

## Studies on the Constituents of *Viburnum* Species. XVIII.<sup>1)</sup> Viburnols: Six New Triterpenoids from *Viburnum dilatatum* THUNB.<sup>2)</sup>

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Six new triterpenoids, viburnols F, G, H, I, J and K, were isolated from the leaves of *Viburnum dilatatum* THUNB. (Caprifoliaceae). The structures were determined by extensive spectroscopic studies. Viburnols F, G and I are the first example of a new class of modified dammarane-type triterpenes.

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

We have recently reported the isolation of five new triterpenoids, viburnols A, B, C, D and E, from the CHCl<sub>3</sub> extract of the leaves of *Viburnum dilatatum* THUNB.<sup>1)</sup> In a previous communication,<sup>2)</sup> we reported the isolation and structural elucidation of six new triterpenoids, viburnols F—K, obtained from the remaining triterpenic fractions of the same extract. In this paper, we present a full account of the structure elucidations of viburnols F (1), G (2), H (3), I (4), J (5) and K (6).

Viburnol F (1) was obtained as its methyl ester **1a**, [ $\alpha$ ]<sub>D</sub> +43.5° (CHCl<sub>3</sub>). The molecular formula of **1a** was assigned as C<sub>31</sub>H<sub>50</sub>O<sub>7</sub> on the basis of the MS and <sup>13</sup>C-NMR spectral data. Its <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were similar to those of viburnol E.<sup>1)</sup> The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of **1a**, however, lacked the signals due to a methylene (C-1) and a cyclic ketone (C-2) of viburnol E and instead showed signals characteristic of two oxygenated carbons [a methine ( $\delta_H$  4.37,  $\delta_C$  82.5) and a quaternary carbon ( $\delta_C$  85.5)], a methoxycarbonyl group ( $\delta_H$  3.76,  $\delta_C$  174.9, 51.9) and two hydroxyl groups ( $\delta_H$  4.68, 4.28, each 1H, disappearing on D<sub>2</sub>O exchange). These findings suggested that the two hydroxy groups are located at the C-1 and -2 positions, and the methoxycarbonyl group is located at the hydroxy-bearing quaternary carbon ( $\delta_C$  85.5), in the five-membered A-ring. The location of

the methoxycarbonyl on C-2 was deduced from the heteronuclear multiple bond coherence (HMBC) spectrum. The quaternary carbon at  $\delta_C$  85.5 showed HMBC correlations with the methyl protons at  $\delta$  1.05 (28-CH<sub>3</sub>) and 0.84 (29-CH<sub>3</sub>), which are also correlated to the quaternary carbon at  $\delta$  46.7 (C-4). On the other hand, the methine carbon at  $\delta$  82.5 showed a correlation with the methyl protons at  $\delta$  1.09 (19-CH<sub>3</sub>), which are also correlated to the quaternary carbon at  $\delta$  46.0 (C-10). Thus, the structure of ring A of **1a** was indicated. The stereochemistry of **1a** was deduced from the difference nuclear Overhauser effect (NOE) spectra. The observation of NOE enhancements between 1-H/19-CH<sub>3</sub> (but not between 1-OH/19-CH<sub>3</sub>), 19-CH<sub>3</sub>/29-CH<sub>3</sub>, 29-CH<sub>3</sub>/2-COOCH<sub>3</sub> and 2-COOCH<sub>3</sub>/1-H indicated that they were all on the same face ( $\beta$ ) of the molecule, while the presence of interactions between 1-OH/9-H and 2-OH/28-CH<sub>3</sub> revealed that these were on the same face ( $\alpha$ ), opposite to the  $\beta$ -face. The signal of 9-H of **1a** was shifted to a lower field ( $\Delta \delta$  +0.46) than that of viburnol E indicating the presence of steric compression between 1 $\alpha$ -OH and 9-H. Moreover, the carbon signal of C-9 was shifted upfield from that of viburnol E by  $\Delta \delta$  -7.4 due to the  $\gamma$ -gauche effect with 1 $\alpha$ -OH (C-19 seems not to be affected by 1-OH). All other HMBC (Fig. 1) and NOE

