Studies on the Constituents from the Aerial Part of *Baccharis dracunculifolia* DC.

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Ten new glycosides, named dracunculifosides A—J, were isolated along with sixteen known glycosides from the aerial part of *Baccharis dracunculifolia* DC. (Compositae). The structures of these glycosides were determined on the basis of spectral and chemical evidence. These new glycosides consisted of β-D-glucopyranose or β-D-apiofuranosyl-(1→6)-β-D-glucopyranose, and most possess an (*E*)-caffeoyl group.

Key words *Baccharis dracunculifolia* DC.; Compositae; dracunculifoside; phenolic glycoside

Baccharis dracunculifolia DC. is indigenous throughout the southeast parts of Latin America and is used by local people in traditional medicine.[1)] Phytochemical investigation of the essential oil has been reported,[1)] but investigation of its glycosides has not been reported. Thus, we have started a study of its constituents in the course of our research on the phytochemicals of Brazilian plants. This paper describes the isolation and structural determination of ten new compounds, named dracunculifosides A—J, along with 16 known ones (**1**,[2)] **2**,[3)] **3**,[4)] **4**,[5)] **5**,[5)] **6**,[5)] **7**,[6,7)] **8**,[6)] **9**,[8,9)] **10**,[10)] **11**,[11)] **12**,[12)] **13**,[13)] **14**,[14)] **15**,[15)] **16**,[16)]).

The MeOH extract from the dried aerial part of *B. dracunculifolia* DC. was suspended in water. The suspension was then extracted with diethyl ether and partitioned into an ether-soluble fraction and a water-soluble fraction. The water-soluble fraction was passed through a Mitsubishi Diaion HP-20 column and the adsorbed material was subsequently eluted with 50% MeOH in water, 70% MeOH in water and MeOH. The 50% MeOH eluate from the Diaion HP-20 column was concentrated and the residue rechromatographed on a silica gel column and by semi-preparative HPLC to give compounds (**1**—**26**).

Dracunculifoside A (**17**) was suggested to have the molecular formula, $C_{28}H_{40}O_{11}$, based on a high resolution (HR)-FAB-MS [positive HR-FAB-MS ion at *m/z* 553.2638 $[M+H]^+$, 575.2489 $[M+Na]^+$]. The ^{1}H-NMR spectrum showed AMX type-aromatic proton signals [δ 7.06 (1H, d, J=2.0 Hz), 6.95 (1H, dd, J=8.0, 2.0 Hz), 6.79 (1H, d, J=8.0 Hz)] which had correlations in the ^{1}H–^{1}H correlation spectroscopy (COSY) spectrum, two *trans*-olefinic proton signals [δ 7.57 (1H, d, J=16.0 Hz), 6.31 (H, d, J=16.0 Hz)], and one anomeric proton signal [δ 4.38 (1H, d, J=8.0 Hz)]. On the other hand, the ^{13}C-NMR spectrum exhibited one carbonyl carbon signal (δ 169.2), two sp^2 carbon signals (δ 147.1, 115.0), aromatic carbon signals (δ 149.6, 146.8, 127.1, 123.0, 116.6, 115.2), and six carbon signals due to the sugar moiety (δ 102.9, 78.2, 75.4, 75.3, 71.6, 64.7) together with the signals due to the aglycone moiety. Thus, compound **17** was considered to consist of an aglycone, one monosaccharide and an (*E*)-caffeoyl group. Since 13 carbon signals and four methyl proton signals [δ 1.30 (3H, d, J=6.5 Hz), 0.93 (3H, s), 0.88 (3H, s), 0.77 (3H, d, J=6.5 Hz)] were assigned to the aglycone moiety in the ^{13}C- and ^{1}H-NMR spectra, the aglycone of **17** was deduce to be an ionone derivative.

Mild alkaline hydrolysis of compound **17** afforded alangionoside A (**17a**).[17)] On comparison of the ^{1}H-NMR spectrum of **17** with that of **17a**, the H-6 signals of β-D-glucopyranose of **17** were shifted downfield, which indicated that the (*E*)-caffeoyl group was attached to C-6 of the β-D-glucopyranose of **17a**. This was confirmed by the ^{1}H-detected heteronuclear multiple-bond connectivity (HMBC) spectrum. On the basis of the above evidence, the structure of dracunculifoside A (**17**) was determined as shown in Chart 1.

Dracunculifoside B (**18**) had the molecular formula, $C_{22}H_{22}O_{12}$, on a HR-FAB-MS [positive HR-FAB-MS ion at *m/z* 501.1036 $[M+Na]^+$]. The ^{1}H- and ^{13}C-NMR spectra of **18** showed signals due to an (*E*)-caffeoyl group and glucopyranose. The J value of the anomeric proton signal of glucopyranose (J=8.0 Hz) and acid hydrolysis of compound **18** suggested that this glucopyranose had a β-D-configuration. In addition to the signals of the (*E*)-caffeoyl group and β-D-glucopyranose, ABX type-aromatic proton signals were observed at δ 7.49 (1H, d, J=2.0 Hz), 7.46 (1H, dd, J=8.0, 2.0 Hz) and 7.19 (1H, d, J=8.0 Hz), and aromatic and one carboxylic carbon signals were shown at δ 150.5, 147.9, 126.9, 123.2, 118.4, 117.2 and 169.6. This suggested that the aglycone of **18** was protocatechuic acid, which was confirmed by acid hydrolysis of **18**.

In the nuclear Overhauser effect (NOE) difference spectrum, irradiation at the anomeric proton signal of β-D-glucopyranose [δ 4.93 (1H, d, J=8.0 Hz)] caused enhancement at δ 7.19 (1H, d, J=8.0 Hz, H-5 of the aglycone). In the HMBC experiment, long-range correlation was observed between the C-4 signal of the aglycone (δ 150.5) and the H-1 signal of β-D-glucopyranose [δ 4.93 (1H, d, J=8.0 Hz)]. Moreover, the carbonyl carbon signal of the (*E*)-caffeoyl group (δ 168.9) exhibited long-range correlations with the H-6 signals of β-D-glucopyranose [δ 4.58 (1H, dd, J=12.0, 2.0 Hz), 4.35 (1H, dd, J=12.0, 5.5 Hz)]. These indicated that β-D-glucopyranose was attached at the C-4 position of the aglycone, and the (*E*)-caffeoyl group was bound to C-6 of β-D-glucopyranose. Therefore, the structure of dracunculifoside B (**18**) was deduced to be 3-hydroxy-4-[(6-*O*-(*E*)-caffeoyl)-β-D-glucopyranosyl]oxybenzoic acid.

