.66 (d, 2.2)	6.65 (d, 1.8)
3b	6.65 (d, 8.8)	6.64 (d, 8.8)				
4b						
5b	6.65 (d, 8.8)	6.64 (d, 8.8)	6.617 (d, 8.8)	6.60 (d, 8.8)	6.68 (d, 8.4)	6.68 (d, 8.4)
6b	6.98 (d, 8.8)	7.03 (d, 8.8)	6.66 (dd, 8.8, 1.8)	6.73 (dd, 8.8, 2.0)	6.91 (dd, 8.4, 2.2)	6.98 (dd, 8.4, 1.8)
7b	6.94 (d, 16.3)	6.56 (d, 16.1)	6.75 (d, 16.1)	6.32 (d, 16.3)	6.90 (d, 16.5)	6.50 (d, 16.5)
8b	6.85 (d, 16.3)	6.81 (d, 16.1)	6.30 (d, 16.1)	6.27 (d, 16.3)	6.71 (d, 16.5)	6.68 (d, 16.5)
9b						
10b						
11b						
12b	6.80 (d, 2.0)	6.24 (d, 2.2)	6.73 (d, 2.2)	6.19 (d, 2.2)	6.80 (d, 2.2)	6.24 (d, 1.8)
13b						
14b	6.99 (d, 2.0)	6.62 (d, 2.2)	6.81 (d, 2.2)	6.44 (d, 2.2)	6.95 (d, 2.2)	6.58 (d, 1.8)
1c						
2c			7.00 (d, 7.7)	7.00 (d, 8.8)	6.61 (d, 8.4)	6.58 (d, 8.8)
3c			6.616 (d, 7.7)	6.62 (d, 8.8)	6.54 (d, 8.4)	6.52 (d, 8.8)
4c						
5c			6.616 (d, 7.7)	6.62 (d, 8.8)	6.54 (d, 8.4)	6.52 (d, 8.8)
6c			7.00 (d, 7.7)	7.00 (d, 8.8)	6.61 (d, 8.4)	6.58 (d, 8.8)
7c			5.26 (d, 3.7)	5.25 (d, 3.2)	5.41 (d, 4.8)	5.42 (d, 5.1)
8c			5.42 (d, 3.7)	5.42 (d, 3.2)	4.29 (d, 4.8)	4.25 (d, 5.1)
9c						
10c						
11c						
12c			6.05 (s)	6.07 (d, 2.0)	6.27 (d, 2.2)	6.28 (d, 2.2)
13c						
14c			6.05 (s)	6.05 (d, 2.0)	6.09 (d, 2.2)	6.09 (d, 2.2)
1d						
2d			7.06 (d, 8.8)	7.07 (d, 8.8)	7.19 (d, 8.4)	7.13 (d, 8.4)
3d			6.70 (d, 8.8)	6.71 (d, 8.8)	6.82 (d, 8.4)	6.76 (d, 8.4)
4d						
5d			6.70 (d, 8.8)	6.71 (d, 8.8)	6.82 (d, 8.4)	6.76 (d, 8.4)
6d			7.06 (d, 8.8)	7.07 (d, 8.8)	7.19 (d, 8.4)	7.13 (d, 8.4)
7d			5.81 (d, 11.4)	5.81 (d, 11.5)	5.34 (d, 4.8)	5.36 (d, 6.2)
8d			4.13 (d, 11.4)	4.12 (d, 11.5)	4.41 (d, 4.8)	4.33 (d, 6.2)
9d						
10d					6.00 (d, 2.2)	6.14 (d, 1.5)
11d						
12d			5.97 (d, 2.2)	5.96 (d, 2.2)	6.05 (t, 2.2)	6.13 (t, 1.5)
13d						
14d			6.13 (d, 2.2)	6.13 (d, 2.2)	6.00 (d, 2.2)	6.14 (d, 1.5)

Table 2. ^{13}C-NMR Data of Some Oligostilbenes (**1** - **6**)

	Viniferifuran (**1**)	ε-Viniferin (**4**)	Vitisifuran A (**2**)	Vitisin A (**5**)	Vitisifuran B (**3**)	Vitisin B (**6**)
1a	123.8 s	133.9 s	123.9 s	134.0 s	123.8 s	134.6 s
2a	128.4 d	128.2 d	128.4 d	128.2 d	128.5 d	127.8 d
3a	116.2 d	116.3 d	116.1 d	116.3 d	116.2 d	116.5 d
4a	158.4 s	158.4 s	158.4 s	158.5 s	158.4 s	158.3 s
5a	116.2 d	116.3 d	116.1 d	116.3 d	116.2 d	116.5 d
6a	128.4 d	128.2 d	128.4 d	128.2 d	128.5 d	127.8 d
7a	150.6 s	94.8 d	150.5 s	94.7 d	150.6 s	94.7 d
8a	117.4 s	58.3 d	117.4 s	58.2 d	117.4 s	57.9 d
9a	138.7 s	147.4 s	138.7 s	147.2 s	138.6 s	147.7 s
10a	110.2 d	107.5 d	110.2 d	107.4 d	110.2 d	107.0 d
11a	160.6 s	160.1 s	160.5 s	159.9 s	160.6 s	160.1 s
12a	103.1 d	102.2 d	103.0 d	102.2 d	103.2 d	102.5 d
13a	160.6 s	160.1 s	160.5 s	159.9 s	160.6 s	160.1 s
14a	110.2 d	107.5 d	110.2 d	107.4 d	110.2 d	107.0 d
1b	130.7 s	130.4 s	129.5 s	129.3 s	133.2 s	132.7 s
2b	128.8 d	128.8 d	133.6 d	132.7 d	125.7 d	125.5 d
3b	116.3 d	116.4 d	132.7 s	132.9 s	132.6 s	132.3 s
4b	158.2 s	158.5 s	155.3 s	155.6 s	160.0 s	160.2 s
5b	116.3 d	116.4 d	115.7 d	115.6 d	110.7 d	110.7 d
6b	128.8 d	128.8 d	123.0 d	123.6 d	126.6 d	126.8 d
7b	123.3 d	123.7 d	121.8 d	122.5 d	123.9 d	124.2 d
8b	129.3 d	130.4 d	130.2 d	131.3 d	129.4 d	130.5 d
9b	133.3 s	136.9 s	133.5 s	137.2 s	132.7 s	136.8 s
10b	122.5 s	120.1 s	122.2 s	119.4 s	122.6 s	120.1 s
11b	156.4 s	162.8 s	156.36 s	162.7 s	156.4 s	162.8 s
12b	97.3 d	96.9 d	97.0 d	96.6 d	97.4 d	96.9 d
13b	156.5 s	159.8 s	156.39 s	159.6 s	156.3 s	159.6 s
14b	107.4 d	104.4 d	107.0 d	104.4 d	107.5 d	104.6 d
1c			136.1 s	136.0 s	132.8 s	132.7 s
2c			129.2 d	129.2 d	127.9 d	127.8 d
3c			115.6 d	115.6 d	116.1 d	116.0 d
4c			155.9 s	155.9 s	158.0 s	158.0 s
5c			115.6 d	115.6 d	116.1 d	116.0 d
6c			129.2 d	129.2 d	127.9 d	127.8 d
7c			41.2 d	41.1 d	92.3 d	92.2 d
8c			41.7 d	41.7 d	52.7 d	53.0 d
9c			141.8 s	141.7 s	142.7 s	142.5 s
10c			121.0 s	121.0 s	120.1 s	120.0 s
11c			158.8 s	158.4 s	162.8 s	162.7 s
12c			96.1 d	96.1 d	96.7 d	96.7 d
13c			160.4 s	160.3 s	160.5 s	160.5 s
14c			110.5 d	110.5 d	107.5 d	107.5 d
1d			131.1 s	131.1 s	134.6 s	133.9 s
2d			130.3 d	130.3 d	127.9 d	128.2 d
3d			116.2 d	116.2 d	116.5 d	116.3 d
4d			158.8 s	158.8 s	158.4 s	158.5 s
5d			116.2 d	116.2 d	116.5 d	116.3 d
6d			130.3 d	130.3 d	127.9 d	128.2 d
7d			89.2 d	89.1 d	94.8 d	94.8 d
8d			49.8 d	49.7 d	57.9 d	58.2 d
9d			142.6 s	142.5 s	147.7 s	147.2 s
10d			121.2 s	121.1 s	107.1 d	107.5 d
11d			158.6 s	158.8 s	160.1 s	160.0 s
12d			101.0 d	101.0 d	102.5 d	102.3 d
13d			156.9 s	156.8 s	160.1 s	160.0 s
14d			104.7 d	104.7 d	107.1 d	107.5 d

and H-2d (6d) and between C-8d and H-10d (14d) were observed. These indicated (-)-vitisifuran B (**3**) to be a structure dehydrogenated between H-7a and H-8a of (-)-vitisin B (**6**).[6] This was further supported by the following chemical evidence. The methylation of **3** with methyl iodide and potassium carbonate in acetone gave a nonamethyl ether (**17**) (*m/z* 1031 [MH$^+$]). The ether (**17**) was oxidized with ozone followed by treatment with dimethyl sulfide to give three degradative products **9**, **10** and **18** in 33.6 %, 22.9 % and 59.6 % yields, respectively. The product **18** was identical with an aldehyde derived from (-)-vitisin B (**6**).[6] Finally, (-)-vitisifuran B (**3**) was successfully converted from (-)-vitisin B (**6**) as follows. (-)-Vitisin B (**6**) was acetylated with acetic anhydride and pyridine to give (-)-vitisin B nonaacetate (**19**) (*m/z* 1285 [MH$^+$], δ_C 92.59 (C-7a), 56.0, (C-8a), 90.7 (C-7c), 52.1 (C-8c), 92.62 (C-7d), 56.6 (C-8d)). The nonaacetate (**19**) was oxidized with DDQ in toluene to give three dehydrogenated esters **20** (*m/z* 1283 [MH$^+$], δ_C 92.6 (C-7a), 56.3 (C-8a), 150.4 (C-7c), 114.2 (C-8c), 92.4 (C-7d), 56.0 (C-8d)), **21** (*m/z* 1283 [MH$^+$], δ_C 150.6 (C-7a), 116.1 (C-8a), 90.6 (C-7c), 51.6 (C-8c), 92.6 (C-7d), 56.1 (C-8d)) and **22** (*m/z* 1281 [MH$^+$], δ_C 150.6 (C-7a), 116.1 (C-8a), 150.3 (C-7c), 114.3 (C-8c), 92.4 (C-7d), 56.2 (C-8d)) in 8.4 %, 9.5 % and 1.5 % yields, respectively.