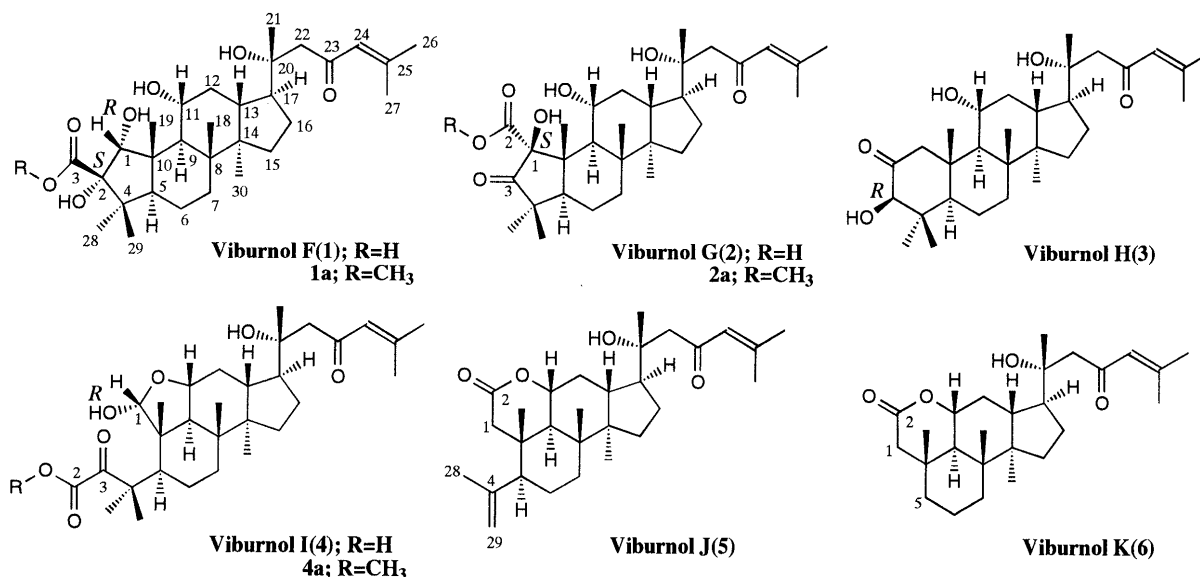
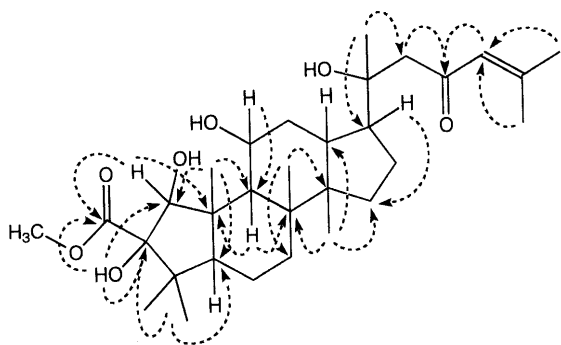
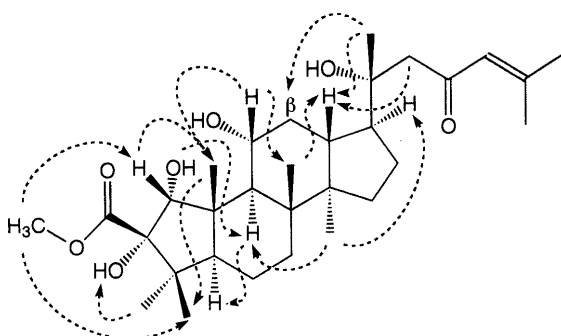


Chart 1

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Fig. 1. HMBC Correlations of **1a**Fig. 2. NOE Enhancements of **1a**

(Fig. 2) correlations of **1a** were the same as those of viburnol E. On the basis of the above data, the structure of viburnol F (**1**) was established as depicted in the formula.

Viburnol G (**2**) was obtained as its methyl ester **2a**,  $[\alpha]_D +73.8^\circ$  ( $\text{CHCl}_3$ ). The molecular formula of **2a** was assigned as  $\text{C}_{31}\text{H}_{48}\text{O}_7$  on the basis of the MS and  $^{13}\text{C}$ -NMR spectral data. From comparison of the NMR spectral data of **2a** with those of viburnol E, it was deduced that **2a** possesses an oxygenated quaternary carbon ( $\delta_{\text{C}} 89.2$ ), a methoxycarbonyl group ( $\delta_{\text{H}} 3.76$ ,  $\delta_{\text{C}} 172.4$ ,  $52.9$ ) and a hydroxyl group ( $\delta_{\text{H}} 5.64$ , 1H, disappearing on  $\text{D}_2\text{O}$  exchange) instead of a methylene (C-1) group in viburnol E. These findings suggested that a tertiary alcohol and a methoxycarbonyl group are located at the C-1 position in the five-membered A-ring. This deduction was supported by the HMBC spectrum. The carbon at  $\delta 89.2$  showed a correlation with the methyl protons at  $\delta 1.02$  (19- $\text{CH}_3$ ), which are also correlated to the quaternary carbon at  $\delta 49.0$  (C-10). Furthermore, correlations were observed between the carbon at  $\delta 217.3$  (C-3) and the protons of 1-OH ( $\delta 5.64$ ), 28- $\text{CH}_3$  and 29- $\text{CH}_3$  ( $\delta 1.07$ ,  $1.17$ ). Thus, the structure **2a** was indicated. The hydroxyl group at C-1 was determined to be on the same side as 19- $\text{CH}_3$  from the NOE difference spectrum. The C-19 signal of **2a** was shifted upfield from that of viburnol E by  $\Delta \delta -3.3$  due to the  $\gamma$ -gauche effect of  $1\beta$ -OH. All other HMBC and NOE correlations of **2a** were the same as those of viburnol E. On the basis of the above data, the structure of viburnol G (**2**) was established to be as depicted.