Dracunculifosides C—E (**19**—**21**) had the molecular formulae, $C_{24}H_{26}O_{12}$, $C_{26}H_{30}O_{11}$ and $C_{18}H_{24}O_{10}$, respectively, based on HR-FAB-MS. The ^{1}H- and ^{13}C-NMR spectral data of compounds **19**—**21** were similar with those of **18** except for the aglycone moiety. Accordingly, compounds **19**—**21** had β-D-glucopyranose and an (*E*)-caffeoyl group as the

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sugar and ester moieties, but the alycone moieties were different from that of **18**.

In the ^{1}H-NMR spectrum of compound **19**, AMX type-aromatic proton signals were observed at δ 7.04 (1H, d, J=8.0 Hz), 6.71 (1H, d, J=2.0 Hz) and 6.53 (1H, dd, J=8.0, 2.0 Hz). The ^{13}C-NMR spectrum showed a carboxylic carbon signal (δ 176.7), two methylene carbon signals (δ 36.7, 31.4) along with the aromatic carbon signals in regard to the aglycone moiety. These facts indicated that the aglycone of **19** was dihydrocaffeic acid, and this was confirmed by acid hydrolysis. The NOE difference experiment irradiating at the anomeric proton signal of β-D-glucopyranose [δ 4.70 (1H, d, J=8.0 Hz)] exhibited an NOE to δ 7.04 (1H, d, J=8.0 Hz, H-5 of the aglycone). Thus, the structure of dracunculifoside C (**19**) was determined to be 3-[3-hydroxy-4-[(6-*O*-(*E*)-caffeoyl)-β-D-glucopyranosyl]]oxyphenylpropionic acid.

Concerning the aglycone moiety of compound **20**, the ^{1}H- and ^{13}C-NMR spectra showed two *trans*-olefinic proton signals [δ 6.40 (1H, d, J=16.0 Hz), 5.99 (1H, dt, J=16.0, 6.0 Hz)], a methylene proton signal [δ 4.00 (2H, d, J=6.0 Hz)], two methoxyl proton signals [δ 3.85 (3H, s), 3.35 (3H, s)] and two sp^2 carbon signals (δ 133.3, 125.7), one carbinol carbon signal (δ 74.1), two methoxyl carbon signals (δ 58.1, 56.8) along with the aromatic proton and carbon signals. The ^{1}H–^{1}H COSY and ^{1}H-detected heteronuclear multiple quantum coherency (HMQC) spectra made it possible to assign each carbon and proton signal, as shown in Tables 2 and 3. In the HMBC spectrum, long-range correlations were observed as follows, δ 3.35 (3H, s –OCH_3)/δ 74.1 (C-9), δ 4.00 (2H, d, J=6.0 Hz, H-9)/δ 125.7 (C-8) and 133.3 (C-7), δ 6.99 (1H, d, J=2.0 Hz, H-2) and 6.78 (1H, br d, J=8.0 Hz, H-6)/δ 133.3 (C-7), δ 4.86 (1H, d, J=8.0 Hz, H-1 of β-D-glucopyranose) and δ 147.5 (C-4). In addition, the NOE difference spectra showed NOEs between δ 3.85 (3H, s, –OCH_3) and 6.99 (1H, d, J=2.0 Hz, H-2), δ 4.86 (1H, d, J=8.0 Hz, H-1 of β-D-glucopyranose) and 7.02 (1H, d, J=8.0 Hz, H-5). These results indicated that the aglycone of **20** was 3-(4-hydroxy-3-methoxyphenyl)-2-propenyl methyl ether, and β-D-glucopyranose was attached to the C-4 position of this aglycone. Accordingly, the structure of dracunculifoside D (**20**) was determined as shown in Chart 1.

Dracunculifoside E (**21**) had propylene glycol as the aglycone, because of observations of one methyl proton signal [δ 1.20 (3H, d, J=6.5 Hz)] and two carbinol carbon signals (δ 78.0, 67.2) in the ^{1}H- and ^{13}C-NMR spectra and the results of acid hydrolysis. In the NOE difference experiment, irradiation of the anomeric proton signal for β-D-glucopyranose [δ 4.40 (1H, d, J=8.0 Hz)] displayed an NOE to the H-2 signal [δ 3.89 (1H, m)]. Thus, β-D-glucopyranose was bound to the C-2 position of the aglycone moiety and the structure of dracunculifoside E (**21**) was elucidated as shown in Chart 1.

On comparison of the ^{13}C chemical shifts of **21** and propylene glycol measured in pyridine-d_5 solution, glycosylation shifts were observed at C-1 (−1.9 ppm), C-2 (+9.1 ppm) and C-3 (−2.8 ppm). These $\Delta\delta_C$ values suggested that the aglycone of **21** was (*S*)-propylene glycol.[18] However, comparing the ^{13}C-NMR spectral data of **21** with those of 2-(*R*)-(β-D-galactopyranosyl)oxy-1-propanol[19] and 2-(*S*)-(β-D-galactopyranosyl)oxy-1-propanol,[19] the ^{13}C chemical shifts of the signals due to the aglycone moiety of **21** resembled those of 2-(*R*)-(β-D-galactopyranosyl)oxy-1-propanol. Therefore, the absolute configuration of the C-2 position in **21** remains to be determined.

The molecular formula of dracunculifoside F (**22**) was suggested to be $C_{24}H_{34}O_{13}$ based on a HR-FAB-MS [positive HR-FAB-MS ion at m/z 553.1927 $[M+Na]^+$]. The ^{1}H- and ^{13}C-NMR spectra showed two anomeric proton and carbon signals [δ 5.03 (1H, d, J=2.0 Hz), 110.7, δ 4.30 (1H, d, J=8.0 Hz), 103.9] together with the signals due to the (*E*)-caffeoyl group and the aglycone, which was deduced to be 2-butanol from the ^{1}H-, ^{13}C-NMR and ^{1}H–^{1}H COSY spectra. Acid hydrolysis of **22** afforded D-glucose and apiose suggesting the presence of one D-glucose and one apiose as sugar moieties. The ^{1}H–^{1}H COSY and HMQC spectra for the anomeric proton and carbon signals at δ 4.30 (1H, d, J=8.0 Hz) and δ 103.9 were assigned to H-1 and C-1 of β-D-glucopyranose, and at δ 5.03 (1H, d, J=2.0 Hz) and δ 110.7 were due to H-1 and C-1 of apiofuranose. In the NOE difference spectra, irradiation of the anomeric proton signals of β-D-glucopyranose [δ 4.30 (1H, d, J=8.0 Hz)] and apiofuranose [δ 5.03 (1H, d, J=2.0 Hz)] showed NOEs to the H-2 signal of the aglycone [δ 3.70 (1H, m)] and the H-6 signals of β-D-glucopyranose [δ 3.99 (1H, dd, J=11.5, 2.0 Hz), 3.60 (1H, dd, J=11.5, 6.0 Hz)], respectively. The HMBC experiment showed long-range correlations between δ 4.30 (H-1 of β-D-glucopyranose) and δ 79.0 (C-2), δ 5.03 (H-1 of apiofuranose) and δ 68.8 (C-6 of β-D-glucopyranose), δ 168.9 [C-