The first compound was assigned to a benzofuran (**20**) dehydrogenated between H-7c and H-8c of (-)-vitisin B nonaacetate (**19**) on the basis of the HMBC spectral analysis.[7] The second compound was assigned to a benzofuran (**21**) dehydrogenated between H-7a and H-8a of (-)-vitisin B nonaacetate (**19**) on the basis of the HMBC spectral analysis.[8] Compound **21** was treated with potassium hydroxide in methanol to give a phenol, which was completely identical with natural (-)-vitisifuran B (**3**), including the sign of the optical rotation. Thus, the absolute structure of (-)-vitisifuran B is represented as **3**. The third compound was assigned to a benzofuran (**22**) further dehydrogenated between H-7a and H-8a of **20** and between H-7c and H-8c of **21** on the basis of the spectral and chemical evidence.[9] Both compounds **20** and **21** were treated with DDQ in toluene to give the same product **22**, respectively.

EXPERIMENTAL

General procedure. IR spectra were recorded on JASCO FT/IR-5000 and FT/IR-410 infrared spectrophotometers. UV spectra were recorded on a JASCO Ubest V-560 spectrophotometer (cell length 10 mm, unless otherwise indicated). Optical rotations were determined on a JASCO P-1020 polarimeter (cell length 100 mm, unless otherwise indicated). CD spectra were taken on JASCO J-600 and J-720 spectropolarimeters (cell length 10 mm, unless otherwise indicated). FABMS were measured with a JEOL HX-110 using *m*-nitrobenzyl alcohol as a matrix unless otherwise indicated. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL A-600 spectrometer.

Isolation of viniferifuran and (-)-vitisifuran B. The newly prepared ethyl acetate soluble fraction (414 mg) corresponding to the third fraction of the acetone extract of the cork of the plant *Vitis vinifera* 'Kyohou' described previously[2] was subjected to reversed-phase MPCC (Nomura Chemical Co. Ltd., Develosil Lop C8-45S (ϕ4.5 x 45 cm, methanol - water (6 : 4), flow rate: 2 ml/min)) to give 10 fractions (9 mg, 61 mg, 61 mg, 177 mg, 59 mg, 9 mg, 4 mg, 2 mg, 9 mg and 15 mg, respectively). The fifth fraction (59 mg) was mainly composed of (-)-vitisin B. The sixth fraction (9 mg) was further subjected to preparative TLC [Merck, 1.05715 (0.25 mm, 20 x 20 cm), chloroform - methanol (5 : 1)] to give viniferifuran (**1**) and (-)-vitisifuran B (**3**) in yields of 1.3 mg and 1.9 mg, respectively.

Isolation of (+)-vitisifuran A and (-)-vitisifuran B. The eluting fraction (580 mg) after (+)-vitisin C and (-)-vitisin B from the ethyl acetate soluble fraction of the methanol extract of the cork of the plant *Vitis vinifera* 'Kyohou' described previously[1] was subjected to reversed phase MPCC (Nomura Chemical Co. Ltd., Develosil Lop C8-45S (ϕ4.5 x 45 cm, methanol - water (6 : 4), flow rate: 3 ml/min)) to give 5 fractions (442 mg, 20 mg, 5 mg, 3 mg and 11 mg, respectively). The first fraction (442 mg) was mainly composed of (-)-vitisin B. The second fraction (20 mg) was further subjected to preparative TLC [Merck, 1.05715 (0.25 mm, 20 x 20 cm), chloroform - methanol (4 : 1)] to give (-)-vitisifuran B (**3**) and (+)-vitisifuran A (**2**) in yields of 14 mg and 0.3 mg, respectively.

Physical properties of viniferifuran.

1: A colorless amorphous powder; Rf 0.31 [TLC (Merck, 1.05715 (0.25 mm)), chloroform - methanol (4 : 1)]; UV (MeOH) λ_{max} nm (log ε): 209 (4.79), 227 sh (4.62), 258 (4.33), 289 sh (4.44), 308 (4.53), 317 (4.54), 337 (4.53), 350 sh (4.52); IR ν_{max} (KBr) cm^{-1}: 3400 br, 1605; HR-FABMS *m/z*: 453.1341 (MH^+; $C_{28}H_{21}O_6$), calcd. 453.1338; ^{1}H-NMR (CD_3OD) given in Table 1; ^{13}C-NMR (CD_3OD) given in Table 2.

Physical properties of (+)-vitisifuran A.

2: A colorless amorphous powder; Rf 0.11 [TLC (Merck, 1.05715 (0.25 mm)), chloroform - methanol (4 : 1)]; $[\alpha]_D$ +236.1° (*c* 0.44, MeOH); UV (MeOH) λ_{max} nm (log ε); 208 (5.07), 232 sh (4.82), 286 (4.41), 313 (4.39), 322 (4.39), 340 sh (4.45), 356 (4.50); CD (MeOH) Δε (nm); +19 (292), +75 (237), +70 (209); IR ν_{max} (KBr) cm^{-1}: 3300 br, 1610; HR-FABMS *m/z*: 905.2593 (MH^+; $C_{56}H_{41}O_{12}$), calcd. 905.2598; ^{1}H-NMR (CD_3OD) given in Table 1; ^{13}C-NMR (CD_3OD) given in Table 2.

Physical properties of (-)-vitisifuran B.

3: A colorless amorphous powder; Rf 0.30 [TLC (Merck, 1.05715 (0.25 mm)), chloroform - methanol (4 : 1)]; $[\alpha]_D$ -133.7° (*c* 0.12, MeOH); UV (MeOH) λ_{max} nm (log ε); 204 (4.99), 228 sh (4.75), 287 (4.29), 297 (4.28), 324 (4.31), 357 sh (4.25); CD (MeOH) Δε (nm); +1.3 (367), -5.0 (304), +7.3 (252), +6.0 (237), -16.0 (220), +13.3 (208); IR ν_{max} (KBr) cm^{-1}: 3400 br, 1615; HR-FABMS *m/z*: 905.2618 (MH^+; $C_{56}H_{41}O_{12}$), calcd. 905.2598; ^{1}H-NMR (CD_3OD) given in Table 1; ^{13}C-NMR (CD_3OD) given in Table 2.

Methylation of viniferifuran. A mixture of viniferifuran (**1**) (3.0 mg, 6.6 μmol), methyl iodide (96 mg) and potassium carbonate (94 mg) in acetone (1 ml) was stirred under nitrogen atmosphere at room temperature for 2 days. The reaction mixture was diluted by ethyl acetate (20 ml), washed with brine and then dried over sodium sulfate. After evaporation of the solvent, the residue was subjected to preparative TLC [Merck, 1.05715 (0.25 mm, 20 x 20 cm), hexane - acetone (2 : 1)] to give a pentamethyl derivative (**7**) in a yield of 2.4 mg (69.3 %).

7: HR-FABMS *m/z*: 523.2124 (MH^+; $C_{33}H_{31}O_6$), calcd. 523.2121; IR ν_{max} (film) cm^{-1}: 3020, 1605; ^{1}H-NMR ($CDCl_3$) δ_H 7.52 (2H, d, *J*=9.2 Hz, H-2a,6a), 6.81 (2H, d, *J*=9.2 Hz, H-3a,5a), 6.65 (2H, d, *J*=2.2 Hz, H-10a,14a), 6.62 (1H, t, *J*=2.2 Hz, H-12a), 7.01 (2H, d, *J*=8.8 Hz, H-2b,6b), 6.77 (2H, d, *J*=8.8 Hz, H-3b,5b), 6.87 (1H, d, *J*=16.1 Hz, H-7b), 6.84 (1H, d, *J*=16.1 Hz, H-8b), 6.99 (1H, d, *J*=2.2 Hz, H-12b), 7.09 (1H, d, *J*=2.2 Hz, H-14b), 3.78 (3H, s, MeO-4a), 3.73 (6H, s, MeO-11a,13a), 3.79 (3H, s, MeO-4b), 3.90 (3H, s, MeO-13b); ^{13}C-NMR ($CDCl_3$) δ_C 123.5 (s, C-1a), 127.5 (d, C-2a,6a), 113.9 (d, C-3a,5a), 159.2 (s, C-4a), 149.7 (s, C-7a), 116.3 (s, C-8a), 136.9 (s, C-9a), 108.5 (d, C-10a,14a), 161.4 (s, C-11a,13a), 100.4 (d, C-

12a), 130.1 (s, C-1b), 127.6 (s, C-2b,6b), 113.8 (d, C-3b,5b), 159.1 (s, C-4b), 123.1 (d, C-7b), 128.5 (d, C-8b), 132.0 (s, C-9b), 122.0 (s, C-10b), 154.9 (s, C-11b), 94.8 (d, C-12b), 158.0 (s, C-13b), 106.6 (d, C-14b), 55.2 (q, MeO-4a), 55.4 (q, MeO-11a,13a), 55.3 (q, MeO-4b), 55.8 (q, MeO-13b).[10]

Ozonolysis of pentamethyl viniferifuran. A solution of pentamethyl viniferifuran (**7**) (30 mg, 57.5 μmol) in ethyl acetate (30 ml) was cooled at -78 ℃, treated with ozone for 2 min, and then worked up with dimethyl sulfide (0.5 ml) to give a resulting mixture. The mixture was separated by preparative TLC (Merck 1.05744 (0.5 mm, 20 x 20 cm), hexane - acetone (2 : 1)) to give three compounds (**8**, **9** and **10**) in yields of 3.2 mg (40.9 %), 9.4 mg (39.1 %) and 2.5 mg (9.7 %), respectively.