Viburnol H (**3**) was obtained as an amorphous powder,  $[\alpha]_D +43.3^\circ$  ( $\text{CHCl}_3$ ). The molecular formula of **3** was assigned as  $\text{C}_{30}\text{H}_{48}\text{O}_5$  on the basis of the MS and  $^{13}\text{C}$ -NMR spectral data. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectral data of **3** were closely related to those of viburnol D,<sup>1)</sup>

except that **3** had an oxygenated methine ( $\delta 82.4$ ) instead of the methylene group in viburnol D. Thus, **3** may be formulated as a hydroxy derivative of viburnol D at ring A. The  $^1\text{H}$ -NMR spectrum of **3**, however, showed signals of a methine proton at  $\delta 3.89$  (1H, s) and a methylene proton at  $\delta 2.25$  and  $3.48$  (each 1H, d,  $J=13.0$  Hz). The multiplicities of these signals indicated that the keto group is located between a hydroxymethine and a methylene group, possibly on C-2. The location of the hydroxy group on C-3 was deduced from the HMBC spectrum, that is, cross peaks were observed between the methylene protons and C-9, -10 and -19, and between the hydroxymethine proton and C-4, -28 and -29. The stereochemistry of the hydroxyl group at C-3 was determined as  $\beta$  on the basis of the NOE difference spectra, in which NOE enhancements were observed at 3-H and 9-H when one of the methylene protons ( $\delta 2.25$ ) at C-1 was irradiated. All other HMBC and NOE correlations of **3** were the same as those of viburnol D. On the basis of the above data, the structure of viburnol H (**3**) is proposed to be as depicted in the formula.

Viburnol I (**4**) was obtained as its methyl ester **4a**,  $[\alpha]_D +20.0^\circ$  ( $\text{CHCl}_3$ ). The molecular formula of **4a** was assigned as  $\text{C}_{31}\text{H}_{48}\text{O}_7$  on the basis of the MS and  $^{13}\text{C}$ -NMR spectral data. From a comparison of the spectral data of **4a** with those of viburnol B methyl ester,<sup>1)</sup> it was deduced that **4a** possesses a hemiacetal ( $\delta_{\text{H}} 4.99$ ,  $\delta_{\text{C}} 105.2$ ) and a carbonyl ( $1738\text{ cm}^{-1}$ ,  $\delta_{\text{C}} 202.8$ ) instead of methylene (C-1) and  $\delta$ -lactone carbonyl (C-2) groups in viburnol B. The planar structure of **4a** was finally deduced from the HMBC spectrum. The cross peaks between the proton at  $\delta 4.99$  and C-11 ( $\delta 75.8$ ), and between the 19- $\text{CH}_3$  ( $\delta 1.07$ ) and the carbon at  $\delta 105.2$ , suggested the presence of a five-membered hemiacetal ring between C-1 and -11. The cross peaks between the methyl protons at  $\delta 1.25$  and  $1.37$  (28- $\text{CH}_3$ , 29- $\text{CH}_3$ ) and carbon signals at  $\delta 202.8$ ,  $50.3$  (C-4) and  $45.5$  (C-5), respectively, suggested that the carbon signal at  $\delta 202.8$  is assignable to C-3. The remaining methoxycarbonyl moiety should, therefore be connected with this carbonyl. The presence of the  $\alpha$ -ketomethylester moiety was supported by the electron impact (EI) mass fragment at  $m/z 287$  [ $\text{M}^+ - \text{H}_2\text{O} - \text{C}_6\text{H}_5\text{O}$  (C-20/-22 cleavage)- $\text{C}_6\text{H}_{10}\text{O}_3$  (C-4/C-5 cleavage)]. On the basis of the above data, **4a** was suggested to be an A-seco dammarane-type triterpene having a five-membered hemiacetal ring and methoxalyl group. The stereochemistry of the hemiacetal group at C-1 was determined by an NOE experiment; a significant NOE between 1-H and 19- $\text{CH}_3$  was observed. Moreover, the carbon signal of C-5 in **4a** was shifted upfield from that of viburnol B methyl ester by  $\Delta \delta -9.8$  due to the  $\gamma$ -gauche effect of  $1\alpha$ -OH (C-19 seems to be unaffected by the 1-OH). All other HMBC and NOE correlations of **4a** were the same as those of viburnol B methyl ester. On the basis of the above data, the structure of viburnol I (**4**) was established to be as depicted in the formula.

