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Benzyl Benzoate Glycoside and 3-Deoxy-D-manno-2-octulosonic Acid Derivatives from *Solidago decurrens*

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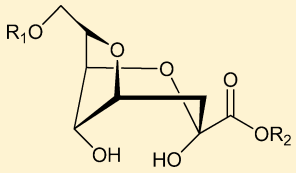
ABSTRACT: A new benzyl benzoate glycoside and five new 3-deoxy-D-manno-2-octulosonic acid derivatives were isolated from the entire plant of *Solidago decurrens* together with three known compounds. Their structures were established by extensive analyses of their 1D and 2D NMR spectra and by comparison with physical data of known compounds.



5 R_1=(*E*)-cinnamoyl, R_2=Butyl
6 R_1=(*E*)-cinnamoyl, R_2=CH_3
7 R_1=(*Z*)-cinnamoyl, R_2=CH_3
8 R_1=benzoyl, R_2=CH_3
9 R_1=benzoyl, R_2=Butyl

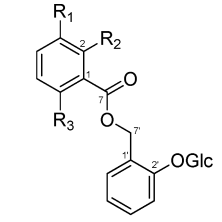
Solidago decurrens Lour. belongs to the genus *Solidago* (Compositae). This genus comprises about 120 species, of which *S. decurrens*, *S. dahurica*, *S. pacifica*, *S. rugosa*, *S. canadensis*, and *S. altissima* are distributed in China. It has been reported that *Solidago* plants have good diuretic, choleretic, antiseptic, and wound-healing activities if used as traditional Chinese medicines. Leiocarposide, *β*-sitosterol, caffeic acid, and chlorogenic acid have been isolated from *S. decurrens*.[1]

In the present study, we describe the isolation and structure determination of six new chemical constituents from *S. decurrens*, i.e., a new benzyl benzoate glycoside, an isomer of leiocarposide, and five new 3-deoxy-D-manno-2-octulosonic acid (KDO) derivatives.

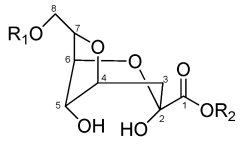
RESULTS AND DISCUSSION

Solidago species have been known to contain several types of benzyl benzoate derivatives such as leiocarposide (**1**).[1,2] The MeOH extract of the entire plant of *S. decurrens* was subjected to a combination of Diaion HP20SS, Sephadex LH-20, and Cosmosil 75C_{18}-OPN column chromatography to obtain leiocarposide (**1**), known benzyl benzoates (**3**, **4**), a new benzyl benzoate derivative (**2**), and five new KDO derivatives (**5**–**9**). The structures of the known compounds (**1**, **3**, **4**) were determined by comparing their physical data with reported data.[3−5] The structures of new compounds (**2**, **5**–**9**) were established by analyses of their 1D and 2D NMR spectra and by comparison with spectroscopic data of known compounds.

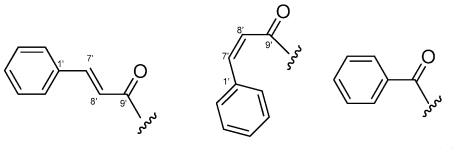
Compound **2** was obtained as a colorless powder. Its molecular formula was determined to be $C_{27}H_{34}O_{16}$, the same as that of leiocarposide (**1**), according to the $[M + H]^+$ ion at *m*/*z* 615.1951 in the HRFABMS together with ^{13}C NMR data. The IR spectrum showed the absorption bands due to hydroxy (3423 cm^{-1}) and carbonyl (1700 cm^{-1}) groups. The ^1H and ^{13}C NMR spectra of compound **2** in methanol-d_4 were similar to those of **1** including sugar moieties, except for the signals of the benzoyl part. The NOESY data of compound **2** in DMSO-d_6 showed the correlations between 3-OH and 4-H, 3-OH and 2-OCH_3, H-4 and H-5, and H-5 and an anomeric proton of glucose moiety attached to C-6, respectively (Figure 2).



1 R_1=OGlc, R_2=OCH_3, R_3=OH
2 R_1=OH, R_2=OCH_3,R_3=OGlc
3 R_1=OGlc, R_2=OCH_3, R_3=OCH_3
4 R_1=H, R_2=OGlc, R_3=OCH_3



5 R_1=a, R_2=Butyl
6 R_1=a, R_2=CH_3
7 R_1=b, R_2=CH_3
8 R_1=c, R_2=CH_3
9 R_1=c, R_2=Butyl



(E)-cinnamoyl (a) (Z)-cinnamoyl (b) benzoyl (c)

Figure 1. Structures of compounds **1**–**9** from *Solidago decurrens*.

Therefore, the structure of compound **2** was elucidated as shown and named isoleiocarposide. The sugar of leiocarposide (**1**) was confirmed to be D-glucose by HPLC analyses of the thiocarbamoyl-thiazolidine derivative of the acid hydrolysis product according to our reported method.[6] Thus, the sugar moiety of **2** was identified as D-glucose by comparison of its 1D NMR data with those of the sugar moiety of leiocarposide (**1**).