8: FABMS *m/z*: 137 (MH^+, $C_8H_9O_2$, using glycerin as a matrix); IR ν_{max} (film) cm^{-1}: 3020, 1700, 1685, 1600; ^{1}H-NMR ($CDCl_3$) δ_H 7.82 (2H, d, *J*=8.8 Hz, H-2b,6b), 6.99 (2H, d, *J*=8.8 Hz, H-3b,5b), 9.87 (1H, s, H-7b), 3.87 (3H, s, MeO-4b). The IR and ^{1}H-NMR spectral data of **8** were identical with those of an authentic sample of *p*-methoxybenzaldehyde.

9: HR-FABMS *m/z*: 419.1506 (MH^+; $C_{25}H_{23}O_6$), calcd. 419.1495; IR ν_{max} (film) cm^{-1}: 3020, 1680, 1610; ^{1}H-NMR ($CDCl_3$) δ_H 7.51 (2H, d, *J*=8.8 Hz, H-2a,6a), 6.81 (2H, d, *J*=8.8 Hz, H-3a,5a), 6.59 (2H, d, *J*=1.8 Hz, H-10a,14a), 6.54 (1H, t, *J*=1.8 Hz, H-12a), 9.75 (1H, s, H-8b), 7.31 (1H, d, *J*=1.8 Hz, H-12b), 7.44 (1H, d, *J*=1.8 Hz, H-14b), 3.78 (3H, s, MeO-4a), 3.77 (6H, s, MeO-11a,13a), 3.90 (3H, s, MeO-13b); ^{13}C-NMR ($CDCl_3$) δ_C 122.6 (s, C-1a), 127.9 (d, C-2a,6a), 114.0 (d, C-3a,5a), 159.9 (s, C-4a), 152.2 (s, C-7a), 114.9 (s, C-8a), 136.4 (s, C-9a), 107.8 (d, C-10a,14a), 161.9 (s, C-11a,13a), 100.6 (d, C-12a), 189.7 (d, C-8b), 129.3 (s, C-9b), 126.8 (s, C-10b), 155.2 (s, C-11b), 103.1 (d, C-12b), 157.4 (s, C-13b), 107.4 (d, C-14b), 55.3 (q, MeO-4a), 55.4 (q, MeO-11a,13a), 56.1 (q, MeO-13b).

10: HR-FABMS *m/z*: 451.1397 (MH^+; $C_{25}H_{23}O_8$), calcd. 451.1393; IR ν_{max} (film) cm^{-1}: 3020, 1735, 1700, 1680, 1605; ^{1}H-NMR ($CDCl_3$) δ_H 7.73 (2H, d, *J*=8.8 Hz, H-2a,6a), 6.80 (2H, d, *J*=8.8 Hz, H-3a,5a), 6.87 (2H, d, *J*=2.2 Hz, H-10a,14a), 6.50 (1H, t, *J*=2.2 Hz, H-12a), 9.88 (1H, s, H-8b), 7.14 (1H, d, *J*=2.6 Hz, H-12b), 7.42 (1H, d, *J*=2.6 Hz, H-14b), 3.82 (3H, s, MeO-4a), 3.71 (6H, s, MeO-11a,13a), 3.93 (3H, s, MeO-13b); ^{13}C-NMR ($CDCl_3$) δ_C 120.4 (s, C-1a), 132.2 (d, C-2a,6a), 113.7 (d, C-3a,5a), 164.1 (s, C-4a), 163.7 (s, C-7a), 193.5 (s, C-8a), 139.8 (s, C-9a), 106.8 (d, C-10a,14a), 160.8 (s, C-11a,13a), 106.3 (d, C-12a), 189.4 (d, C-8b), 137.1 (s, C-9b), 127.0 (s, C-10b), 149.9 (s, C-11b), 114.8 (d, C-12b), 161.2 (s, C-13b), 112.3 (d, C-14b), 55.49 (q, MeO-4a), 55.53 (q, MeO-11a,13a), 56.0 (q, MeO-13b).

Acetylation of (+)-ε-viniferin. A solution of (+)-ε-viniferin (**4**) (64.0 mg, 141 μmol) in acetic anhydride (1.5 ml) and pyridine (1.5 ml) was stirred overnight at room temperature. After the concentration of the reaction mixture under reduced pressure, the residue was subjected to column chromatography over silica gel (Fuji silysia Chemical Co. Ltd., BW-820MH, 1.0 g) using chloroform - acetone (20 : 1) to give an acetate (**11**) in a yield of 92 mg (98.5%).

11: HR-FABMS *m/z*: 665.2017 (MH^+; $C_{38}H_{33}O_{11}$), calcd. 665.2023; IR ν_{max} (film) cm^{-1}: 3020, 1765, 1610; ^{1}H-NMR ($CDCl_3$) δ_H 7.32 (2H, d, *J*=8.8 Hz, H-2a,6a), 7.08 (2H, d, *J*=8.8 Hz, H-3a,5a), 5.59 (1H, d, *J*=6.6 Hz, H-7a), 4.58 (1H, d, *J*=6.6 Hz, H-8a), 6.84 (2H, d, *J*=1.8 Hz, H-10a,14a), 6.88 (1H, t, *J*=1.8 Hz, H-12a), 7.16 (2H, d, *J*=8.4 Hz, H-2b,6b), 6.96 (2H, d, *J*=8.4 Hz, H-3b,5b), 6.52 (1H, d, *J*=16.1 Hz, H-7b), 6.86 (1H, d, *J*=16.1 Hz, H-8b), 6.63 (1H, d, *J*=1.8 Hz, H-12b), 6.93 (1H, d, *J*=1.8 Hz, H-14b), 2.31 (3H, s), 2.27 (3H, s), 2.25 (3H, s), 2.24 (6H, s); ^{13}C-NMR ($CDCl_3$) δ_C 138.0 (s, C-1a), 126.7 (d, C-2a,6a), 121.9 (d,

C-3a,5a), 150.6 (s, C-4a), 92.7 (d, C-7a), 56.6 (d, C-8a), 144.3 (s, C-9a), 118.5 (d, C-10a,14a), 151.6 (s, C-11a,13a), 114.8 (d, C-12a), 134.4 (s, C-1b), 127.7 (d, C-2b,6b), 121.7 (d, C-3b,5b), 150.3 (s, C-4b), 124.0 (d, C-7b), 130.3 (d, C-8b), 135.3 (s, C-9b), 123.8 (s, C-10b), 160.7 (s, C-11b), 102.8 (d, C-12b), 152.0 (s, C-13b), 110.6 (d, C-14b), 169.40 (s), 169.36 (s), 169.33 (s), 168.7 (s), 168.7 (s), 21.2 (q), 21.1 (q), 21.1 (q), 21.0 (q), 21.0 (q).

Oxidation of (+)-ε-viniferin pentaacetate. A mixture of (+)-ε-viniferin pentaacetate (**11**) (92 mg, 139 μmol) and DDQ (50 mg, 220 μmol, 1.6 eq) in toluene (30 ml) was stirred under reflux. Each 50 mg of DDQ (totally 250 mg, 1101 μmol, 7.9 eq) was added into the reaction mixture every 15 hr. After 90 hr, the reaction mixture was subjected to column chromatography over silica gel (Fuji silysia Chemical Co. Ltd., BW-820MH, 0.5 g) using benzene - acetone (20 : 1), to preparative TLC (Merck, 13895 (1.0 mm, 20 x 20 cm), chloroform - acetone (20 : 1)) and then to preparative HPLC (YMC Co. Ltd., YMC-Pack C8 (ϕ20 x 250 mm), acetonitrile - water (9 : 1), flow rate: 3.0 ml/min) to give a dehydro product (**12**) and the starting material (**11**) in yields of 31.4 mg (34.2 %) and 45.0 mg (48.8 %), respectively.

12: HR-FABMS *m/z*: 663.1868 (MH^+; $C_{38}H_{31}O_{11}$), calcd. 663.1866; IR ν_{max} (film) cm^{-1}: 3020, 1770, 1610; ^{1}H-NMR ($CDCl_3$) δ_H 7.55 (2H, d, *J*=8.8 Hz, H-2a,6a), 7.03 (2H, d, *J*=8.8 Hz, H-3a,5a), 7.09 (2H, d, *J*=2.2 Hz, H-10a,14a), 7.18 (1H, t, *J*=2.2 Hz, H-12a), 7.10 (2H, d, *J*=8.4 Hz, H-2b,6b), 6.98 (2H, d, *J*=8.4 Hz, H-3b,5b), 6.86 (1H, d, *J*=16.5 Hz, H-7b), 6.95 (1H, d, *J*=16.5 Hz, H-8b), 7.22 (1H, d, *J*=1.8 Hz, H-12b), 7.23 (1H, d, *J*=1.8 Hz, H-14b), 2.35 (3H, s), 2.267 (3H, s), 2.265 (3H, s), 2.23 (6H, s); ^{13}C-NMR ($CDCl_3$) δ_C 127.5 (s, C-1a), 127.6 (d, C-2a,6a), 121.8 (d, C-3a,5a), 150.7 (s, C-4a), 151.1 (s, C-7a), 116.0 (s, C-8a), 136.0 (s, C-9a), 121.0 (d, C-10a,14a), 151.7 (s, C-11a,13a), 115.7 (d, C-12a), 134.5 (s, C-1b), 127.6 (d, C-2b,6b), 121.7 (d, C-3b,5b), 150.2 (s, C-4b), 123.8 (d, C-7b), 129.6 (d, C-8b), 132.2 (s, C-9b), 125.4 (s, C-10b), 153.9 (s, C-11b), 103.9 (d, C-12b), 148.4 (s, C-13b), 113.2 (d, C-14b) , 169.7 (s), 169.4 (s), 169.2 (s), 168.6 (s), 168.6 (s), 21.13 (q), 21.10 (q), 21.07 (q), 21.01 (q), 21.01 (q).