Viburnol J (**5**) was obtained as an amorphous powder,  $[\alpha]_D +45.5^\circ$  ( $\text{CHCl}_3$ ). The molecular formula of **5** was assigned as  $\text{C}_{29}\text{H}_{44}\text{O}_4$  on the basis of the MS and  $^{13}\text{C}$ -NMR spectral data. From a comparison of the NMR spectral data of **5** with those of viburnol C,<sup>1)</sup> it was

Table 1.  $^{13}\text{C}$ -NMR Chemical Shifts (67.8 MHz,  $\text{CDCl}_3$ )

C	1a	2a	3	4a	5	6
1	82.5	89.2	55.9	105.2	48.9	50.6
2	85.5	172.4	212.3	164.9	170.5	170.4
3	174.9	217.5	82.4	202.8	—	—
4	46.7	44.5	45.3	50.3	144.5	—
5	55.9	51.6	55.3	45.5	56.1	40.2
6	17.9	17.5	18.3	22.7	23.7	18.1
7	35.2	35.0	35.4	34.0	34.1	33.9
8	41.2	41.6	41.0	38.2	39.1	39.2
9	47.3	49.1	55.1	49.8	46.5	45.3
10	46.0	49.0	44.8	47.5	35.7	32.1
11	69.8	69.5	70.3	75.8	78.0	78.6
12	38.2	37.6	39.7	34.5	34.7	34.7
13	41.2	41.4	40.7	43.3	40.9	40.9
14	50.2	50.5	50.1	50.2	50.1	50.0
15	30.9	30.8	30.7	30.9	30.7	30.6
16	25.2	25.2	25.0	26.0	25.0	25.0
17	50.1	50.0	50.2	48.3	49.3	49.3
18	16.8	17.1	16.3	15.3	15.2	15.0
19	16.9	14.5	17.7	17.3	17.2	20.4
20	74.9	74.6	74.8	74.8	74.4	74.4
21	26.5	26.0	26.5	26.1	25.8	25.8
22	50.0	50.9	49.9	50.6	51.0	51.0
23	202.9	202.8	202.8	202.7	202.6	202.6
24	124.9	124.9	124.8	124.8	124.7	124.7
25	157.6	57.8	157.6	157.5	157.8	157.7
26	27.9	28.0	27.8	27.9	27.9	27.9
27	21.0	21.2	21.0	21.0	21.0	21.0
28	25.3	27.6	29.5	20.5	22.9	—
29	21.2	22.3	16.5	23.8	114.6	—
30	16.7	16.7	16.3	16.0	16.4	16.3

Assignments were confirmed by  $^1\text{H}$ - $^1\text{H}$  and  $^{13}\text{C}$ - $^1\text{H}$  COSY, distortionless enhancement by polarization transfer (DEPT) and HMBC methods.

deduced that **5** possesses an isopropenyl group ( $\delta_{\text{H}}$  4.92, 4.68, 1.75,  $\delta_{\text{C}}$  144.5, 114.6, 22.9) instead of a hydroxyl and two methyl (C-28, -29) groups in viburnol C. The isopropenyl group was located at C-5 from the HMBC spectrum. The carbon signal at  $\delta$  56.1 (C-5) showed correlations with the methyl protons ( $\delta$  1.75) and with the olefin protons ( $\delta$  4.92, 4.68). All other HMBC and NOE correlations of **5** were the same as those of viburnol C. On the basis of the above data, the structure of viburnol J (**5**) was established to be as depicted in the formula.

Viburnol K (**6**) was obtained as an amorphous powder,  $[\alpha]_{\text{D}} + 25.5^\circ$  ( $\text{CHCl}_3$ ). The molecular formula of **6** was assigned as  $\text{C}_{26}\text{H}_{40}\text{O}_4$  on the basis of the MS and  $^{13}\text{C}$ -NMR spectral data. From a comparison of the NMR spectral data of **6** with those of viburnol C, it was deduced that **6** possesses a methylene ( $\delta_{\text{C}}$  40.2) group instead of a hydroxyl-bearing carbon (C-4), two methyls (C-28, -29) and a methine (C-5) in viburnol C. The carbon signals of C-6 and -10 in **6** were shifted upfield from those of viburnol C by  $\Delta$   $\delta$  -4.1 and -5.5, respectively, because of the loss of the  $\beta$ -substituent effect. These findings suggested that the methylene carbon at  $\delta$  40.2 could be assigned as C-5. All other HMBC and NOE correlations of **6** were the same as those of viburnol C. On the basis of the above data, the structure of viburnol K (**6**) was established to be as depicted in the formula. Viburnol K (**6**) is the first example of a ring A-tetranor (C-3, -4, -28 and -29)- triterpene isolated from a natural source.

The methyl esters **1a**, **2a** and **4a** may be artifacts formed

from the corresponding acids **1**, **2** and **4** during the extraction and isolation processes.

