Studies on the Constituents of *Viburnum* Species. XVII.[1] New Dammarane-Type Triterpenoids from *Viburnum dilatatum* THUNB.[2]

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Five new dammarane-type triterpenoids, viburnols A, B, C, D and E, were isolated from the leaves of *Viburnum dilatatum* THUNB. (Caprifoliaceae). The structures were determined by extensive spectroscopic studies. Viburnols A, B and C are the first examples of a new class of modified dammarane triterpene.

Key words *Viburnum dilatatum*; Caprifoliaceae; triterpene; dammarane; viburnol

The deciduous shrub *Viburnum dilatatum* THUNB. is widely distributed in Japan and China.[3] The leaves have been utilized in traditional Chinese medicine (Chinese name, Jia mi).[4] Rice[5] reported that *V. dilatatum* exhibited allelopathic activity, injuring adjacent vegetation. In a survey to detect growth and germination inhibitors from the leaves of this plant grown in Japan, we found that the $CHCl_3$ extract showed growth and germination inhibitory effects towards the seeds of head lettuce. From this extract, we isolated a new norisoprenoid along with seven known norisoprenoids and eight known phenolic compounds.[6] Among these compounds, nine compounds were shown to be growth and germination inhibitors of lettuce, alfalfa and cress seeds. Furthermore, in a previous communication,[2] we reported the isolation and structural elucidation of five new dammarane-type triterpenoids, viburnols A—E obtained from the remaining fractions of the same extract. In this paper, we present a full account of the structure elucidations of viburnols A (**1**), B (**2**), C (**3**), D (**4**) and E (**5**). The isolation procedure is described in detail in the experimental section.

Viburnol A (**1**) was obtained as an amorphous powder, $[\alpha]_D$ +26.4° ($CHCl_3$). The molecular formula of **1** was assigned as $C_{30}H_{44}O_6$ on the basis of MS and ^{13}C-NMR spectral data. The ^{13}C-NMR spectrum showed signals of 30 carbons including three oxygenated carbons (two methine and one quaternary) and eight methyl groups. The spectral data of **1** revealed the presence of an α,β-unsaturated ketone [240 nm; 1674, 1614 cm^{-1}; δ_H 6.05 (1H, br s). δ_C 202.5 (s), 124.7 (d), 158.1 (s)] and two δ-lactones [1749, 1746 cm^{-1}; δ_H 4.52 (1H, ddd, J=11.7, 11.5, 4.8 Hz), 4.41 (1H, s). δ_C 175.1 (s), 165.3 (s), 82.9 (d), 79.3 (d)]. The ^{1}H-NMR spectrum of **1** showed signals of two vinyl methyl groups at δ 2.17 (3H, s) and 1.92 (3H, d, J=1.5 Hz) and a methylene group adjacent to an α,β-unsaturated ketone [δ 2.56 (2H, s)]. The IR spectrum showed hydroxyl group absorption (3507 cm^{-1}). In addition, the ^{13}C-NMR spectrum showed the presence of an oxygenated quaternary carbon (δ 74.4). Five of the six oxygens are accounted for in the α,β-unsaturated ketone and two δ-lactone rings and the remaining oxygen must therefore be present as a tertiary alcohol unit. These data suggest that **1** has a 20-hydroxy-24-en-23-one-type side chain. Furthermore, the molecular formula of **1** required 9 degrees of unsaturation. The α,β-unsaturated ketone has 2 degrees of unsaturation, and therefore **1** must have a five-ring system including two δ-lactone rings of the skeleton itself. Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra of **1** were undertaken with the aid of ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY), ^{1}H–^{13}C COSY