Deacetylation of the dehydro product. A solution of the dehydro product (**12**) (11.4 mg, 17.2 μmol) and potassium hydroxide (119 mg, 2.12 mmol) in methanol (15 ml) was stirred at room temperature. After 1 hr, the solution was diluted with cooled water (15 ml) and then neutralized with 1 % hydrochloric acid. The solution was extracted with ethyl acetate (each 20 ml, 3 times). The extract was washed with brine and then dried over sodium sulfate. After evaporation of the solvent, the residue was subjected to preparative TLC (Merck, 1.05715 (0.25 mm, 20 x 20 cm), chloroform - methanol (4 : 1)) to give a product (**1**) in a yield of 6.1 mg (51.5 %). The ^{1}H- and ^{13}C-NMR spectral data of the product were completely identical with those of natural viniferifuran (**1**).

Methylation of (+)-vitisifuran A. A mixture of (+)-vitisifuran A (**2**) (5.0 mg, 5.5 μmol), methyl iodide (164 mg, 1.1 mmol) and potassium carbonate (160 mg, 1.1 mmol) in acetone (2 ml) was stirred under nitrogen atmosphere at room temperature. Each 250 mg of methyl iodide (totally 750 mg, 5.3 mmol) and 250 mg of potassium carbonate (totally 750 mg, 5.4 mmol) were added into the reaction mixture every one day. After 5 days, the reaction mixture was diluted by ethyl acetate (20 ml), washed with brine and then dried over sodium sulfate. After evaporation of the solvent, the residue was subjected to preparative TLC [Merck, 1.05715 (0.25 mm, 20 x 20 cm), hexane - acetone (2 : 1)] to give a decamethyl derivative (**13**) in a yield of 3.1 mg (53.7 %).

13: HR-FABMS *m/z*: 1045.4167 (MH^+; $C_{66}H_{61}O_{12}$), calcd. 1045.4163; IR ν_{max} (film) cm^{-1}: 3020, 1605; ^{1}H-

NMR ($CDCl_3$) δ_H 7.50 (2H, d, *J*=8.8 Hz, H-2a,6a), 6.79 (2H, d, *J*=8.8 Hz, H-3a,5a), 6.60 (2H, s, H-10a,14a), 6.60 (1H, s, H-12a), 5.85 (1H, d, *J*=1.5 Hz, H-2b), 6.68 (1H, d, *J*=8.8 Hz, H-5b), 6.65 (1H, dd, *J*=8.8, 1.5 Hz, H-6b), 6.62 (1H, d, *J*=16.1 Hz, H-7b), 6.33 (1H, d, *J*=16.1 Hz, H-8b), 6.93 (1H, d, *J*=2.2 Hz, H-12b), 6.92 (1H, d, *J*=2.2 Hz, H-14b), 7.06 (2H, d, *J*=8.8 Hz, H-2c,6c), 6.71 (2H, d, *J*=8.8 Hz, H-3c,5c), 5.34 (1H, d, *J*=3.7 Hz, H-7c), 5.46 (1H, d, *J*=3.7 Hz, H-8c), 6.26 (1H, d, *J*=2.2 Hz, H-12c), 6.16 (1H, d, *J*=2.2 Hz, H-14c), 7.18 (2H, d, *J*=8.8 Hz, H-2d,6d), 6.82 (2H, d, *J*=8.8 Hz, H-3d,5d), 5.96 (1H, d, *J*=11.7 Hz, H-7d), 4.22 (1H, d, *J*=11.7 Hz, H-8d), 6.01 (1H, d, *J*=2.2 Hz, H-12d), 6.24 (1H, d, *J*=2.2 Hz, H-14d), 3.92 (3H, s), 3.87 (3H, s), 3.78 (3H, s), 3.76 (3H, s), 3.74 (3H, s), 3.72 (6H, s), 3.68 (3H, s), 3.59 (3H, s), 3.14 (3H, s); ^{13}C-NMR ($CDCl_3$) δ_C 123.5 (s, C-1a), 127.5 (d, C-2a,6a), 113.8 (d, C-3a,5a), 159.2 (s, C-4a), 149.6 (s, C-7a), 116.3 (s, C-8a), 137.0 (s, C-9a), 108.4 (d, C-10a,14a), 161.3 (s, C-11a,13a), 100.7 (d, C-12a), 129.0 (s, C-1b), 131.8 (d, C-2b), 132.2 (d, C-3b), 156.3 (s, C-4b), 109.4 (d, C-5b), 121.9 (d, C-6b), 121.8 (d, C-7b), 129.5 (d, C-8b), 132.9 (s, C-9b), 121.7 (s, C-10b), 154.9 (s, C-11b), 94.7 (d, C-12b), 158.0 (s, C-13b), 106.6 (d, C-14b), 135.2 (s, C-1c), 128.0 (d, C-2c,6c), 113.4 (d, C-3c,5c), 157.4 (s, C-4c), 39.8 (d, C-7c), 40.7 (d, C-8c), 139.2 (s, C-9c), 120.7 (s, C-10c), 159.4 (s, C-11c), 94.5 (d, C-12c), 160.5 (s, C-13c), 108.1 (d, C-14c), 130.4 (s, C-1d), 129.1 (d, C-2d,6d), 114.1 (d, C-3d,5d), 159.9 (s, C-4d), 87.7 (d, C-7d), 48.5 (d, C-8d), 140.6 (s, C-9d), 122.6 (s, C-10d), 158.8 (s, C-11d), 95.8 (d, C-12d), 159.1 (s, C-13d), 103.2 (d, C-14d), 55.9 (q), 55.72 (q), 55.68 (q), 55.5 (q), 55.5 (q), 55.35 (q), 55.32 (q), 55.28 (q), 55.23 (q), 55.1 (q).

Ozonolysis of decamethyl (+)-vitisifuran A. A solution of decamethyl-(+)-vitisifuran A (**13**) (20 mg, 19.2 μmol) in ethyl acetate (15 ml) was cooled at -78 ℃, treated with ozone for 1 min, and then worked up with dimethyl sulfide (0.5 ml) to give a resulting mixture. The mixture was separated by preparative TLC (Merck 1.05715 (0.25 mm, 20 x 20 cm), hexane - acetone (2 : 1)) to give three compounds (**9**, **10** and **14**) in yields of 3.8 mg (47.5 %), 1.3 mg (15.1 %) and 6.7 mg (53.2 %), respectively. **9** and **10** were completely identical with the above products derived from viniferifuran (**1**), respectively.

14: $[\alpha]_D$ +247.5° (*c* 0.5, $CHCl_3$); FABMS *m/z*: 659 (MH^+; $C_{41}H_{39}O_8$); IR ν_{max} (film) cm^{-1}: 1690, 1600; ^{1}H-NMR ($CDCl_3$) δ_H 6.52 (1H, d, *J*=2.2 Hz, H-2b), 6.95 (1H, d, *J*=8.8 Hz, H-5b), 7.64 (1H, dd, *J*=8.8, 2.2 Hz, H-6b), 9.37 (1H, s, H-7b), 7.06 (2H, d, *J*=8.1 Hz, H-2c,6c), 6.72 (2H, d, *J*=8.1 Hz, H-3c,5c), 5.38 (1H, d, *J*=4.4 Hz, H-7c), 5.50 (1H, d, *J*=4.4 Hz, H-8c), 6.27 (1H, d, *J*=2.2 Hz, H-12c), 6.16 (1H, d, *J*=2.2 Hz, H-14c), 7.17 (2H, d, *J*=8.8 Hz, H-2d,6d), 6.82 (2H, d, *J*=8.8 Hz, H-3d,5d), 5.94 (1H, d, *J*=11.7 Hz, H-7d), 4.23 (1H, d, *J*=11.7 Hz, H-8d), 5.98 (1H, d, *J*=2.2 Hz, H-12d), 6.23 (1H, d, *J*=2.2 Hz, H-14d), 4.00 (3H, s, MeO-4b) , 3.75 (3H, s, MeO-4c), 3.68 (3H, s, MeO-13c), 3.76 (3H, s, MeO-4d), 3.18 (3H, s, MeO-11d), 3.61 (3H, s, MeO-13d); ^{13}C-NMR ($CDCl_3$) δ_C 128.9 (s, C-1b), 133.9 (d, C-2b), 133.9 (s, C-3b), 161.5 (s, C-4b), 109.3 (d, C-5b), 128.0 (d, C-6b), 191.1 (d, C-7b), 134.6 (s, C-1c), 127.9 (d, C-2c,6c), 113.5 (d, C-3c,5c), 157.5 (s, C-4c), 39.4 (d, C-7c), 40.9 (d, C-8c), 138.4 (s, C-9c), 120.7 (s, C-10c), 159.3 (s, C-11c), 94.7 (d, C-12c), 160.6 (s, C-13c), 108.0 (d, C-14c), 130.2 (s, C-1d), 129.1 (d, C-2d,6d), 114.1 (d, C-3d,5d), 159.9 (s, C-4d), 87.8 (d, C-7d), 48.5 (d, C-8d), 140.6 (s, C-9d), 121.9 (s, C-10d), 159.0 (s, C-11d), 95.3 (d, C-12d), 158.9 (s, C-13d), 103.1 (d, C-14d), 55.9 (q, MeO-4b) , 55.30 (q, MeO-4c), 55.27 (q, MeO-13c), 55.33 (q, MeO-4d), 55.4 (q, MeO-11d), 55.1 (q, MeO-13d).