Table 1. ^{13}C- and ^{1}H-NMR Spectral Data of Compound **17**

	C	H
Aglycone moiety		
-1	78.2	—
-2	35.4	1.86 (m)
-3	39.8	1.64 *c)*
		1.35 (t, 12.0)
-4	67.5	3.74 (m)
-5	45.9	1.64 (t, 12.0)
		1.38 *c)*
-6	40.5	—
-7	136.2	5.60 (d, 16.0)
-8	133.3	5.75 (dd, 16.0, 6.5)
-9	78.0	4.36 (m)
-10	21.7	1.30 (d, 6.5)
-11	25.3 *a)*	0.88 (s) *a)*
-12	26.1 *a)*	0.93 (s) *a)*
-13	16.5	0.77 (d, 6.5)
Suger moiety		
Glu-1′	102.9	4.38 (d, 8.0)
-2′	75.3 *b)*	3.22 (t, 8.0)
-3′	78.2	3.38 *c)*
-4′	71.6	3.38 *c)*
-5′	75.4 *b)*	3.46 (m)
-6′	64.7	4.44 (dd, 12.0, 2.0)
		4.29 (dd, 12.0, 5.5)
Ester moiety		
-1‴	169.2	—
-2‴	115.0	6.31 (d, 16.0)
-3‴	147.1	7.57 (d, 16.0)
-4‴	127.1	—
-5‴	115.2	7.06 (d, 2.0)
-6‴	149.6	—
-7‴	146.8	—
-8‴	116.6	6.79 (d, 8.0)
-9‴	123.0	6.95 (dd, 8.0, 2.0)

Measured in MeOH-d_4 solution at 35 °C. *a*, *b*) Interchageable in each column. *c*) Overlapping with other signals. Glc: β-D-glucopyranosyl.

Table 2. ^{13}C-NMR Spectral Data of Compounds **18**—**25**

Carbon No.	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
Aglycone moiety								
C-1	126.9	138.1	133.2[a)]	67.2	21.5	22.2[a)]	139.0	134.2
-2	118.4	117.1	111.9	78.0	79.0	72.9	129.3	119.5
-3	147.9	148.4	151.0	16.8	30.2	23.9[a)]	129.3	146.8
-4	150.5	145.0	147.5	—	10.0	—	128.7	146.6
-5	117.2	119.3	118.4	—	—	—	129.3	117.2
-6	123.2	120.7	120.7	—	—	—	129.3	124.7
-7	169.6	31.4	133.3[a)]	—	—	—	71.9	30.3
-8	—	36.7	125.7	—	—	—	—	46.0
-9	—	176.7	74.1	—	—	—	—	211.3
-10	—	—	-	—	—	—	—	30.1
-OMe	—	—	56.8	—	—	—	—	—
-OMe′	—	—	58.1	—	—	—	—	—
Sugar moiety								
Glc-1′	103.1	104.6	102.6	103.0	103.9	102.7	103.3	104.6
-2′	74.8	74.9	74.9	74.9	75.3	75.1	75.1	75.1
-3′	77.5	77.6	77.9	77.8	78.2	78.2	78.1	77.6
-4′	71.8	71.9	72.1	71.8	71.9	71.9	71.9	71.6
-5′	75.9	75.8	75.6	75.5	76.7	76.8	77.0	77.1
-6′	64.6	64.6	64.6	64.7	68.8	68.8	68.7	68.5
Api-1″	—	—	—	—	110.7	110.7	110.7	110.6
-2″	—	—	—	—	78.5	78.5	78.5	78.7
-3″	—	—	—	—	79.0	79.0	79.0	79.0
-4″	—	—	—	—	75.0	75.0	75.1	74.9
-5″	—	—	—	—	67.5	67.5	67.5	67.6
Ester moiety								
-1‴	168.9	168.9	168.9	169.1	168.9	168.9	168.9	169.0
-2‴	114.9	115.0	115.1	114.9	114.8	114.8	114.8	114.9
-3‴	147.3	147.2	147.1	147.3	147.4	147.4	147.4	147.3
-4‴	127.7	127.8	127.8	127.8	127.8	127.8	127.8	127.8
-5‴	115.1	115.2	115.2	115.2	115.3	115.3	115.3	115.3
-6‴	149.7	149.7	149.7	149.6	149.7	149.7	149.6	149.6
-7‴	146.8	146.9	146.8	146.8	146.8	146.8	146.8	146.8
-8‴	116.6	116.6	116.6	116.5	116.5	116.5	116.5	116.5
-9‴	123.1	123.1	123.1	123.0	123.0	123.0	123.0	123.0

Measured in MeOH-d_4 solution at 35 °C. *a*) Interchangeable in each column. Glc: β-D-glucopyranosyl; Api: β-D-apiofuranosyl.

1‴ of (*E*)-caffeoyl group] and δ 4.27 (2H, s, H-5 of apiofuranose). On the basis of these results, β-D-glucopyranose and apiofuranose were attached to the C-2 position of the aglycone and the C-6 position of β-D-glucopyranose, respectively, and the (*E*)-caffeoyl group was bound to C-5 of apiofuranose.

On comparison of the ^{1}H- and ^{13}C-NMR spectral data of the sugar moiety of **22** with those of osmanthusides I and J,[20] the signals due to apiofuranose of **22** were in good agreement. Thus, this apiofuranose was deduced to have the β-D-configuration, and compound **22** was identified to be 2-[(5-*O*-(*E*)-caffeoyl)-β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl]oxybutane.

In the ^{13}C-NMR spectrum of **22** measured in pyridine-d_5 solution, glycosylation shifts were observed at C-1 (−2.0 ppm), C-2 (+8.9 ppm) and C-3 (−3.2 ppm) of the aglycone moiety. These $\Delta\delta_C$ values suggested that the aglycone was 2-(*S*)-butanol.[18] Moreover, the ^{13}C-NMR spectral data of the aglycone of **22** were consistent with those of 2-(*S*)-(β-D-glucopyranosyl)oxybutane.[21] Based on these results, the structure of dracunculifoside F (**22**) was determined as shown in Chart 1.