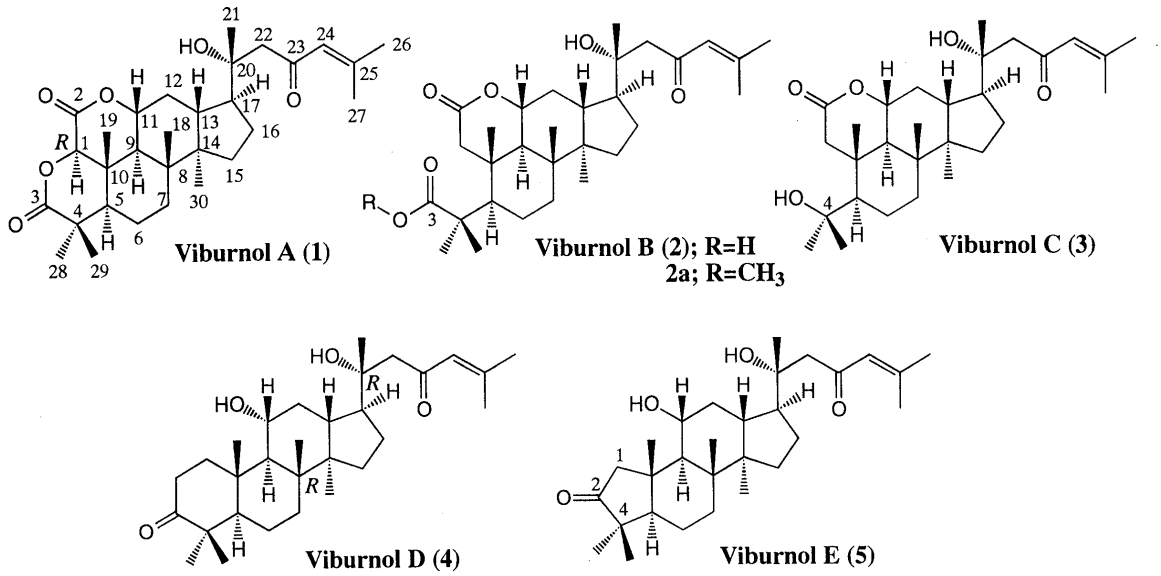

Chart 1

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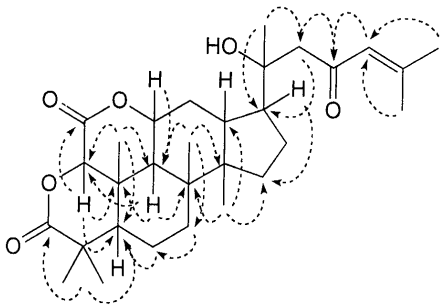

Fig. 1. HMBC Correlations of **1**

and homonuclear 2-dimensional J (2DJ) spectral data. The connectivities of the five rings and five methyl groups through the quaternary carbons, and the side chain were revealed by interpretation of the heteronuclear multiple bond coherence (HMBC) spectrum (Fig. 1). On the basis of the above data, viburnol A (**1**) was suggested to be a modified dammarane-type triterpene having two δ-lactone rings. The relative stereochemistry of **1** was clarified by the difference in nuclear Overhauser effect (NOE) spectra. As shown in Fig. 2, NOEs were observed between 11-H/13-H, 18-CH_3 and 19-CH_3 (β-side); 9-H/1-H and 30-CH_3 and 17-H/30-CH_3 (α-side). These NOE results suggested that the two δ-lactone rings should be fused *trans* at C-1 and C-10. The presence of the 1β-oxygen atom produced a γ-gauche shielding effect on the 19-methyl carbon (δ_C 10.6). Furthermore, as can be seen in Fig. 2, NOE enhancements between 21-CH_3/12-H_β and 13-H and 22-CH_2/13-H were observed. Thus, the structure of viburnol A (**1**), including the side chain, is established as depicted in the formula.