Viburnols F (**1**), G (**2**), H (**3**), I (**4**), J (**5**) and K (**6**) were presumably biosynthesized from viburnol D (Fig. 3), so all the chiral centers of **1** (except C-1 and -2), **2** (except C-1), **3** (except C-3), **4** (except C-1), **5** and **6** are expected to coincide with those of viburnol D, whose absolute configuration was elucidated from the circular dichroism (CD) spectrum.<sup>1)</sup> Based on this assumption, the full structures of viburnols F—K (**1**—**6**) are as shown in Chart 1.

Compounds **1**—**6** are new dammarane-type triterpenes, and compounds **1**, **2** and **4** are the first examples of a new class of modified dammarane-type triterpenes. Furthermore, the occurrence of compounds **1** and **2** gives important clues to the biosynthesis of the A-nor-triterpenoid, viburnol E.

It is likely that all viburnols (except viburnols D and H) are biosynthesized from the postulated intermediate (**7**; dammar-24-ene-2,3,23-trione-1 $\alpha$ ,11 $\alpha$ ,20 $\alpha$ -triol). Bonds cleavages at ring A followed by recyclization would afford viburnols F (route A), G (route B), A (route C) and I (route D) (Fig. 3).<sup>3)</sup>

#### Experimental

The instruments, materials and experimental conditions were the same as in our previous paper.<sup>1)</sup>

**Extraction and Isolation** The extraction and isolation procedures were as described in our previous paper.<sup>1)</sup> Compounds **1a** (10.0 mg), **2a** (7.0 mg), **3** (30.0 mg), **4a** (6.5 mg), **5** (10.0 mg) and **6** (9.5 mg) were isolated from frs. 3-2-4—3-2-8 by preparative HPLC.

Viburnol F Methyl Ester (**1a**): An amorphous powder,  $[\alpha]_{\text{D}} + 43.5^\circ$  ( $c = 0.3$ ,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3421, 2954, 1727, 1672, 1613. UV  $\lambda_{\text{max}}$  (MeOH) nm (log  $\epsilon$ ): 241.0 (3.89). EI-MS  $m/z$ : 516 ( $\text{M} - \text{H}_2\text{O}$ )<sup>+</sup>. FAB-MS  $m/z$ : 535 ( $\text{M} + \text{H}$ )<sup>+</sup>. HR-MS  $m/z$ : 516.3459 ( $\text{M}^+ - \text{H}_2\text{O}$ , Calcd for  $\text{C}_{31}\text{H}_{48}\text{O}_6$ ; 516.3451).  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.07 (1H, br t,  $J = 1.2$  Hz, 24-H), 4.68 (1H, br s, 1-OH), 4.40 (1H, s, 20-OH), 4.37 (1H, s, 1-H), 4.28 (1H, s, 2-OH), 3.99 (1H, ddd,  $J = 11.2, 10.5, 5.0$  Hz, 11-H), 3.76 (3H, s,  $\text{COOCH}_3$ ), 2.54, 2.61 (2H, d,  $J = 16.4$  Hz, 22- $\text{CH}_2$ ), 2.42 (1H, br s, 11-OH), 2.21 (1H, m, 12- $\text{H}_\beta$ ), 2.17 (3H, d,  $J = 1.2$  Hz, 27- $\text{CH}_3$ ), 2.14 (1H, d,  $J = 11.2$  Hz, 9-H), 1.91 (3H, d,  $J = 1.2$  Hz, 26- $\text{CH}_3$ ), 1.21 (3H, s, 21- $\text{CH}_3$ ), 1.09 (3H, s, 19- $\text{CH}_3$ ), 1.05 (3H, s, 28- $\text{CH}_3$ ), 0.97 (6H, s, 18,30- $\text{CH}_3$ ), 0.84 (3H, s, 29- $\text{CH}_3$ ).  $^{13}\text{C}$ -NMR (67.8 MHz,  $\text{CDCl}_3$ ): Table 1.