Acetylation of (+)-vitisin A. A solution of (+)-vitisin A (**5**) (73.1 mg, 80.7 μmol) in acetic anhydride

(1.0 ml) and pyridine (1.0 ml) was stirred overnight at room temperature. After the concentration of the reaction mixture under reduced pressure, the residue was subjected to column chromatography over silica gel (Fuji silysia Chemical Co. Ltd., BW-820MH, 0.3 g) using chloroform to give an acetate (**15**) in a yield of 103.5 mg (96.7 %).

15: HR-FABMS *m/z*: 1327.3812 (MH^+; $C_{76}H_{63}O_{22}$), calcd. 1327.3811; IR ν_{max} (film) cm^{-1}: 3020, 1765, 1615; ^{1}H-NMR ($CDCl_3$) δ_H 7.29 (2H, d, *J*=8.8 Hz, H-2a,6a), 7.07 (2H, d, *J*=8.8 Hz, H-3a,5a), 5.52 (1H, d, *J*=6.6 Hz, H-7a), 4.55 (1H, d, *J*=6.6 Hz, H-8a), 6.78 (2H, d, *J*=2.2 Hz, H-10a,14a), 6.85 (1H, t, *J*=2.2 Hz, H-12a), 5.82 (1H, d, *J*=2.2 Hz, H-2b), 6.90 (1H, d, *J*=8.8 Hz, H-5b), 7.00 (1H, dd, *J*=8.8, 2.2 Hz, H-6b), 6.313 (1H, d, *J*=16.1 Hz, H-7b), 6.40 (1H, d, *J*=16.1 Hz, H-8b), 6.57 (1H, d, *J*=1.9 Hz, H-12b), 6.87 (1H, d, *J*=1.9 Hz, H-14b), 7.13 (2H, d, *J*=8.8 Hz, H-2c,6c), 6.89 (2H, d, *J*=8.8 Hz, H-3c,5c), 4.86 (1H, d, *J*=3.7 Hz, H-7c), 5.14 (1H, d, *J*=3.7 Hz, H-8c), 6.46 (1H, d, *J*=1.8 Hz, H-12c), 6.309 (1H, d, *J*=1.8 Hz, H-14c), 7.19 (2H, d, *J*=8.4 Hz, H-2d,6d), 7.05 (2H, d, *J*=8.4 Hz, H-3d,5d), 6.06 (1H, d, *J*=11.4 Hz, H-7d), 4.20 (1H, d, *J*=11.4 Hz, H-8d), 6.61 (1H, d, *J*=2.2 Hz, H-12d), 6.78 (1H, d, *J*=2.2 Hz, H-14d), 2.300 (3H, s), 2.296 (3H, s), 2.28 (3H, s), 2.264 (3H, s), 2.256 (3H, s), 2.24 (6H, s), 2.172 (3H, s), 2.169 (3H, s), 2.00 (3H, s); ^{13}C-NMR ($CDCl_3$) δ_C 138.1 (s, C-1a), 126.7 (d, C-2a,6a), 121.8 (d, C-3a,5a), 150.6 (s, C-4a), 92.6 (d, C-7a), 56.5 (d, C-8a), 144.4 (s, C-9a), 118.4 (d, C-10a,14a), 151.5 (s, C-11a,13a), 114.6 (d, C-12a), 134.6 (s, C-1b), 131.4 (d, C-2b), 137.2 (s, C-3b), 147.6 (s, C-4b), 122.0 (d, C-5b), 123.4 (d, C-6b), 123.9 (d, C-7b), 130.2 (d, C-8b), 135.3 (s, C-9b), 123.6 (s, C-10b), 160.7 (s, C-11b), 102.6 (d, C-12b), 152.0 (s, C-13b), 110.8 (d, C-14b), 138.2 (s, C-1c), 127.7 (d, C-2c,6c), 121.9 (d, C-3c,5c), 149.2 (s, C-4c), 42.7 (d, C-7c), 40.4 (d, C-8c), 134.9 (s, C-9c), 124.4 (s, C-10c), 158.7 (s, C-11c), 102.5 (d, C-12c), 151.4 (s, C-13c), 116.0 (d, C-14c), 135.0 (s, C-1d), 128.6 (d, C-2d,6d), 122.0 (d, C-3d,5d), 151.0 (s, C-4d), 86.7 (d, C-7d), 48.5 (d, C-8d), 140.6 (s, C-9d), 129.4 (s, C-10d), 150.6 (s, C-11d), 114.2 (d, C-12d), 149.5 (s, C-13d), 116.1 (d, C-14d), 169.6 (s), 169.44 (s), 169.37 (s), 169.32 (s), 169.2 (s), 169.1 (s), 168.7 (s), 168.7 (s), 168.5 (s), 168.5 (s), 21.14 (q), 21.10 (q), 21.10 (q), 21.07 (q), 21.07 (q), 21.05 (q), 21.05 (q), 21.05 (q), 21.02 (q), 20.4 (q).

Oxidation of (+)-vitisin A decaacetate. A mixture of (+)-vitisin A decaacetate (**15**) (103.5 mg, 78.2 μmol) and DDQ (22 mg, 97 μmol, 1.2 eq) in toluene (70 ml) was stirred under reflux. Each 22 mg of DDQ (totally 350 mg, 1.54 mmol, 19.7 eq) was added into the reaction mixture every 14 hr. After 10 days, the reaction mixture was subjected to column chromatography over silica gel (Fuji silysia Chemical Co. Ltd., BW-820MH, 3.5 g) using benzene - acetone (10 : 1)), to preparative TLC (Merck, 13895 (1.0 mm, 20 x 20 cm), hexane - acetone (1 : 1)) and then to preparative HPLC (YMC Co. Ltd., YMC-Pack C8 (ϕ20 x 250 mm), acetonitrile - water (9 : 1), flow rate: 3.0 ml/min) to give a dehydro product (**16**) and the starting material (**15**) in yields of 32.3 mg (31.3%) and 32.9 mg (31.8 %), respectively.

16: HR-FABMS *m/z*: 1325.3654 (MH^+; $C_{76}H_{61}O_{22}$), calcd. 1325.3654; IR ν_{max} (film) cm^{-1}: 3020, 1765, 1605; ^{1}H-NMR ($CDCl_3$) δ_H 7.51 (2H, d, *J*=8.8 Hz, H-2a,6a), 7.01 (2H, d, *J*=8.8 Hz, H-3a,5a), 7.06 (2H, d, *J*=2.2 Hz, H-10a,14a), 7.19 (1H, t, *J*=2.2 Hz, H-12a), 5.83 (1H, d, *J*=2.2 Hz, H-2b), 6.94 (1H, d, *J*=8.4 Hz, H-5b), 6.81 (1H, dd, *J*=8.4, 2.2 Hz, H-6b), 6.72 (1H, d, *J*=16.1 Hz, H-7b), 6.44 (1H, d, *J*=16.1 Hz, H-8b), 7.16 (1H, d, *J*=2.2 Hz, H-12b), 7.214 (1H, d, *J*=2.2 Hz, H-14b), 7.15 (2H, d, *J*=8.8 Hz, H-2c,6c), 6.90 (2H, d, *J*=8.8 Hz, H-3c,5c), 4.85 (1H, d, *J*=3.7 Hz, H-7c), 5.16 (1H, d, *J*=3.7 Hz, H-8c), 6.46 (1H, d, *J*=1.8 Hz, H-12c), 6.35 (1H, d, *J*=1.8 Hz, H-14c), 7.209 (2H, d, *J*=8.8 Hz, H-2d,6d), 7.05 (2H, d, *J*=8.8 Hz, H-3d,5d),

6.10 (1H, d, *J*=11.4 Hz, H-7d), 4.23 (1H, d, *J*=11.4 Hz, H-8d), 6.62 (1H, d, *J*=2.2 Hz, H-12d), 6.79 (1H, d, *J*=2.2 Hz, H-14d), 2.34 (3H, s), 2.32 (3H, s), 2.27 (3H, s), 2.262 (3H, s), 2.262 (3H, s), 2.260 (3H, s), 2.260 (3H, s), 2.20 (3H, s), 2.17 (3H, s), 2.03 (3H, s); ^{13}C-NMR ($CDCl_3$) δ_C 127.5 (s, C-1a), 127.6 (d, C-2a,6a), 121.78 (d, C-3a,5a), 150.6 (s, C-4a), 150.7 (s, C-7a), 116.0 (s, C-8a), 136.2 (s, C-9a), 121.0 (d, C-10a,14a), 151.6 (s, C-11a,13a), 115.7 (d, C-12a), 134.7 (s, C-1b), 131.5 (d, C-2b), 134.8 (s, C-3b), 147.5 (s, C-4b), 122.2 (d, C-5b), 123.6 (d, C-6b), 123.2 (d, C-7b), 129.7 (d, C-8b), 132.1 (s, C-9b), 125.2 (s, C-10b), 153.8 (s, C-11b), 103.8 (d, C-12b), 148.5 (s, C-13b), 113.4 (d, C-14b), 138.2 (s, C-1c), 127.7 (d, C-2c,6c), 121.83 (d, C-3c,5c), 149.2 (s, C-4c), 40.44 (d, C-7c), 40.39 (d, C-8c), 137.3 (s, C-9c), 124.5 (s, C-10c), 158.8 (s, C-11c), 102.5 (d, C-12c), 151.0 (s, C-13c), 115.8 (d, C-14c), 135.0 (s, C-1d), 128.8 (d, C-2d,6d), 122.0 (d, C-3d,5d), 151.0 (s, C-4d), 86.7 (d, C-7d), 48.5 (d, C-8d), 140.6 (s, C-9d), 129.6 (s, C-10d), 151.0 (s, C-11d), 114.3 (d, C-12d), 149.6 (s, C-13d), 116.0 (d, C-14d), 169.7 (s), 169.5 (s), 169.23 (s), 169.18 (s), 169.08 (s), 168.72 (s), 168.66 (s), 168.55 (s), 168.55 (s), 168.51 (s), 21.14 (q), 21.14 (q), 21.11 (q), 21.11 (q), 21.07 (q), 21.07 (q), 21.07 (q), 21.07 (q), 21.00 (q), 20.4 (q).