The molecular formulae of dracunculifosides G—I (**23**—**25**) were considered to be $C_{23}H_{32}O_{13}$, $C_{27}H_{32}O_{13}$ and $C_{30}H_{36}O_{15}$ by the HR-FAB-MS spectra. Comparison of the ^{1}H- and ^{13}C-NMR spectral data of **23**—**25** with those of **22** indicated that the structures of the sugar and ester moieties were the same as those of **22**, but the aglycone moieties were different from those of **22**.

With regards to the aglycone moiety of compound **23**, ^{1}H- and ^{13}C-NMR spectra showed two methyl proton and carbon signals [δ 1.21 (3H, d, J=6.5 Hz), 1.17 (3H, d, J=6.5 Hz), δ 23.9, 22.2], and a set of carbinol proton and carbon signals [δ 3.98 (1H, m), δ 72.9]. As a result, the aglycone moiety of **23** was deduced to be 2-propanol, and this was confirmed by the ^{1}H–^{1}H COSY and HMQC experiments.

The ^{1}H- and ^{13}C-NMR spectra of compound **24** displayed A_2M_2X type-aromatic proton signals [δ 7.39 (2H, br d, J=8.0 Hz), 7.30 (2H, br t, J=8.0 Hz), 7.23 (1H, br t, J=8.0 Hz)], two carbinol proton signals [δ 4.87 (1H, d, J=12.0 Hz), 4.64 (1H, d, J=12.0 Hz)], aromatic carbon signals (δ 139.0, 129.3×4, 128.7) and one carbinol carbon signal (δ 71.9) in addition to the signals due to the sugar and ester moieties. This data led us to conclude that the aglycone moiety of **24** was benzyl alcohol. This was confirmed by acid hydrolysis.

The aglycone of compound **25** was considered to be 4-(3,4-dihydroxyphenyl)butan-2-one based on the similarity of the ^{13}C-NMR spectrum of **25** to that for myzodendrone (**11**).[11] Mild acid hydrolysis of **25** afforded **11**, confirming the above presumption.

Therefore, the structures of dracunculifosides G—I (**23**—**25**) were identified as shown in Chart 1. The glycosidic link-

Table 3. ^{1}H-NMR Spectral Data of Compounds **18**—**25**

Proton No.	**18**	**19**	**20**	**21**
Aglycone moiety				
H-1	—	—	—	3.54 (d, 5.0)
-2	7.49 (d, 2.0)	6.71 (d, 2.0)	6.99 (d, 2.0)	3.89 (m)
-3	—	—	—	1.20 (d, 6.5)
	—	—	—	—
-4	—	—	—	—
-5	7.19 (d, 8.0)	7.04 (d, 8.0)	7.02 (d, 8.0)	—
-6	7.46 (dd, 8.0, 2.0)	6.53 (dd, 8.0, 2.0)	6.78 (br d, 8.0)	—
-7	—	2.73 (t, 7.5)	6.40 (d, 16.0)	—
	—	—	—	—
-8	—	2.47 (t, 7.5)	5.99 (dt, 16.0, 6.0)	—
-9	—	—	4.00 (d, 6.0)	—
-10	—	—	—	—
-OMe	—	—	3.85 (s)	—
-OMe′	—	—	3.35 (s)	—
Sugar moiety				
Glc-1′	4.93 (d, 8.0)	4.70 (d, 8.0)	4.86 (d, 8.0)	4.40 (d, 8.0)
-2′	3.57 (t, 8.0)	3.50[a)]	3.53 (t, 8.0)	3.22 (t, 8.0)
-3′	3.53 (t, 8.0)	3.50[a)]	3.49 (t, 8.0)	3.40 (t, 8.0)
-4′	3.44 (t, 8.0)	3.41 (t, 8.0)	3.39[a)]	3.35 (t, 8.0)
-5′	3.76 (m)	3.67 (m)	3.69 (m)	3.56[a)]
-6′	4.58 (dd, 12.0, 2.0)	4.55 (dd, 12.0, 2.0)	4.51 (dd, 12.0, 2.5)	4.55 (dd, 12.0, 2.0)
	4.35 (dd, 12.0, 5.5)	4.37 (dd, 12.0, 6.5)	4.38 (dd, 12.0, 7.5)	4.28 (dd, 12.0, 5.0)
Api-1″	—	—	—	—
-2″	—	—	—	—
-4″	—	—	—	—
	—	—	—	—
-5″	—	—	—	—
	—	—	—	—
Ester moiety				
-2‴	6.29 (d, 16.0)	6.30 (d, 16.0)	6.25 (d, 16.0)	6.28 (d, 16.0)
-3‴	7.58 (d, 16.0)	7.59 (d, 16.0)	7.53 (d, 16.0)	7.58 (d, 16.0)
-5‴	7.06 (d, 2.0)	7.07 (d, 2.0)	7.05 (d, 2.0)	7.05 (d, 2.0)
-8‴	6.79 (d, 8.0)	6.81 (d, 8.0)	6.80 (d, 8.0)	6.78 (d, 8.0)
-9‴	6.95 (dd, 8.0, 2.0)	6.97 (dd, 8.0, 2.0)	6.94 (dd, 8.0, 2.0)	6.95 (dd, 8.0, 2.0)

ages of each compound were confirmed by NOE difference experiments involving irradiation of the anomeric proton signals.

Dracunculifoside J (**26**) had the molecular formula, $C_{19}H_{24}O_{10}$ by a HR-FAB-MS [positive HR-FAB-MS ion at *m*/*z* 412.1357 $[M]^+$]. The ^{13}C-NMR spectrum of **26** showed aromatic carbon signals (δ 158.7, 153.3, 139.6, 121.0, 115.8, 110.8), two sp^2 carbon signals (δ 144.1, 114.6), three carbinol carbon signals (δ 92.3, 77.3, 70.3) and signals due to an acetyl group (δ 205.9, 27.3), in addition to the signals for β-D-glucopyranose. In the ^{1}H-NMR spectrum, two aromatic proton signals [δ 7.29 (1H, s), 6.94 (1H, s)], an acetyl methyl signal [δ 2.61 (3H, s)], an *exo*-methylene proton signal [δ 5.29 (2H, overlapping with other signals)] and four carbinol proton signals [δ 5.30 (1H, overlapping), 4.99 (1H, d, J=5.0 Hz), 4.48 (1H, d, J=12.5 Hz), 4.30 (1H, d, J=12.5 Hz)] were present along with signals due to β-D-glucopyranose. Based on the ^{1}H-, ^{13}C- and two-dimensional (2D)-NMR (HMQC, HMBC, ^{1}H–^{1}H COSY) spectra and comparison of the NMR spectral data with those of toxol derivatives,[22)] the aglycone of dracunculifoside J (**26**) consisted of benzofuran, –C(CH_2)–CH_2–OH, one acetyl and two hydroxyl groups.