Viburnol G Methyl Ester (**2a**): An amorphous powder,  $[\alpha]_{\text{D}} + 73.8^\circ$  ( $c = 0.4$ ,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3451, 2957, 1755, 1719, 1672, 1613. UV  $\lambda_{\text{max}}$  (MeOH) nm (log  $\epsilon$ ): 240.0 (3.93). EI-MS  $m/z$ : 514 ( $\text{M} - \text{H}_2\text{O}$ )<sup>+</sup>. FAB-MS  $m/z$ : 533 ( $\text{M} + \text{H}$ )<sup>+</sup>. HR-MS  $m/z$ : 514.3303 ( $\text{M}^+ - \text{H}_2\text{O}$ , Calcd for  $\text{C}_{31}\text{H}_{46}\text{O}_6$ ; 514.3295).  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.05 (1H, br t,  $J = 1.2$  Hz, 24-H), 5.64 (1H, s, 1-OH), 4.37 (1H, s, 20-OH), 3.82 (1H, m, 11-H), 3.76 (3H, s,  $\text{COOCH}_3$ ), 3.34 (1H, d,  $J = 8.9$  Hz, 11-OH), 2.57 (2H, s, 22- $\text{CH}_2$ ), 2.32 (1H, m, 12- $\text{H}_\beta$ ), 2.17 (3H, d,  $J = 1.2$  Hz, 27- $\text{CH}_3$ ), 2.06 (1H, d,  $J = 10.9$  Hz, 9-H), 1.92 (3H, d,  $J = 1.2$  Hz, 26- $\text{CH}_3$ ), 1.20 (3H, s, 21- $\text{CH}_3$ ), 1.17 (3H, s, 29- $\text{CH}_3$ ), 1.07 (3H, s, 28- $\text{CH}_3$ ), 1.02 (6H, s, 18,19- $\text{CH}_3$ ), 0.94 (3H, s, 30- $\text{CH}_3$ ).  $^{13}\text{C}$ -NMR (67.8 MHz,  $\text{CDCl}_3$ ): Table 1.

Viburnol H (**3**): An amorphous powder,  $[\alpha]_{\text{D}} + 43.3^\circ$  ( $c = 0.7$ ,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3475, 3019, 2974, 1704, 1674, 1614. UV  $\lambda_{\text{max}}$  (MeOH) nm (log  $\epsilon$ ): 240.0 (3.79). EI-MS  $m/z$ : 470 ( $\text{M} - \text{H}_2\text{O}$ )<sup>+</sup>. FAB-MS  $m/z$ : 489 ( $\text{M} + \text{H}$ )<sup>+</sup>. HR-MS  $m/z$ : 470.3366 ( $\text{M}^+ - \text{H}_2\text{O}$ , Calcd for  $\text{C}_{30}\text{H}_{46}\text{O}_4$ ; 470.3396).  $^1\text{H}$ -NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.06 (1H, br t,  $J = 1.3$  Hz, 24-H), 4.36 (1H, br s, 20-OH), 3.98 (1H, ddd,  $J = 10.6, 10.4, 5.3$  Hz, 11-H), 3.89 (1H, s, 3-H), 3.48 (1H, d,  $J = 13.0$  Hz, 1- $\text{H}_\beta$ ), 2.56 (2H, s, 22- $\text{CH}_2$ ), 2.25 (1H, d,  $J = 13.0$  Hz, 1- $\text{H}_\alpha$ ), 2.22 (1H, m, 12- $\text{H}_\beta$ ), 2.17 (3H, d,  $J = 1.3$  Hz, 27- $\text{CH}_3$ ), 1.92 (3H, d,  $J = 1.3$  Hz, 26- $\text{CH}_3$ ), 1.70 (1H, d,  $J = 10.6$  Hz, 9-H), 1.21 (3H, s, 21- $\text{CH}_3$ ), 1.19 (3H, s, 28- $\text{CH}_3$ ), 0.99 (3H, s, 19- $\text{CH}_3$ ), 0.96 (6H, s, 18,30- $\text{CH}_3$ ), 0.70 (3H, s, 29- $\text{CH}_3$ ).  $^{13}\text{C}$ -NMR (67.8 MHz,  $\text{CDCl}_3$ ): Table 1.