Viburnol B (**2**) was obtained as its methyl ester **2a**, $[\alpha]_D$ +8.1° ($CHCl_3$). The molecular formula of **2a** was assigned as $C_{31}H_{48}O_6$ on the basis of MS and ^{13}C-NMR spectral data. In the NMR spectrum of **2a**, the signal patterns were similar to those of **1**. The ^{1}H- and ^{13}C-NMR spectra of **2a**, however, lacked the signal due to the oxygenated methine moiety at C-1 of **1** and instead showed signals characteristic of a methoxycarbonyl [δ_H 3.70 (3H, s). δ_C 179.1, 51.9] and a methylene moiety adjacent to a carbonyl carbon [δ_H 2.50, 2.28 (each 1H, d, J=16.8 Hz). δ_C 48.3]. These findings were considered to be caused by the opening of the δ-lactone (A ring) of **1**. This deduction was supported by the HMBC spectrum. The carbon resonance at δ 179.1, which revealed a methoxycarbonyl unit, showed HMBC correlations with the methyl protons at δ 1.24 and 1.22 (28-CH_3, 29-CH_3). The remaining methylene moiety was attributed to C-1 on the basis of cross peaks observed in the HMBC spectrum between the methylene protons and both C-2 (δ_C 170.0) and C-19 (δ_C 17.9). The relative stereochemistry of **2a** was ascertained by analysis of the NOE difference spectra. These observations indicated that the relative configurations of the chiral center in **2a** were compatible with those of viburnol A (**1**). Thus, the structure of viburnol B (**2**) including the side chain is established as depicted in the formula. Compound **2a** may be an artifact formed from **2** during the extraction and isolation processes.

Viburnol C (**3**) was obtained as an amorphous powder, $[\alpha]_D$ +20.3° ($CHCl_3$). The spectral data of **3** were similar

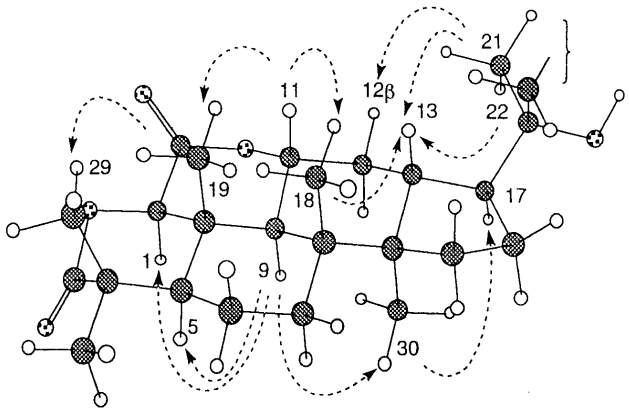

Fig. 2. NOE Enhancements of **1**

to those of **2a**. The ^{1}H- and ^{13}C-NMR spectra of **3** lacked the signals due to the methoxycarbonyl moiety of **2a** and instead showed a signal characteristic of hydroxy-bearing quaternary carbon (δ_C 75.5). The placement of the tertiary hydroxy group on C-4 was deduced from the HMBC spectrum. The signal at δ 75.5 showed HMBC correlations with the methyl protons at δ 1.31 and 1.27 (28,29-CH_3), which are also correlated to the methine carbon at δ 57.9 (C-5). All other HMBC and NOE correlations of **3** were consistent with those of **2a**. On the basis of the above data, the structure of viburnol C (**3**) is established as depicted in the formula. The C-1 signal of **3** appeared at δ 50.5, shifted to lower field by 2.2 ppm from that of **2a**. This shift is attributable to the effect of the hydroxyl-substituent at the δ-position.

Viburnol D (**4**) was obtained as an amorphous powder, $[\alpha]_D$ +51.1° ($CHCl_3$). The NMR signals of **4**, except those of the side chain, were very similar to those of alnuserol isolated from *Alnus serrulatoides*.[7] The IR and ^{13}C-NMR spectra suggested the presence of a six-membered cyclic ketone (1702 cm^{-1}, δ_C 218.7), and the ^{13}C-NMR signal of oxygenated methine carbon (C-11) of **4** was shifted upfield by 8.1 ppm in comparison with that of **1**. These findings suggested that a secondary hydroxy group is located at the C-11 position, and the cyclic ketone group is located at C-3 in the six-membered A-ring. On the basis of the above data, including the HMBC and the NOE difference spectra of **4**, the structure of viburnol D (**4**) is established as depicted in the formula.