In the HMBC experiment for **26**, long-range correlations were observed as follows; δ 92.3 (C-2)/δ 5.29 (2H, overlapping, H-11), 4.48 (1H, d, J=12.5 Hz, H-12), 4.30 (1H, d, J=12.5 Hz, H-12) and δ 4.99 (1H, d, J=5.0 Hz, H-2)/δ 144.1 (C-10), 114.6 (C-11), 70.3 (C-12). Thus, the –C(CH_2)–CH_2–OH group was suggested to be bound to the C-2 position. Similarly, observation of long-range correlation between δ 77.3 (C-3) and δ 6.94 (1H, s) indicated it was possible to assign the signal at δ 6.94 (1H, s) to H-4 of the aromatic ring, and the remaining aromatic proton signal at δ 7.29 (1H, s) belonged to the H-7 position. In the NOE difference experiment, irradiation of the acetyl methyl signal [δ 2.61 (3H, s)] showed an NOE to the H-7 signal [δ 7.29 (1H, s)]. This suggested that the acetyl group was attached to the C-6 position. Moreover, in the NOE difference spectrum irradiating the anomeric proton signal of the β-D-glucopyranose [δ 4.31 (1H, d, J=8.0 Hz)] showed an NOE to the H-12 signal [δ 4.48 (1H, d, J=12.5 Hz)]. On the basis of the above evidence, the structure of dracunculifoside J (**26**) was elucidated as shown in Chart 1. The J value of the H-2 signal indicated the *cis*-form of C-2 and C-3,[22a)] but the absolute configuration of this position remains to be determined.

Experimental

General Procedure Instrumental analyses were carried out as described previously.[23)]

Extraction and Isolation The aerial part of *Baccharis dracunculifolia* DC. (644 g) was extracted three times with MeOH under reflux. The extract was concentrated under reduced pressure and the residue was suspended in H_2O. This suspension was extracted with Et_2O. The H_2O layer was passed through a Mitsubishi Diaion HP-20 column and adsorbed material was eluted with 50% MeOH in water, 70% MeOH in water and MeOH. The 50% MeOH fraction from the HP-20 column was concentrated, and the residue

Table 3. (continued)

Proton No.	**22**	**23**	**24**	**25**
Aglycone moiety				
H-1	1.20 (d, 6.5)	1.17 (d, 6.5)[b]	—	—
-2	3.70 (m)	3.98 (m)	7.39 (br d, 8.0)	7.02 (s)
-3	1.58 (m)	1.21 (d, 6.5)[b]	7.30 (br t, 8.0)	—
	1.45 (m)	—	—	—
-4	0.91 (t, 7.5)	—	7.23 (br t, 8.0)	—
-5	—	—	7.30 (br t, 8.0)	6.73 (br s)
-6	—	—	7.39 (br d, 8.0)	6.73 (br s)
-7	—	—	4.87 (d, 12.0)	2.74[a]
	—	—	4.64 (d, 12.0)	—
-8	—	—	—	2.74[a]
-9	—	—	—	—
-10	—	—	—	2.10 (s)
-OMe	—	—	—	—
-OMe′	-—	—	—	—
Sugar moiety				
Glc-1′	4.30 (d, 8.0)	4.31 (d, 8.0)	4.34 (d, 8.0)	4.68 (d, 8.0)
-2′	3.16 (t, 8.0)	3.14 (t, 8.0)	3.26 (t, 8.0)	3.47[a]
-3′	3.34[a]	3.35[a]	3.35[a]	3.48[a]
-4′	3.25 (t, 8.0)	3.25 (t, 8.0)	3.29[a]	3.37[a]
-5′	3.40 (m)	3.40 (m)	3.42 (m)	3.57 (m)
-6′	3.99 (dd, 11.5, 2.0)	3.99 (dd, 12.0, 2.0)	4.03 (dd, 12.0, 2.0)	4.07 (dd, 11.5, 1.5)
	3.60 (dd, 11.5, 6.0)	3.61 (dd, 12.0, 5.5)	3.65 (dd, 12.0, 5.5)	3.65 (dd, 11.5, 6.0)
Api-1″	5.03 (d, 2.0)	5.03 (d, 2.0)	5.08 (d, 2.0)	5.03 (d, 2.0)
-2″	3.93 (d, 2.0)	3.94 (d, 2.0)	3.98 (d, 2.0)	3.97 (d, 2.0)
-4″	4.03 (d, 10.0)	4.04 (d, 10.0)	4.06 (d, 10.0)	4.03 (d, 10.0)
	3.85 (d, 10.0)	3.85 (d, 10.0)	3.86 (d, 10.0)	3.84 (d, 10.0)
-5″	4.27 (s)	4.25 (s)	4.29 (s)	4.27 (d, 12.0)
	—	—	—	4.26 (d, 12.0)
Ester moiety				
-2‴	6.29 (d, 16.0)	6.29 (d, 16.0)	6.28 (d, 16.0)	6.28 (d, 16.0)
-3‴	7.59 (d, 16.0)	7.69 (d, 16.0)	7.57 (d, 16.0)	7.57 (d, 16.0)
-5‴	7.06 (br s)	7.06 (d, 2.0)	7.03 (br s)	7.04 (d, 2.0)
-8‴	6.78 (d, 8.0)	6.79 (d, 8.0)	6.78 (d, 8.0)	6.77 (d, 8.0)
-9‴	6.96 (br d, 8.0)	6.96 (dd, 8.0, 2.0)	6.93 (br d, 8.0)	6.93 (dd, 8.0, 2.0)

Measured in MeOH-d_4 solution at 35 °C. *a*) Overlapping with other signals. *b*) Interchangeable in each column. Glc: β-D-glucopyranosyl; Api: β-D-apiofranosyl.

rechromatographed on a silica gel column with a $CHCl_3$–MeOH–EtOAc–H_2O system and semi-preparative HPLC (Develosil-ODS-15/30 and -ODS-T-5: 10—23 % MeCN in water, 10—22.5% MeCN in water+2% AcOH, 35—40% MeOH in water and 35—40% MeOH in water+2% AcOH) to give compounds **1** (20 mg), **2** (41 mg), **3** (4 mg), **4** (74 mg), **5** (37 mg), **6** (6 mg), **7** (4 mg), **8** (4 mg), **9** (4 mg), **10** (9 mg), **11** (34 mg), **12** (3 mg), **13** (5 mg), **14** (12 mg), **15** (12 mg), **16** (6 mg), **17** (75 mg), **18** (4 mg), **19** (6 mg), **20** (7 mg), **21** (7 mg), **22** (15 mg), **23** (5 mg), **24** (23 mg), **25** (6 mg) and **26** (9 mg).