Deacetylation of the dehydro product. A solution of the dehydro product (**16**) (15.2 mg, 11.5 μmol) and potassium hydroxide (109 mg, 1.6 mmol) in methanol (15 ml) was stirred at room temperature. After 1.5 hr, the solution was diluted with cooled water (15 ml) and then neutralized with 1 % cooled hydrochloric acid. The solution was extracted with ethyl acetate (each 20 ml, 3 times). The extract was washed with brine and then dried over sodium sulfate. After evaporation of the solvent, the residue was subjected to preparative TLC (Merck, 1.05715 (0.25 mm, 20 x 20 cm), chloroform - methanol (4 : 1)) to give a product (**2**) in a yield of 6.2 mg (59.7 %). The product was completely identified with natural (+)-vitisifuran A (**2**) by comparison with the optical rotation as well as the ^{1}H-NMR spectral data.

Methylation of (-)-vitisifuran B. A mixture of (-)-vitisifuran B (**3**) (14.8 mg, 16.4 μmol), methyl iodide (480 mg, 3.4 mmol) and potassium carbonate (470 mg, 3.4 mmol) in acetone (10 ml) was stirred under nitrogen atmosphere at room temperature. After 22 hr, the reaction mixture was diluted by ethyl acetate (50 ml), washed with brine and then dried over sodium sulfate. After evaporation of the solvent, the residue was subjected to preparative TLC [Merck, 1.05715 (0.25 mm, 20 x 20 cm), chloroform] to give a nonamethyl derivative (**17**) in a yield of 13.8 mg (81.8 %).

17: HR-FABMS *m/z*: 1031.4003 (MH^+; $C_{65}H_{59}O_{12}$), calcd. 1031.4007; IR ν_{max} (film) cm^{-1}: 3020, 1610; ^{1}H-NMR ($CDCl_3$) δ_H 7.50 (2H, d, *J*=8.4 Hz, H-2a,6a), 6.80 (2H, d, *J*=8.4 Hz, H-3a,5a), 6.58 (2H, d, *J*=1.1 Hz, H-10a,14a), 6.49 (1H, t, *J*=1.1 Hz, H-12a), 6.59 (1H, d, *J*=1.8 Hz, H-2b), 6.675 (1H, d, *J*=8.1 Hz, H-5b), 6.81 (1H, dd, *J*=8.1, 1.8 Hz, H-6b), 6.682 (1H, d, *J*=17.2 Hz, H-7b), 6.72 (1H, d, *J*=17.2 Hz, H-8b), 6.96 (1H, brs, H-12b), 7.00 (1H, brs, H-14b), 6.74 (2H, d, *J*=8.4 Hz, H-2c,6c), 6.61 (2H, d, *J*=8.4 Hz, H-3c,5c), 5.43 (1H, d, *J*=5.1 Hz, H-7c), 4.32 (1H, d, *J*=5.1 Hz, H-8c), 6.46 (1H, d, *J*=1.8 Hz, H-12c), 6.23 (1H, d, *J*=1.8 Hz, H-14c), 7.22 (2H, d, *J*=8.4 Hz, H-2d,6d), 6.87 (2H, d, *J*=8.4 Hz, H-3d,5d), 5.43 (1H, d, *J*=5.1 Hz, H-7d), 4.43 (1H, d, *J*=5.1 Hz, H-8d), 6.08 (2H, s, H-10d,14d), 6.08 (1H, s, H-12d), 3.89 (3H, s), 3.78 (3H, s), 3.76 (3H, s), 3.743 (3H, s), 3.735 (3H, s), 3.60 (3H, s), 3.60 (3H, s), 3.60 (3H, s), 3.60 (3H, s); ^{13}C-NMR ($CDCl_3$) δ_C 123.5 (s, C-1a), 127.5 (d, C-2a,6a), 113.9 (d, C-3a,5a), 159.2 (s, C-4a), 149.7 (s, C-7a), 116.4 (s, C-8a), 136.7 (s, C-9a), 108.4 (d, C-10a,14a), 161.3 (s, C-11a,13a), 100.6 (d, C-12a), 131.0 (s, C-1b), 123.8 (d, C-2b), 130.8 (s, C-3b), 158.7 (s, C-4b), 109.8 (d, C-5b), 126.3 (d, C-6b), 123.0 (d, C-7b),

129.0 (d, C-8b), 132.2 (s, C-9b), 121.9 (s, C-10b), 154.9 (s, C-11b), 94.8 (d, C-12b), 158.0 (s, C-13b), 106.7 (d, C-14b), 132.4 (s, C-1c), 126.8 (d, C-2c,6c), 113.6 (d, C-3c,5c), 159.2 (s, C-4c), 91.2 (d, C-7c), 51.8 (d, C-8c), 140.7 (s, C-9c), 120.0 (s, C-10c), 161.3 (s, C-11c), 94.4 (d, C-12c), 161.7 (s, C-13c), 106.2 (d, C-14c), 133.9 (s, C-1d), 126.6 (d, C-2d,6d), 114.1 (d, C-3d,5d), 159.6 (s, C-4d), 93.1 (d, C-7d), 56.7 (d, C-8d), 146.0 (s, C-9d), 105.4 (d, C-10d,14d), 161.0 (s, C-11d,13d), 98.8 (d, C-12d), 55.8 (q), 55.4 (q), 55.3 (q), 55.3 (q), 55.2 (q), 55.2 (q), 55.1 (q), 55.0 (q), 55.0 (q).

Ozonolysis of nonamethyl (-)-vitisifuran B. A solution of nonamethyl-(-)-vitisifuran B (**17**) (11.0 mg, 10.7 μmol) in ethyl acetate (7 ml) was cooled at -78 ℃, treated with ozone for 1 min, and then worked up with dimethyl sulfide (0.5 ml) to give a resulting mixture. The mixture was separated by preparative TLC (Merck 1.05715 (0.25 mm, 20 x 20 cm), hexane - acetone (2 : 1)) to give three compounds (**9**, **10** and **18**) in yields of 1.5 mg (33.6 %), 1.1 mg (22.9 %) and 4.1 mg (59.6 %), respectively. **9** and **10** were completely identical with the above products derived from viniferifuran (**1**), respectively. **18** was also identified with an authentic sample derived from (-)-vitisin B (**6**) including the sign of the optical rotation.[6]

Acetylation of (-)-vitisin B. A solution of (-)-vitisin B (**6**) (121.3 mg, 133.9 μmol) in acetic anhydride (1.5 ml) and pyridine (1.5 ml) was stirred overnight at room temperature. After the concentration of the reaction mixture under reduced pressure, the residue was subjected to column chromatography over silica gel (Fuji silysia Chemical Co. Ltd., BW-820MH, 2 g) using chloroform - methanol (10 : 1) to give an acetate (**19**) in a yield of 171.2 mg (99.6 %).

19: HR-FABMS *m/z*: 1285.3710 (MH^+; $C_{74}H_{61}O_{21}$), calcd. 1285.3705; IR ν_{max} (film) cm^{-1}: 3020, 1765, 1615; ^{1}H-NMR ($CDCl_3$) δ_H 7.30 (2H, d, *J*=8.8 Hz, H-2a,6a), 7.06 (2H, d, *J*=8.8 Hz, H-3a,5a), 5.51 (1H, d, *J*=5.1 Hz, H-7a), 4.51 (1H, d, *J*=5.1 Hz, H-8a), 6.58 (2H, d, *J*=1.5 Hz, H-10a,14a), 6.78 (1H, t, *J*=1.5 Hz, H-12a), 6.62 (1H, brs, H-2b), 6.73 (1H, d, *J*=8.4 Hz, H-5b), 6.99 (1H, brd, *J*=8.4 Hz, H-6b), 6.33 (1H, d, *J*=16.1 Hz, H-7b), 6.69 (1H, d, *J*=16.1 Hz, H-8b), 6.58 (1H, d, *J*=1.8 Hz, H-12b), 6.83 (1H, d, *J*=1.8 Hz, H-14b), 6.75 (2H, d, *J*=8.8 Hz, H-2c,6c), 6.82 (2H, d, *J*=8.8 Hz, H-3c,5c), 5.36 (1H, d, *J*=4.8 Hz, H-7c), 4.22 (1H, d, *J*=4.8 Hz, H-8c), 6.68 (1H, d, *J*=2.2 Hz, H-12c), 6.35 (1H, d, *J*=2.2 Hz, H-14c), 7.28 (2H, d, *J*=8.4 Hz, H-2d,6d), 7.08 (2H, d, *J*=8.4 Hz, H-3d,5d), 5.55 (1H, d, *J*=6.6 Hz, H-7d), 4.53 (1H, d, *J*=6.6 Hz, H-8d), 6.80 (2H, s, H-10d,14d), 6.80 (1H, s, H-12d), 2.30 (3H, s), 2.284 (3H, s), 2.276 (3H, s), 2.24 (3H, s), 2.22 (3H, s), 2.203 (3H, s), 2.203 (3H, s), 2.199 (3H, s), 2.199 (3H, s); ^{13}C-NMR ($CDCl_3$) δ_C 138.4 (s, C-1a), 126.5 (d, C-2a,6a), 121.9 (d, C-3a,5a), 150.61 (s, C-4a), 92.59 (d, C-7a), 56.0 (d, C-8a), 144.9 (s, C-9a), 117.6 (d, C-10a,14a), 151.6 (s, C-11a,13a), 114.7 (d, C-12a), 130.5 (s, C-1b), 124.8 (d, C-2b), 130.0 (s, C-3b), 159.0 (s, C-4b), 110.3 (d, C-5b), 127.0 (d, C-6b), 121.8 (d, C-7b), 131.2 (d, C-8b), 135.9 (s, C-9b), 123.3 (s, C-10b), 160.6 (s, C-11b), 102.3 (d, C-12b), 152.0 (s, C-13b), 110.6 (d, C-14b), 137.7 (s, C-1c), 126.7 (d, C-2c,6c), 121.5 (d, C-3c,5c), 150.3 (s, C-4c), 90.7 (d, C-7c), 52.1 (d, C-8c), 141.3 (s, C-9c), 123.7 (s, C-10c), 160.8 (s, C-11c), 102.8 (d, C-12c), 152.5 (s, C-13c), 113.8 (d, C-14c), 138.1 (s, C-1d), 126.2 (d, C-2d,6d), 122.0 (d, C-3d,5d), 150.59 (s, C-4d), 92.62 (d, C-7d), 56.6 (d, C-8d), 144.4 (s, C-9d), 118.6 (d, C-10d,14d), 151.5 (s, C-11d,13d), 114.6 (d, C-12d), 169.3 (s), 169.3 (s), 169.3 (s), 169.0 (s), 169.0 (s), 168.7 (s), 168.7 (s), 168.5 (s), 168.5 (s), 21.17 (q), 21.15 (q), 21.14 (q), 21.11 (q), 21.09 (q), 21.08 (q), 21.08 (q), 21.01 (q), 21.01 (q).