Viburnol E (**5**) was obtained as an amorphous powder, $[\alpha]_D$ +76.4° ($CHCl_3$). The spectral data of **5** corresponding to rings B, C, and D and the side chain are in fair agreement with those of **4**. The major difference of **5** from **4** was the absence of a methylene group, and the signal of the cyclic ketone (δ_C 225.7) was shifted downfield by 7.0 ppm in comparison with that of **4**. Furthermore, the carbon resonance at δ 225.7 showed HMBC correlations with the methylene protons at δ 2.15 and 2.58 (each 1H, d, J=16.5 Hz, 1-CH_2), which are also correlated to the methyl carbon at δ 17.8 (C-19). The relative stereochemistry of **5** was ascertained by analysis of the NOE difference spectra. These observations indicated that the relative configurations of the chiral center are compatible with those of viburnol D (**4**). On the basis of the above data, viburnol E (**5**) was suggested to be a rearranged

Table 1. ^{13}C-NMR Chemical Shifts (67.8 MHz, $CDCl_3$)

C	1	2a	3	4	5
1	82.9	48.3	50.5	42.0	58.6
2	165.3	170.0	171.1	34.2	225.7
3	175.1	179.1	—	218.7	—
4	41.7	45.4	75.5	47.7	43.9
5	53.2	55.3	57.9	55.2	59.8
6	18.6	19.9	22.2	19.6	17.9
7	34.4	34.9	34.6	35.1	35.3
8	39.2	39.4	39.3	40.6	40.1
9	47.3	47.3	47.2	54.7	54.7
10	35.7	38.1	37.6	38.2	41.2
11	79.3	77.2	77.1	71.2	69.7
12	33.8	35.0	35.1	39.7	38.3
13	41.2	40.7	40.7	41.2	41.1
14	49.7	50.1	50.1	49.97	50.1
15	30.7	30.6	30.7	30.7	30.7
16	25.1	25.0	25.0	25.0	25.2
17	49.1	49.3	49.3	50.1	50.1
18	15.8	15.3	15.2	16.2	16.9
19	10.6	17.9	17.4	16.8	17.8
20	74.4	74.4	74.4	74.8	74.8
21	26.3	25.8	25.7	26.5	26.4
22	50.4	51.1	51.2	50.0	50.1
23	202.5	202.6	202.6	202.8	202.8
24	124.7	124.7	124.4	124.9	124.8
25	158.1	157.8	157.8	157.6	157.6
26	27.9	27.9	27.9	27.8	27.9
27	21.1	21.0	21.0	21.0	21.0
28	29.8	27.9[a)]	33.8[b)]	27.5	27.6
29	23.3	22.7[a)]	28.1[b)]	20.7	20.9
30	16.3	16.4	16.3	16.1	16.6

Assignments were confirmed by ^{1}H–^{1}H and ^{13}C–^{1}H COSY and HMBC methods. *a,b*) Signals may be interchanged.

dammarane-type triterpene having a five-membered cyclic ketone (A-ring).

The structures of viburnols A (**1**), B (**2**), C (**3**), D (**4**) and E (**5**), including the side chain, were elucidated on the basis of spectral data. Viburnols A (**1**), B (**2**), C (**3**) and E (**5**) were presumably biosynthesized from viburnol D (**4**), so all the chiral centers of **1** (except C-1), **2**, **3** and **5** coincided with those of **4**. [It is expected that viburnol A (**1**) is biosynthesized from the postulated intermediate (dammar-24-ene-2,3,23-trione-1α,11α,20α-triol) derived from viburnol D (**4**), whose C-2 and C-3 bond cleavage followed by recyclization would afford viburnol A (**1**).] The circular dichroism (CD) spectrum of **4** showed a positive Cotton effect, $\Delta\varepsilon + 1.06$ (289.5 nm), suggesting that C-8 should have the *R*-configuration.[8)] Consequently, the configurations at C-1 of **1** and C-20 of **1**—**5** were determined as *R*. Thus, the full structures of viburnols A—E (**1**—**5**) were established to be as shown in Chart 1.