Dracunculifoside A (**17**): Amorphous powder. $[\alpha]_D^{26}$ −24.4° (c=0.75, MeOH). UV λ_{max}^{MeOH} nm (log ε): 201 (4.15), 218 (4.05), 245 (3.91), 303 (sh), 329 (4.15). FAB-MS *m/z*: 553 $[M+H]^+$, 575 $[M+Na]^+$. HR-FAB-MS *m/z*: 553.2638 (Calcd for $C_{28}H_{41}O_{11}$: 553.2649), 575.2489 (Calcd for $C_{28}H_{40}O_{11}Na$: 575.2468). ^{13}C- and ^1H-NMR: shown in Table 1.

Dracunculifoside B (**18**): Amorphous powder. $[\alpha]_D^{26}$ −72.9° (c=0.40, MeOH). UV λ_{max}^{MeOH} nm (log ε): 202 (4.58), 204 (4.59), 214 (sh), 246 (4.24), 295 (4.16), 331 (4.20). FAB-MS *m/z*: 501 $[M+Na]^+$. HR-FAB-MS *m/z*: 501.1036 (Calcd for $C_{22}H_{22}O_{12}Na$: 501.1009). ^{13}C- and ^1H-NMR: shown in Tables 2 and 3.

Dracunculifoside C (**19**): Amorphous powder. $[\alpha]_D^{25}$ −58.9° (c=0.59, MeOH). UV λ_{max}^{MeOH} nm (log ε): 203 (4.82), 218 (4.29), 247 (sh), 287 (sh), 301 (4.11), 329 (4.20). FAB-MS *m/z*: 529 $[M+Na]^+$. HR-FAB-MS *m/z*: 529.1334 (Calcd for $C_{24}H_{26}O_{12}Na$: 529.1322). ^{13}C- and ^1H-NMR: shown in Tables 2 and 3.

Dracunculifoside D (**20**): Amorphous powder. $[\alpha]_D^{26}$ −6.7° (c=0.36., MeOH). UV λ_{max}^{MeOH} nm (log ε): 203 (4.53), 214 (sh), 252 (4.28), 265 (sh), 297 (4.19), 330 (4.19). FAB-MS *m/z*: 541 $[M+Na]^+$. HR-FAB-MS *m/z*: 541.1683 (Calcd for $C_{26}H_{30}O_{11}Na$: 541.1686). ^{13}C- and ^1H-NMR: shown in Tables 2 and 3.

Dracunculifoside E (**21**): Amorphous powder. $[\alpha]_D^{26}$ −19.9° (c=0.68, MeOH). UV λ_{max}^{MeOH} nm (log ε): 203 (4.07), 219 (4.11), 244 (3.97), 302 (sh), 329 (4.21). FAB-MS *m/z*: 423 $[M+Na]^+$. HR-FAB-MS *m/z*: 423.1287 (Calcd for $C_{18}H_{24}O_{10}Na$: 423.1267). ^{13}C- and ^1H-NMR: shown in Tables 2 and 3. ^{13}C-NMR (pyridine-d_5 at 30 °C): δ 167.6 (C-1‴), 150.5 (C-6‴), 147.7 (C-7‴), 146.1 (C-3‴), 127.0 (C-4‴), 122.0 (C-9‴), 116.7 (C-8‴), 115.9 (C-5‴), 114.9 (C-2‴), 103.7 (C-1′), 78.3 (C-3′), 77.9 (C-2), 75.5 (C-5′), 74.9 (C-2′), 71.7 (C-4′), 66.8 (C-1), 64.5 (C-6′), 17.6 (C-3); (D_2O at 35 °C): d 169.8 (C-1‴), 147.9 (C-6‴), 147.0 (C-3‴), 145.0 (C-7‴), 127.6 (C-4‴), 123.4 (C-9‴), 116.9 (C-8‴), 115.9 (C-5‴), 114.8 (C-2‴), 101.5 (C-1′), 77.5 (C-3′), 76.4 (C-2), 73.8 (C-5′), 74.2 (C-2′), 70.6 (C-4′), 65.9 (C-1), 64.0 (C-6′), 16.2 (C-3). (The signal of dioxane at δ 67.3 was used as the internal standard in D_2O solution.)

Dracunculifoside F (**22**): Amorphous powder. $[\alpha]_D^{26}$ −41.9° (c=0.95, MeOH). UV λ_{max}^{MeOH} nm (log ε): 202 (4.36), 219 (4.18), 244 (sh), 305 (sh), 331 (4.18). FAB-MS *m/z*: 553 $[M+Na]^+$. HR-FAB-MS *m/z*: 553.1927 (Calcd for $C_{24}H_{34}O_{13}Na$: 553.1897). ^{13}C- and ^1H-NMR: shown in Tables 2 and 3. ^{13}C-NMR (pyridine-d_5 at 30 °C): δ 167.4 (C-1‴), 147.7 (C-7‴), 146.1 (C-3‴), 126.9 (C-4‴), 122.1 (C-9‴), 116.7 (C-8‴), 115.9 (C-5‴), 114.7 (C-2‴), 110.7 (C-1″), 104.2 (C-1′), 78.6×2 (C-3′, 3″), 78.2 (C-2″), 77.3 (C-2), 77.0 (C-5′), 75.4 (C-2′), 74.9 (C-4″), 72.0 (C-4′), 69.0 (C-6′), 67.4 (C-5″), 29.7 (C-3), 21.7 (C-1), 9.8 (C-4), (C-6‴ signal was overlapping with pyridine-d_5 signals); (D_2O at 35 °C): δ 169.7 (C-1‴), 148.0 (C-6‴), 147.2 (C-3‴), 145.1 (C-7‴), 127.6 (C-4‴), 123.5 (C-9‴), 117.0 (C-8‴), 115.9 (C-5‴), 114.8 (C-2‴), 109.6 (C-1″), 102.3 (C-1′), 79.8 (C-2), 78.6 (C-3″),77.5 (C-3′), 76.6 (C-2″),75.4 (C-5′), 74.2 (C-2′), 74.0 (C-4″), 70.8 (C-4′), 68.5 (C-6′), 66.7 (C-5″), 29.2 (C-3), 20.8 (C-1), 9.5 (C-4). (The signal of dioxane at δ 67.3 was used as the internal standard in D_2O solution.)