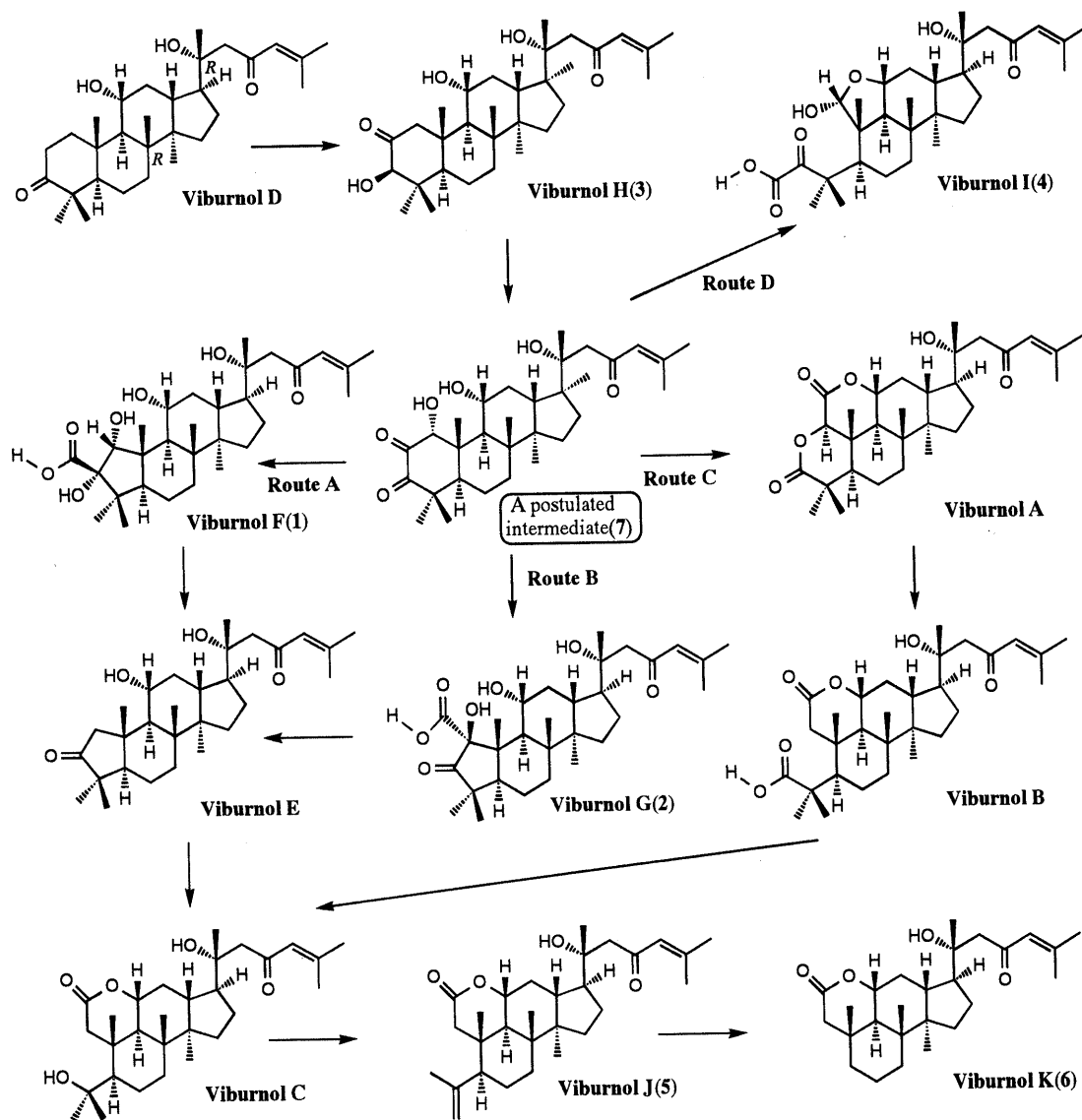


Fig. 3. Possible Biosynthetic Pathways of Viburnols

**Viburnol I Methyl Ester (4a):** An amorphous powder,  $[\alpha]_D +20.0^\circ$  ( $c=0.3$ ,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3452, 2958, 2928, 1738, 1713, 1673, 1612. UV  $\lambda_{\text{max}}$  (MeOH) nm ( $\log \epsilon$ ): 241.0 (3.94). EI-MS  $m/z$ : 514 ( $\text{M}-\text{H}_2\text{O}$ )<sup>+</sup>. FAB-MS  $m/z$ : 533 ( $\text{M}+\text{H}$ )<sup>+</sup>. HR-MS  $m/z$ : 514.3322 ( $\text{M}^+-\text{H}_2\text{O}$ , Calcd for  $\text{C}_{31}\text{H}_{46}\text{O}_6$ ; 514.3295),  $m/z$ : 417.2674 ( $\text{M}^+-\text{H}_2\text{O}-\text{C}_6\text{H}_9\text{O}$ , Calcd for  $\text{C}_{25}\text{H}_{37}\text{O}_5$ ; 417.2641),  $m/z$ : 287.1970 ( $\text{M}^+-\text{H}_2\text{O}-\text{C}_6\text{H}_9\text{O}-\text{C}_6\text{H}_{10}\text{O}_3$ , Calcd for  $\text{C}_{19}\text{H}_{27}\text{O}_2$ ; 287.2011). <sup>1</sup>H-NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.04 (1H, br t,  $J=1.0$  Hz, 24-H), 4.99 (1H, d,  $J=2.5$  Hz, 1-H), 4.33 (1H, s, 20-OH), 3.84 (3H, s,  $\text{COOCH}_3$ ), 3.73 (1H, ddd,  $J=11.9, 11.0, 5.0$  Hz, 11-H), 2.61, 2.53 (2H, d,  $J=16.5$  Hz, 22- $\text{CH}_2$ ), 2.36 (1H, m, 12- $\text{H}_\beta$ ), 2.34 (1H, d,  $J=2.5$  Hz, 1-OH), 2.16 (3H, d,  $J=1.0$  Hz, 27- $\text{CH}_3$ ), 2.10 (1H, d,  $J=11.9$  Hz, 9-H), 1.91 (3H, d,  $J=1.0$  Hz, 26- $\text{CH}_3$ ), 1.37 (3H, s, 29- $\text{CH}_3$ ), 1.25 (3H, s, 28- $\text{CH}_3$ ), 1.19 (3H, s, 21- $\text{CH}_3$ ), 1.07 (3H, s, 19- $\text{CH}_3$ ), 0.97 (3H, s, 18- $\text{CH}_3$ ), 0.96 (3H, s, 30- $\text{CH}_3$ ). <sup>13</sup>C-NMR (67.8 MHz,  $\text{CDCl}_3$ ): Table 1.