Compounds **1**—**5** are new dammarane-type triterpenes (**1** and **2** are A-seco-dammarane-type triterpenes and **3** and **5** are A-nor-dammarane-type triterpenes). Compound **5** is the first naturally occurring dammarane-type triterpene having a five-membered cyclic ketone in ring-A. These compounds are the first examples of a new class of modified dammarane-type triterpene.

Experimental

Optical rotations were determined with a JASCO DIP-360 digital polarimeter. IR spectra were recorded with a Perkin-Elmer 1725X FT-IR instrument. UV spectra were recorded with a Beckman DU-64 spectrometer. The CD spectra were obtained with a JASCO J-700 spectropolarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded with JEOL JNX-EX 270 (270 and 67.8 MHz, respectively) and JEOL JNM-GSX 400 (400 and 100 MHz, respectively) spectrometers. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; dd, double doublet; ddd, double double doublet; m, multiplet, br; broad). MS were recorded on a JEOL JMS-DX 303 mass spectrometer. Column chromatography was carried out on Kieselgel 60 (Merck; 70-230 mesh) and Cosmosil 75C_{18}-OPN (Nacalai Tesque). Preparative HPLC was carried out on a Tosoh HPLC system (pump, CCPD; detector, UV-8010) using Cosmosil 5C18-AR (Nacalai Tesque, 10 mm i.d. × 25 cm) and TSK gel OH-120 (Tosoh, 7.8 mm i.d. × 30 cm) columns. TLC was carried out with precoated Kieselgel 60 plates (Merck) and detection was achieved by spraying 50% H_2SO_4 followed by heating.

Plant Material The leaves of *Viburnum dilatatum* THUNB. were collected near Sendai, Miyagi prefecture, Japan, in August 1995 and identified by one of the authors (M. Kikuchi). A voucher specimen is held in the laboratory of M. Kikuchi.

Extraction and Isolation Fresh leaves of *V. dilatatum* (4.4 kg) were extracted with MeOH at room temperature for two months. The MeOH extract was concentrated under reduced pressure and the residue was suspended in a small excess of water. This suspension was successively extracted with $CHCl_3$, Et_2O, AcOEt and *n*-BuOH. The $CHCl_3$-soluble fraction was concentrated under reduced pressure to produce a residue (92.5 g). This residue was chromatographed on a silica gel column using hexane–Me_2CO (4 : 1) and the eluate was separated into four fractions [frs. 1—4: fr. 1 (5.5 g), fr. 2 (10.7 g), fr. 3 (14.3 g), fr. 4 (55.0 g)]. Fr. 3 (MeOH–H_2O, 3 : 1 soluble material; 6.3 g) was rechromatographed on a C18 open column using MeOH–H_2O (3 : 1) and the eluate was separated into six fractions {frs. 3-1—3-6: fr. 3-1 [0.25 g; UV λ_{max} (MeOH) nm: 220], fr. 3-2 [1.25 g; UV λ_{max} (MeOH) nm: 240], fr. 3-3 [0.13 g; UV λ_{max} (MeOH) nm: 244], fr. 3-4 [0.84 g; UV λ_{max} (MeOH) nm: 270], fr. 3-5 [1.31 g; UV λ_{max} (MeOH) nm: 267, 231], fr. 3-6 [1.80 g; UV λ_{max} (MeOH) nm: 227]}. Fr. 3-2 was rechromatographed on a silica gel column using hexane–Me_2CO (3 : 1) and the eluate was separated into twenty-eight fractions (frs. 3-2-1—3-2-28). Frs. 3-2-4—3-2-8 were subjected to preparative HPLC [5C18-AR column; MeOH–H_2O (3 : 1), OH-120 column; hexane–Me_2CO (4 : 1), each flow rate: 1.5 ml/min], respectively, to give compounds **1** (80.5 mg), **2a** (240.5 mg), **3** (48.0 mg), **4** (25.5 mg) and **5** (35.0 mg).