Dracunculifoside G (**23**): Amorphous powder. $[\alpha]_D^{26}$ −51.8° (c=0.46, MeOH). UV λ_{max}^{MeOH} nm (log ε): 218 (4.10), 245 (3.96), 302 (4.08), 330 (4.21). FAB-MS *m/z*: 539 $[M+Na]^+$. HR-FAB-MS *m/z*: 539.1762 (Calcd for $C_{23}H_{32}O_{13}Na$: 539.1741). ^{13}C- and ^1H-NMR: shown in Tables 2 and 3.

Dracunculifoside H (**24**): Amorphous powder. $[\alpha]_D^{26}$ −64.0° (c=0.84, MeOH). UV λ_{max}^{MeOH} nm (log ε): 208 (4.26), 245 (4.02), 301 (4.12), 330

Table 4. ^{13}C- and ^{1}H-NMR Spectral Data of Compound **26**

	C	H
Aglycone moiety		
-2	92.3	4.99 (d, 5.0)
-3	77.3	5.30[b]
-4	115.8	6.94 (s)
-5	158.7	-
-6	121.0	-
-7	110.8	7.29 (s)
-8	153.3	-
-9	139.6	-
-10	144.1	-
-11	114.6	5.29[b]
-12	70.3	4.48 (d, 12.5)
		4.30 (d, 12.5)
-13	205.9	-
-14	27.3	2.61 (s)
Sugar moiety		
Glc-1′	103.7	4.31 (d, 8.0)
-2′	75.1	3.22 (t, 8.0)
-3′	78.1[a]	3.35[b]
-4′	71.7	3.28[b]
-5′	78.0[a]	3.27[b]
-6′	62.8	3.87 (dd, 12.0, 2.0)
		3.67 (dd, 12.0, 5.0)

Measured in MeOH-d_4 solution at 35°C. *a*) Interchangeable in each column. *b*) Overlapping with other signals.

(4.24). FAB-MS *m/z*: 587 $[M+Na]^+$. HR-FAB-MS *m/z*: 587.1750 (Calcd for $C_{27}H_{32}O_{13}Na$: 587.1741). ^{13}C- and ^{1}H -NMR: shown in Tables 2 and 3.

Dracunculifoside I (**25**): Amorphous powder. $[\alpha]_D^{26}$ −77.6° (*c*=0.59, MeOH). UV λ_{max}^{MeOH} nm (log ε): 202 (4.60), 218 (4.37), 243 (4.08), 289 (4.14), 304 (4.18), 329 (4.30). FAB-MS *m/z*: 659 $[M+Na]^+$. HR-FAB-MS *m/z*: 659.1938 (Calcd for $C_{30}H_{36}O_{15}Na$: 659.1952). ^{13}C- and ^{1}H-NMR: shown in Tables 2 and 3.

Dracunculifoside J (**26**): Amorphous powder. $[\alpha]_D^{26}$ −18.8° (*c*=0.86, MeOH). UV λ_{max}^{MeOH} nm (log ε): 202 (4.17), 212 (4.19), 231 (4.27), 260 (3.89), 368 (3.72). FAB-MS *m/z*: 412 $[M]^+$, 435 $[M+Na]^+$. HR-FAB-MS *m/z*: 412.1357 (Calcd for $C_{19}H_{24}O_{10}$: 412.1369). ^{13}C- and ^{1}H-NMR: shown in Table 4.

Mild Alkaline Hydrolysis of Compound 17 Compound **17** (10 mg) in 0.1% NaOH (1 ml) was treated for 6 h at room temperature with stirring under a N_2 gas atmosphere. The reaction mixture was passed through an Amberlite IR-120B column and the eluate was concentrated to dryness. The residue was partitioned between EtOAc and H_2O. Both layers were concentrated to dryness, and HPLC analysis of the residue from the EtOAc layer suggested that (*E*)-caffeic acid was produced from **17**. Conditions: column; YMC-ODS 4.6 mm×25 cm. flow rate; 1.0 ml/min. 15% MeCN+0.05% trifluoroacetic acid (TFA); t_R, (*E*)-caffeic acid 11.8 min. Purification of the residue from the H_2O layer by HPLC (YMC-ODS 20 mm×25 cm, 37.5% MeOH in water) afforded alangionoside A (**17a**, 1 mg) which was identified by comparison of the ^{13}C-NMR spectral data and the optical rotation value with the reported ones.[17]

Acid Hydrolysis of Compounds 20 and 21 Compounds **20** and **21** (*ca.* 1 mg) were refluxed in AcCl–MeOH (1 : 10) (1 ml) for 5 h and 6.5 h, respectively. After being neutralized with Ag_2CO_3, the reaction mixture was taken to dryness. Gas chromatography (GC) analysis detected propylene glycol from the residue of compound **21**. CG conditions: column; GL capillary col-