Oxidation of (-)-vitisin B nonaacetate. A mixture of (-)-vitisin B nonaacetate (**19**) (171.2 mg, 133.3 μmol) and DDQ (31 mg, 133.3 μmol, 1.0 eq) in toluene (30 ml) was stirred under reflux. Furthermore, each 21 mg of DDQ (totally 63 mg, 267 μmol, 2.1 eq) was added into the reaction mixture every 14 hr. After 69 hr, the reaction mixture was subjected to column chromatography over silica gel (Fuji silysia Chemical Co. Ltd., BW-820MH, 1.8 g) using benzene - acetone (20 : 1)), to preparative TLC (Merck, 13895 (1.0 mm, 20 x 20 cm), hexane - acetone (1 : 1)) and then to preparative HPLC (YMC Co. Ltd., YMC-Pack C8 (ϕ20 x 250 mm), acetonitrile - water (8 : 2), flow rate: 3.0 ml/min) to give three dehydrogenated products (**20**, **21**, **22**) and the starting material (**19**) in yields of 14.1 mg (8.4 %), 16.2 mg (9.5 %), 2.6 mg (1.5 %), and 80.8 mg (47.2 %), respectively.

20: HR-FABMS *m/z*: 1283.3546 (MH^+; $C_{74}H_{59}O_{21}$), calcd. 1283.3549; IR ν_{max} (film) cm^{-1}: 3020, 1765, 1615; ^{1}H-NMR ($CDCl_3$) δ_H 7.34 (2H, d, *J*=8.8 Hz, H-2a,6a), 7.09 (2H, d, *J*=8.8 Hz, H-3a,5a), 5.60 (1H, d, *J*=5.9 Hz, H-7a), 4.66 (1H, d, *J*=5.9 Hz, H-8a), 6.86 (2H, d, *J*=2.2 Hz, H-10a,14a), 6.85 (1H, t, *J*=2.2 Hz, H-12a), 7.05 (1H, d, *J*=2.2 Hz, H-2b), 7.20 (1H, d, *J*=8.8 Hz, H-5b), 7.08 (1H, dd, *J*=8.8, 2.2 Hz, H-6b), 6.58 (1H, d, *J*=16.1 Hz, H-7b), 6.94 (1H, d, *J*=16.1 Hz, H-8b), 6.63 (1H, d, *J*=2.2 Hz, H-12b), 6.96 (1H, d, *J*=2.2 Hz, H-14b), 7.42 (2H, d, *J*=8.8 Hz, H-2c,6c), 6.97 (2H, d, *J*=8.8 Hz, H-3c,5c), 6.81 (1H, d, *J*=2.2 Hz, H-12c*), 6.82 (1H, d, *J*=2.2 Hz, H-14c*), 7.10 (2H, d, *J*=8.8 Hz, H-2d,6d), 7.01 (2H, d, *J*=8.8 Hz, H-3d,5d), 5.41 (1H, d, *J*=7.0 Hz, H-7d), 3.79 (1H, d, *J*=7.0 Hz, H-8d), 6.15 (2H, d, *J*=2.2 Hz, H-10d,14d), 6.40 (1H, t, *J*=2.2 Hz, H-12d), 2.32 (3H, s), 2.29 (3H, s), 2.29 (3H, s), 2.29 (3H, s), 2.27 (3H, s), 2.22 (3H, s), 2.22 (3H, s), 1.96 (3H, s), 1.96 (3H, s); ^{13}C-NMR ($CDCl_3$) δ_C 138.3 (s, C-1a), 126.6 (d, C-2a,6a), 122.0 (d, C-3a,5a), 150.6 (s, C-4a), 92.6 (d, C-7a), 56.3 (d, C-8a), 144.8 (s, C-9a), 118.4 (d, C-10a,14a), 151.6 (s, C-11a,13a), 114.7 (d, C-12a), 131.7 (s, C-1b), 118.9 (d, C-2b), 129.5 (s, C-3b), 153.6 (s, C-4b), 111.3 (d, C-5b), 122.6 (d, C-6b), 122.3 (d, C-7b), 131.6 (d, C-8b), 135.5 (s, C-9b), 123.7 (s, C-10b), 160.9 (s, C-11b), 102.5 (d, C-12b), 152.1 (s, C-13b), 110.4 (d, C-14b), 127.8 (s, C-1c), 127.2 (d, C-2c,6c), 121.9 (d, C-3c,5c), 150.9 (s, C-4c), 150.4 (s, C-7c), 114.2 (s, C-8c), 130.5 (s, C-9c), 125.7 (s, C-10c), 161.0 (s, C-11c), 103.8 (d, C-12c), 152.2 (s, C-13c), 116.4 (d, C-14c), 137.1 (s, C-1d), 127.0 (d, C-2d,6d), 121.9 (d, C-3d,5d), 150.6 (s, C-4d), 92.4 (d, C-7d), 56.0 (d, C-8d), 142.1 (s, C-9d), 117.4 (d, C-10d,14d), 150.5 (s, C-11d,13d), 113.6 (d, C-12d), 169.3 (s), 169.3 (s), 169.2 (s), 169.1 (s), 168.9 (s), 168.7 (s), 168.7 (s), 168.3 (s), 168.3 (s), 21.20 (q), 21.17 (q), 21.14 (q), 21.11 (q), 21.11 (q), 21.0 (q), 21.0 (q), 20.9 (q), 20.9 (q). * The assignments may be interchangeable.

21: HR-FABMS *m/z*: 1283.3549 (MH^+; $C_{74}H_{59}O_{21}$), calcd. 1283.3549; IR ν_{max} (film) cm^{-1}: 3020, 1765, 1605; ^{1}H-NMR ($CDCl_3$) δ_H 7.53 (2H, d, *J*=8.8 Hz, H-2a,6a), 7.02 (2H, d, *J*=8.8 Hz, H-3a,5a), 7.03 (2H, brs, H-10a,14a), 7.00 (1H, brs, H-12a), 6.62 (1H, brs, H-2b), 6.74 (1H, d, *J*=8.8 Hz, H-5b), 6.90 (1H, brd, *J*=8.8 Hz, H-6b), 6.63 (1H, d, *J*=16.1 Hz, H-7b), 6.73 (1H, d, *J*=16.1 Hz, H-8b), 7.17 (1H, brs, H-12b), 7.14 (1H, brs, H-14b), 6.80 (2H, d, *J*=8.4 Hz, H-2c,6c), 6.84 (2H, d, *J*=8.4 Hz, H-3c,5c), 5.37 (1H, d, *J*=4.4 Hz, H-7c), 4.31 (1H, d, *J*=4.4 Hz, H-8c), 6.71 (1H, brs, H-12c), 6.38 (1H, brs, H-14c), 7.29 (2H, d, *J*=8.4 Hz, H-2d,6d), 7.07 (2H, d, *J*=8.4 Hz, H-3d,5d), 5.54 (1H, d, *J*=4.8 Hz, H-7d), 4.55 (1H, d, *J*=4.8 Hz, H-8d), 6.62 (2H, brs, H-10d,14d), 6.77 (1H, brs, H-12d), 2.34 (3H, s), 2.26 (3H, s), 2.25 (3H, s), 2.25 (3H, s), 2.24 (3H, s), 2.21 (3H, s), 2.21 (3H, s), 2.15 (3H, s), 2.15 (3H, s); ^{13}C-NMR ($CDCl_3$) δ_C 127.6 (s, C-1a), 127.6 (d, C-2a,6a), 121.5 (d, C-3a,5a), 150.9 (s, C-4a), 150.6 (s, C-7a), 116.1 (s, C-8a), 136.0 (s, C-9a), 121.1 (d, C-10a,14a), 151.51 (s, C-11a,13a), 115.6 (d, C-12a), 130.6 (s, C-1b), 124.2 (d, C-2b), 130.0 (s, C-3b), 158.8 (s, C-4b), 110.3 (d, C-5b), 127.2 (d, C-6b), 121.9 (d, C-7b), 130.6 (d, C-8b), 132.8 (s, C-9b), 125.0 (s, C-

10b), 153.9 (s, C-11b), 103.4 (d, C-12b), 148.5 (s, C-13b), 113.1 (d, C-14b), 137.7 (s, C-1c), 126.6 (d, C-2c,6c), 121.8 (d, C-3c,5c), 150.3 (s, C-4c), 90.6 (d, C-7c), 51.6 (d, C-8c), 141.3 (s, C-9c), 123.9 (s, C-10c), 160.6 (s, C-11c), 102.8 (d, C-12c), 152.5 (s, C-13c), 113.7 (d, C-14c), 138.4 (s, C-1d), 126.2 (d, C-2d,6d), 122.1 (d, C-3d,5d), 150.6 (s, C-4d), 92.6 (d, C-7d), 56.1 (d, C-8d), 144.9 (s, C-9d), 117.6 (d, C-10d,14d), 151.54 (s, C-11d,13d), 114.5 (d, C-12d), 169.7 (s), 169.3 (s), 169.2 (s), 169.0 (s), 169.0 (s), 168.6 (s), 168.5 (s), 168.5 (s), 168.5 (s), 21.14 (q), 21.14 (q), 21.14 (q), 21.08 (q), 21.08 (q), 21.08 (q), 21.08 (q), 20.9 (q), 20.9 (q).