Viburnol A (1) An amorphous powder, $[\alpha]_D$ +26.4° (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3507, 3019, 2970, 1749, 1746, 1674, 1614. UV λ_{max} (MeOH) nm (log ε): 240.0 (3.87). EI-MS *m/z*: 482 $(M-H_2O)^+$. FAB-MS *m/z*: 501 $(M+H)^+$, 523 $(M+Na)^+$. HR-MS *m/z*: 482.3010 ($M^+ - H_2O$, Calcd for $C_{30}H_{42}O_5$; 482.3032). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 6.05 (1H, br s, 24-H), 4.52 (1H, ddd, *J* = 11.7, 11.5, 4.8 Hz, 11-H), 4.41 (1H, s, 1-H), 2.56 (2H, s, 22-CH_2), 2.45 (1H, ddd, *J* = 12.0, 4.8, 2.9 Hz, 12-H_β), 2.17 (3H, s, 27-CH_3), 1.97 (1H, d, *J* = 11.7 Hz, 9-H), 1.92 (3H, d, *J* = 1.5 Hz, 26-CH_3), 1.34 (3H, s, 28-CH_3), 1.27 (3H, s, 29-CH_3), 1.21 (3H, s, 21-CH_3), 1.15 (3H, s, 19-CH_3), 1.10 (3H, s, 18-CH_3), 1.00 (3H, s, 30-CH_3). ^{13}C-NMR (67.8 MHz, $CDCl_3$): Table 1.

Viburnol B Methyl Ester (2a) An amorphous powder, $[\alpha]_D$ +8.1° (*c* = 1.6, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3483, 3019, 2974, 1719, 1676, 1615. UV λ_{max} (MeOH) nm (log ε): 241.0 (3.95). EI-MS *m/z*: 498 $(M-H_2O)^+$. FAB-MS *m/z*: 517 $(M+H)^+$. HR-MS *m/z*: 498.3299 ($M^+ - H_2O$, Calcd for $C_{31}H_{46}O_5$; 498.3345). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 6.04 (1H, s, 24-H), 4.39 (1H, ddd, *J* = 11.9, 10.7, 5.0 Hz, 11-H), 3.70 (3H, s, $COOCH_3$), 2.56 (2H, s, 22-CH_2), 2.50 (1H, s, *J* = 16.8 Hz, 1-H_β), 2.38 (1H, ddd, *J* = 12.0, 5.0, 3.0 Hz, 12-H_β), 2.28 (1H, d, *J* = 16.8 Hz, 1-H_α), 2.17 (3H, s, 27-CH_3), 1.92 (3H, s, 26-CH_3), 1.78 (1H, d, *J* = 11.9 Hz, 9-H), 1.24, 1.22 (each 3H, s, 28, 29-CH_3), 1.20 (3H, s, 21-CH_3), 1.18 (3H, s, 19-CH_3), 1.02 (3H, s, 18-CH_3), 0.95 (3H, s, 30-CH_3). ^{13}C-NMR (67.8 MHz, $CDCl_3$): Table 1.