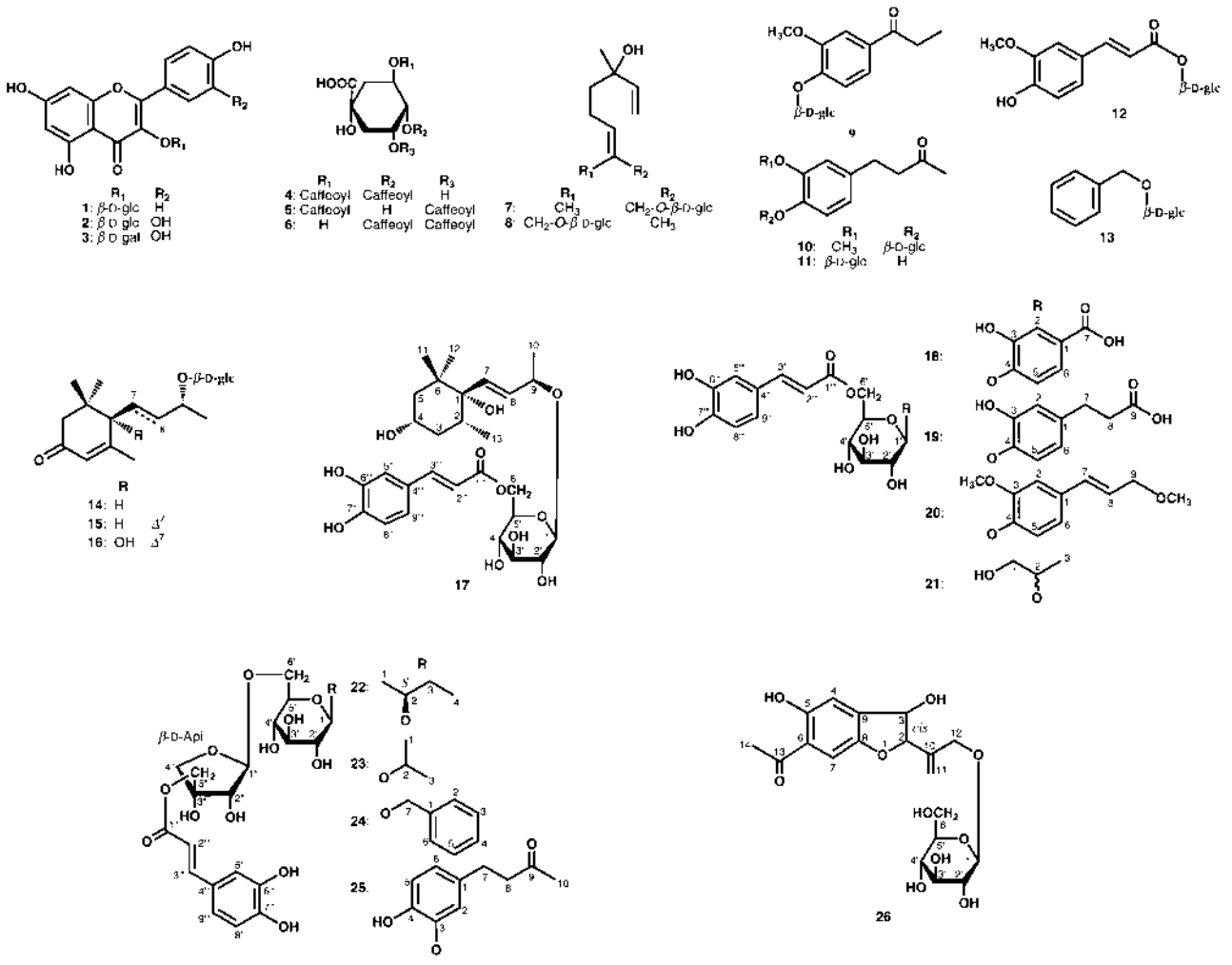

Chart 1

umn TC-1 (GL Science, Inc.) 0.25 mm×30 m, carrier gas N_2, column temperature 70 °C; t_R propylene glycol 3.3 min. The residues of **20** and **21** were partitioned between EtOAc and H_2O. The EtOAc layer was concentrated to dryness and HPLC used to analyze the residue with an authentic sample. HPLC conditions: column; YMC-ODS 4.6 mm×25 cm. flow rate; 1.0 ml/min. 30% MeCN; t_R methyl caffeate 9.8 min. The H_2O layer was also concentrated to dryness and each residue in 5% H_2SO_4 (5 drops) was heated at 100 °C for 1 h. The solution was passed through an Amberlite IRA-60E column. The eluate was concentrated to dryness and the residue was stirred with D-cysteine methyl ester hydrochloride, hexamethyldisilazane and trimethylsilylchloride in pyridine using the same procedur as in previous reports.[24,25] After the reactions, the supernatant was subjected to GC analysis. GC conditions: column; GL capillary column TC-1 (GL Science, Inc.) 0.25 mm×30 m, carrier gas N_2, column temperature 230 °C; t_R D-glucose 21.0 min, L-glucose 20.2 min. D-Glucose was detected from compounds **20** and **21**.

Alkaline and Acid Hydrolysis of Compounds 18, 19, 22—25 Compounds **18**, **19**, **22**—**25** (*ca*. 2 mg) were dissolved in 0.1% NaOH, and stirred for 2 to 6 h at room temperature under a N_2 gas atmosphere. The procedures after hydrolysis were carried out as described above. (*E*)-Caffeic acid was detected from the residue of the EtOAc layer of each compound by HPLC analysis under the same conditions.

The residues of the H_2O layers from compounds **18** and **19** were dissolved in dioxane and 0.05 N HCl (50 μl each) and heated at 95 °C for 1.5 h. After hydrolysis, H_2O and EtOAc were added to the reaction mixture, and the EtOAc layer was subjected to HPLC analysis. Protocatechuic acid and dihydrocaffeic acid were detected from compounds **18** and **19**, respectively. HPLC conditions: column; YMC-ODS 4.6 mm×25 cm, flow rate; 1.0 ml/min. 12.5% MeCN+0.05% TFA; t_R protocatechuic acid (3,4-dihydroxybenzoic acid) 8.4 min, 15% MeCN+0.05% TFA; t_R dihydrocaffeic acid (3-(3,4-dihydroxyphenyl)-propanoic acid) 9.6 min.

The H_2O layer was neutralized with an Amberlite IRA-60E column and the eluate was concentrated to dryness. The residue with D-cysteine methyl ester hydrochloride, hexamethyldisilazane and trimethylsilylchloride succeeded in the same manner. GC analysis was carried out under the same conditions described above. D-Glucose was detected from compounds **18** and **19**.

The residues of the H_2O layers from compounds **22**—**25** were divided into two parts, which were dissolved in dioxane and 2 N HCl (30 μl each). One was heated at 100 °C for 1 h, and the reaction mixture passed through an Amberlite IRA-60E column. The eluate was concentrated to dryness and the residue was partitioned between EtOAc and H_2O. By HPLC analysis, benzyl alcohol was detected from the EtOAc layer of compound **24**. Conditions: column; YMC-ODS 4.6 mm×25 cm. flow rate; 1.0 ml/min. 30% MeCN; t_R, benzyl alcohol 7.4 min. From the H_2O layer of each compound, D-glucose was observed by the same procedures mentioned above.

The remaining residue was dissolved in dioxane and 2 N HCl and was heated at 100 °C for 5 min. The procedures following hydrolysis were the same as described above, and HPLC analysis detected myzodendrone (**11**) from compound **25**. Conditions: column; YMC-ODS 4.6 mm×25 cm, flow rate; 1.0 ml/min. 12.5% MeCN+0.05% TFA; t_R myzodendrone 16.6 min. Subsequently, the H_2O layer was reduced with $NaBH_4$ (*ca*. 1 mg) for 1 h at room temperature. The reaction mixture was passed through an Amberlite IR-120B column and the eluate was concentrated to dryness. Boric acid was removed by co-distillation with MeOH, and the residue was acetylated overnight with acetic anhydride and pyridine (5 drops each) at room temperature. After evaporation of the reagents under a stream of air, apiitol acetate was detected by GC analysis. GC conditions: column; Supelco SP-2380TM capillary column 0.25 mm×30 m, carrier gas N_2, column temperature 250 °C; t_R apiitol acetate 8.9 min

Acid Hydrolysis of Compound 26 Compound **26** (*ca*. 1 mg) in 5% H_2SO_4 (5 drops) was heated at 100 °C for 1 h. The procedures to analyze the sugar moiety were the same as described above. D-Glucose was detected from compound **26**.

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