22: HR-FABMS *m/z*: 1281.3392 (MH^+; $C_{74}H_{57}O_{21}$), calcd. 1281.3392; IR ν_{max} (film) cm^{-1}: 3020, 1765, 1610; ^{1}H-NMR ($CDCl_3$) δ_H 7.55 (2H, d, *J*=8.8 Hz, H-2a,6a), 7.03 (2H, d, *J*=8.8 Hz, H-3a,5a), 7.109 (2H, d, *J*=2.2 Hz, H-10a,14a), 7.17 (1H, t, *J*=2.2 Hz, H-12a), 6.92 (1H, d, *J*=1.8 Hz, H-2b), 7.207 (1H, d, *J*=8.4 Hz, H-5b), 6.94 (1H, dd, *J*=8.4, 1.8 Hz, H-6b), 6.83 (1H, d, *J*=17.6 Hz, H-7b), 6.98 (1H, d, *J*=17.6 Hz, H-8b), 7.206 (1H, d, *J*=1.8 Hz, H-12b), 7.26 (1H, d, *J*=1.8 Hz, H-14b), 7.42 (2H, d, *J*=8.8 Hz, H-2c,6c), 6.99 (2H, d, *J*=8.8 Hz, H-3c,5c), 6.86 (1H, d, *J*=2.2 Hz, H-12c), 6.82 (1H, d, *J*=2.2 Hz, H-14c), 7.110 (2H, d, *J*=8.8 Hz, H-2d,6d), 7.00 (2H, d, *J*=8.8 Hz, H-3d,5d), 5.44 (1H, d, *J*=7.7 Hz, H-7d), 3.81 (1H, d, *J*=7.7 Hz, H-8d), 6.20 (2H, d, *J*=2.2 Hz, H-10d,14d), 6.40 (1H, t, *J*=2.2 Hz, H-12d), 2.359 (3H, s), 2.357 (3H, s), 2.30 (3H, s), 2.272 (3H, s), 2.272 (3H, s), 2.266 (3H, s), 2.266 (3H, s), 2.02 (3H, s), 2.02 (3H, s); ^{13}C-NMR ($CDCl_3$) δ_C 127.56 (s, C-1a), 127.61 (d, C-2a,6a), 121.8 (d, C-3a,5a), 151.1 (s, C-4a), 150.6 (s, C-7a), 116.1 (s, C-8a), 136.0 (s, C-9a), 121.2 (d, C-10a,14a), 151.8 (s, C-11a,13a), 115.7 (d, C-12a), 131.9 (s, C-1b), 119.1 (d, C-2b), 129.4 (s, C-3b), 153.5 (s, C-4b), 111.3 (d, C-5b), 122.5 (d, C-6b), 122.0 (d, C-7b), 131.4 (d, C-8b), 132.6 (s, C-9b), 125.2 (s, C-10b), 154.0 (s, C-11b), 103.6 (d, C-12b), 148.5 (s, C-13b), 113.4 (d, C-14b), 127.9 (s, C-1c), 127.12 (d, C-2c,6c), 121.8 (d, C-3c,5c), 150.8 (s, C-4c), 150.3 (s, C-7c), 114.3 (s, C-8c), 130.7 (s, C-9c), 126.2 (s, C-10c), 160.9 (s, C-11c), 103.9 (d, C-12c), 152.2 (s, C-13c), 116.2 (d, C-14c), 137.0 (s, C-1d), 127.09 (d, C-2d,6d), 121.9 (d, C-3d,5d), 150.7 (s, C-4d), 92.4 (d, C-7d), 56.2 (d, C-8d), 141.9 (s, C-9d), 117.5 (d, C-10d,14d), 150.5 (s, C-11d,13d), 113.5 (d, C-12d), 169.7 (s), 169.2 (s), 169.1 (s), 169.1 (s), 168.5 (s), 168.5 (s), 168.3 (s), 168.3 (s), 168.3 (s), 21.18 (q), 21.18 (q), 21.14 (q), 21.14 (q), 21.13 (q), 21.04 (q), 21.00 (q), 20.97 (q), 20.97 (q).

*Deacetylation of compound **21**.* A solution of compound **21** (6.2 mg, 4.8 μmol) and potassium hydroxide (112 mg, 1.7 mmol) in methanol (10 ml) was stirred at room temperature. After 1.5 hr, the solution was diluted with cooled water (10 ml) and then neutralized with 1 % cooled hydrochloric acid. The solution was extracted with ethyl acetate (each 20 ml, 3 times). The extract was washed with brine and then dried over sodium sulfate. After evaporation of the solvent, the residue was subjected to preparative TLC (Merck, 1.05715 (0.25 mm, 20 x 20 cm), chloroform - methanol (4 : 1)) to give a product (**3**) in a yield of 2.8 mg (64.0 %). The product was completely identified with natural (-)-vitisifuran B (**3**) by comparison with the optical rotation as well as the ^{1}H-NMR spectral data.

*Oxidation of compound **20**.* A mixture of compound **20** (5.0 mg, 3.9 μmol) and DDQ (1.5 mg) in toluene (5 ml) was stirred under reflux in a nitrogen atomosphere. Furthermore, each 1.5 mg of DDQ (totally 9.1 mg, 40.1 μmol, 10.3 eq) was added into the reaction mixture every 10 hr. After 62 hr, the reaction mixture was subjected to column chromatography over silica gel (Fuji silysia Chemical Co. Ltd., BW-820MH, 1.5 g) using benzene - acetone (20 : 1)) and then to preparative HPLC (YMC Co. Ltd., YMC-Pack C8 (φ20 x 250 mm),

acetonitrile - water (8 : 2), flow rate: 3.0 ml/min) to give a dehydrogenated products (0.7 mg) with the recovered starting material (**20**, 3.0 mg). The product was completely identified with compound **22** by comparison with the IR and ^{1}H-NMR spectral data.

Oxidation of compound 21. A mixture of compound **21** (5.0 mg, 3.9 μmol) and DDQ (1.5 mg) in toluene (5 ml) was stirred under reflux in a nitrogen atomosphere. Furthermore, each 1.5 mg of DDQ (totally 9.2 mg, 40.5 μmol, 10.4 eq) was added into the reaction mixture every 10 hr. After 62 hr, the reaction mixture was subjected to column chromatography over silica gel (Fuji silysia Chemical Co. Ltd., BW-820MH, 1.5 g) using benzene - acetone (20 : 1) and then to preparative HPLC (YMC Co. Ltd., YMC-Pack C8 (φ20 x 250 mm), acetonitrile - water (8 : 2), flow rate: 3.0 ml/min) to give a dehydrogenated products (0.3 mg) with the recovered starting material (**21**, 3.3 mg). The product was completely identified with compound **22** by comparison with the IR and ^{1}H-NMR spectral data.

Acknowledgments. This research was financially supported by Grants-in-Aid for Scientific Research (No. 09672174) and for High-Tech Research Center Project from the Ministry of Education, Science, Sports and Culture of Japan which are gratefully acknowledged. We also thank Mrs. F. Yamahata (Wakayama Prefecture) for collection of the plant material ('Kyohou'), Professor A. Nagatsu (Nagoya City University) for the CD spectra and Mr. K. Terashima (Meijo University) for the high resolution FAB-MS.

REFERENCES AND NOTES

1. Ito, J.; Niwa, M. *Tetrahedron* **1996**, *52*, 9991.
2. Ito, J.; Niwa, M.; Oshima, Y. *Heterocycles* **1997**, *45*, 1809.
3. Shinoda, K.; Takaya, Y.; Ohta, T.; Niwa, M.; Hisamichi, K.; Takeshita, M.; Oshima, Y. *Heterocycles* **1997**, *46*, 169.
4. Ito, J.; Gobaru, K.; Shimamura, T., Niwa, M.; Takaya, Y.; Oshima, Y.*Tetrahedron* **1998**, *54*, 6651.
5. Langcake, P.; Pryce, R. J. *Experientia* **1977**, *33*, 151.
6. Oshima, Y.; Kamijou, A.; Ohizumi, Y.; Niwa, M.; Ito, J.; Hisamichi, K.; Takeshita, M. *Tetrahedron* **1995**, *51*, 11979.
7. In the HMBC spectrum of **20**, cross peaks between H-14c and C-8c, H-2b and C-8c, H-7d and C-2d (6d), and H-8d and C-10d (14d) were respectively observed.
8. In the HMBC spectrum of **21**, cross peaks between H-10a (14a) and C-8a, H-2a (6a) and C-7a, H-7d and C-2d (6d), and H-8d and C-10d (14d) were respectively observed.
9. In the HMBC spectrum of **22**, cross peaks between H-7d and C-2d (6d), and H-8d and C-10d (14d) were respectively observed.
10. Kurihara, H; Kawabata, J; Ichikawa, S; Mizutani, J. *Agric. Biol. Chem.* **1990**, *54*, 1097.