Viburnol C (3) An amorphous powder, $[\alpha]_D$ +20.3° (*c* = 2.9, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3474, 2978, 2971, 1713, 1676, 1614. UV λ_{max} (MeOH) nm (log ε): 240.0 (4.05). EI-MS *m/z*: 438 $(M-2H_2O)^+$. FAB-MS *m/z*: 475 $(M+H)^+$. HR-MS *m/z*: 438.3143 ($M^+ - 2H_2O$, Calcd for $C_{29}H_{42}O_3$; 438.3134). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 6.04 (1H, s, 24-H), 4.42 (1H, ddd, *J* = 11.8, 11.2, 5.0 Hz, 11-H), 3.46 (1H, d, *J* = 18.2 Hz, 1-H_β), 2.57 (2H, s, 22-CH_2), 2.37 (1H, ddd, *J* = 12.2, 5.0, 3.0 Hz, 12-H_β), 2.28 (1H, d, *J* = 18.2 Hz, 1-H_α), 2.17 (3H, s, 27-CH_3), 1.92 (3H, s, 26-CH_3), 1.76 (1H, d, *J* = 11.8 Hz, 9-H), 1.31, 1.27 (each 3H, s, 28, 29-CH_3), 1.26 (3H, s, 19-CH_3), 1.21 (3H, s, 21-CH_3), 1.04 (3H, s, 18-CH_3), 0.94 (3H,

s, 30-CH_3). ^{13}C-NMR (67.8 MHz, $CDCl_3$): Table 1.

Viburnol D (4) An amorphous powder, $[\alpha]_D$ +51.1° (c=1.0, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3475, 3020, 2970, 1702, 1676, 1614. UV λ_{max} (MeOH) nm (log ε): 241.0 (3.98). EI-MS m/z: 454 $(M-H_2O)^+$. FAB-MS m/z: 473 $(M+H)^+$. HR-MS m/z: 454.3483 (M^+-H_2O, Calcd for $C_{30}H_{46}O_3$; 454.3447). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 6.07 (1H, s, 24-H), 3.95 (1H, ddd, J=10.7, 10.6, 5.0 Hz, 11-H), 2.66 (1H, ddd, J=13.5, 8.1, 5.4 Hz, 1-H_β), 2.57 (2H, s, 22-CH_2), 2.45 (2H, m, 2-CH_2), 2.22 (1H, m 12-H_β), 2.17 (3H, s, 27-CH_3), 1.92 (3H, s, 26-CH_3), 1.54 (1H, d, J=10.7 Hz, 9-H), 1.21 (3H, s, 21-CH_3), 1.10 (3H, s, 28-CH_3), 1.07 (6H, s, 19, 29-CH_3), 1.00 (3H, s, 18-CH_3), 0.92 (3H, s, 30-CH_3). ^{13}C-NMR (67.8 MHz, $CDCl_3$): Table 1. CD $\Delta\varepsilon$ (nm) (MeOH): +1.06 (289.5).

Viburnol E (5) An amorphous powder, $[\alpha]_D$ +76.4° (c=2.2, $CHCl_3$). IR ($CHCl_3$) cm^{-1} 3474, 3014, 2967, 1728, 1674, 1614. UV λ_{max} (MeOH) nm (log ε): 241.0 (3.95). EI-MS m/z: 440 $(M-H_2O)^+$. FAB-MS m/z: 459 $(M+H)^+$. HR-MS m/z: 440.3271 (M^+-H_2O, Calcd for $C_{29}H_{44}O_3$; 440.3291). ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 6.07 (1H, s, 24-H), 3.90 (1H, ddd, J=10.9, 10.6, 5.3 Hz, 11-H), 2.58 (1H, d, J=16.5 Hz, 1-H_β), 2.57 (2H, s, 22-CH_2), 2.22 (1H, m 12-H_β), 2.17 (3H, s, 27-CH_3), 2.15 (1H, d, J=16.5 Hz, 1-H_α), 1.91 (3H, s, 26-CH_3), 1.68 (1H, d, J=10.7 Hz, 9-H), 1.21 (3H, s, 21-CH_3), 1.006, 0.997, 0.989, 0.975 (15H, 18, 19, 28, 29, 30-CH_3). ^{13}C-NMR (67.8 MHz, $CDCl_3$): Table 1. CD $\Delta\varepsilon$ (nm) (MeOH): +2.79 (300.5).

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