**Viburnol J (5)** An amorphous powder,  $[\alpha]_D +45.5^\circ$  ( $c=0.2$ ,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3456, 2965, 1718, 1673, 1611. UV  $\lambda_{\text{max}}$  (MeOH) nm ( $\log \epsilon$ ): 241.0 (3.93). EI-MS  $m/z$ : 438 ( $\text{M}-\text{H}_2\text{O}$ )<sup>+</sup>. FAB-MS  $m/z$ : 457 ( $\text{M}+\text{H}$ )<sup>+</sup>. HR-MS  $m/z$ : 438.3112 ( $\text{M}^+-\text{H}_2\text{O}$ , Calcd for  $\text{C}_{29}\text{H}_{42}\text{O}_3$ ; 438.3134). <sup>1</sup>H-NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.05 (1H, br s, 24-H), 4.92 (1H, t,  $J=1.7$  Hz, 29- $\text{H}_\beta$ ), 4.68 (1H, br s, 29- $\text{H}_\alpha$ ), 4.42 (1H, ddd,  $J=11.6, 11.4, 5.0$  Hz, 11-H), 4.38 (1H, s, 20-OH), 2.57 (2H, s, 22- $\text{CH}_2$ ), 2.54 (1H, d,  $J=16.0$  Hz, 1- $\text{H}_\beta$ ), 2.39 (1H, ddd,  $J=12.0, 5.0, 3.0$  Hz, 12- $\text{H}_\beta$ ), 2.17 (3H, s, 27- $\text{CH}_3$ ), 2.16 (1H, d,  $J=16.0$  Hz, 1- $\text{H}_\alpha$ ), 1.92 (3H, d,  $J=1.3$  Hz, 26- $\text{CH}_3$ ), 1.79 (1H, d,  $J=11.6$  Hz, 9-H), 1.75 (3H, br s, 28- $\text{CH}_3$ ), 1.21

(3H, s, 21- $\text{CH}_3$ ), 1.06 (6H, s, 18, 19- $\text{CH}_3$ ), 0.97 (3H, s, 30- $\text{CH}_3$ ). <sup>13</sup>C-NMR (67.8 MHz,  $\text{CDCl}_3$ ): Table 1.

**Viburnol K (6)** An amorphous powder,  $[\alpha]_D +25.5^\circ$  ( $c=0.4$ ,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3452, 2943, 1718, 1674, 1614. UV  $\lambda_{\text{max}}$  (MeOH) nm ( $\log \epsilon$ ): 241.0 (3.80). EI-MS  $m/z$ : 398 ( $\text{M}-\text{H}_2\text{O}$ )<sup>+</sup>. FAB-MS  $m/z$ : 417 ( $\text{M}+\text{H}$ )<sup>+</sup>. HR-MS  $m/z$ : 398.2831 ( $\text{M}^+-\text{H}_2\text{O}$ , Calcd for  $\text{C}_{26}\text{H}_{38}\text{O}_3$ ; 398.2821). <sup>1</sup>H-NMR (270 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.04 (1H, br t,  $J=1.0$  Hz, 24-H), 4.39 (1H, ddd,  $J=11.9, 10.6, 5.0$  Hz, 11-H), 4.37 (1H, s, 20-OH), 2.56 (2H, s, 22- $\text{CH}_2$ ), 2.38 (1H, m, 12- $\text{H}_\beta$ ), 2.34 (1H, d,  $J=17.2$  Hz, 1- $\text{H}_\beta$ ), 2.17 (3H, d,  $J=1.0$  Hz, 27- $\text{CH}_3$ ), 2.16 (1H, d,  $J=17.2$  Hz, 1- $\text{H}_\alpha$ ), 1.92 (3H, d,  $J=1.0$  Hz, 26- $\text{CH}_3$ ), 1.78 (1H, d,  $J=11.9$  Hz, 9-H), 1.21 (3H, s, 21- $\text{CH}_3$ ), 1.12 (3H, s, 19- $\text{CH}_3$ ), 1.04 (3H, s, 18- $\text{CH}_3$ ), 0.95 (3H, s, 30- $\text{CH}_3$ ). <sup>13</sup>C-NMR (67.8 MHz,  $\text{CDCl}_3$ ): Table 1.

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#### References and Notes

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