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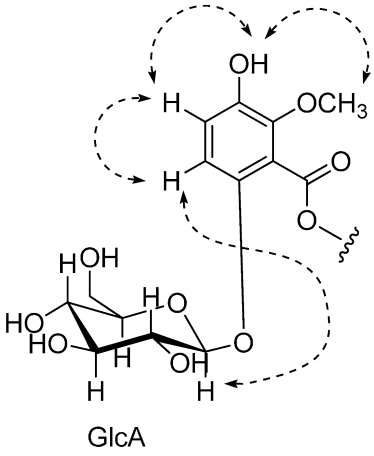

Figure 2. Key NOE correlations for **2** in DMSO-d_6.

Compound **5** was obtained as a colorless powder. The molecular formula was deduced to be $C_{21}H_{26}O_8$ by HRFABMS at m/z 407.1721 $[M + H]^+$ together with the ^{13}C NMR data. The IR spectrum showed the absorption bands due to hydroxy (3410 cm^{-1}) and carbonyl (1754, 1712 cm^{-1}) groups. The ^{13}C NMR spectrum showed 21 carbon signals, which were assignable to six aromatic carbons, two olefinic carbons, a methyl carbon, five methylene carbons, four methine carbons, and three quaternary carbons, two of which were ester carbonyl carbons. The presence of a cinnamoyl moiety in **5** was suggested by the ^1H NMR data. The ^1H NMR data showed the signals from the five aromatic protons around δ_H 7.38 (3H) and around δ_H 7.57 (2H), suggesting the presence of a monosubstituted benzene ring. Moreover, the presence of an *E* double bond was suggested by two olefinic proton signals at δ_H 6.53 (d, J = 16.0 Hz, H-8′) and 7.70 (d, J = 16.0 Hz, H-7′). In addition, the HMBC spectrum showed correlations between H-7′ and an ester carbonyl carbon C-9′ (δ_C 168.4) and between H-8′ and C-1′ (δ_C 135.7) and C-9′. The presence of a butoxy moiety was suggested by the correlations between H-4″ (δ_H 0.93, t, J = 7.5 Hz) and H-3″ (δ_H 1.39, sext, J = 7.5 Hz), H-3″ and H-2″ (δ_H 1.65, qui, J = 7.5 Hz), and H-2″ and oxygenated proton H-1″ (δ_H 4.19, t, J = 7.5 Hz) in the $^1H-^1H$ COSY spectrum (Figure 3).

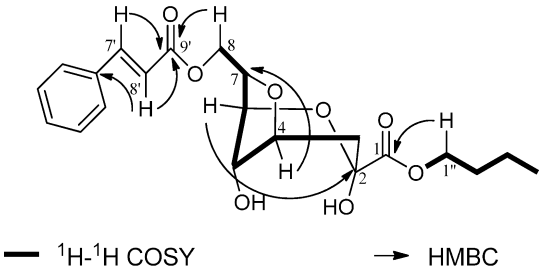

Figure 3. Key $^1H-^1H$ COSY and HMBC correlations for **5**.

Other than the two moieties mentioned above, the remaining ^1H and ^{13}C NMR signals indicated the existence of the KDO skeleton. Thus, the $^1H-^1H$ COSY spectrum showed correlations between H_2-3 (δ_H 2.25, dd, J = 15.5, 5.0 Hz and δ_H 2.31, dd, J = 15.5, 1.0 Hz) and H-4 (δ_H 4.16, br t, J = 5.0 Hz), H-4 and H-5 (δ_H 4.04, t, J = 5.0 Hz), H-5 and H-6 (δ_H 4.49, t, J = 5.0 Hz), H-6 and H-7 (δ_H 4.43, ddd, J = 8.5, 5.0, 2.5 Hz), and H-7 and H_2-8 (δ_H 4.79, dd, J = 12.5, 2.5 Hz and δ_H 5.01, dd, J = 12.5, 8.5 Hz), respectively. Together with the results stated above, the presence of the remaining two carbon signals (acetal carbon C-2 at δ_C 104.9 and ester carbonyl carbon C-1 at δ_C 169.2) confirmed a KDO structure. The molecular formula and degree of unsaturation suggested this KDO moiety had a bicyclic system. The HMBC correlation between H-4 and C-7 indicated that the ether bond was formed between C-4 and C-7 by dehydroxylation of the KDO skeleton. The cinnamoyl and butoxy substituents were attached to C-8 and C-1, respectively, as deduced by the HMBC correlations between H-1″ and C-1, and H-8 and C-9′, respectively. Finally, the NOESY spectrum of compound **5** was measured in DMSO-d_6 to determine the configurations at C-2 and C-5. A NOESY correlation was observed between 2-OH and 5-OH, which confirmed that the hydroxy groups at C-2 and C-5 were *endo* orientated (Figure 4). Therefore, the structure of compound **5**

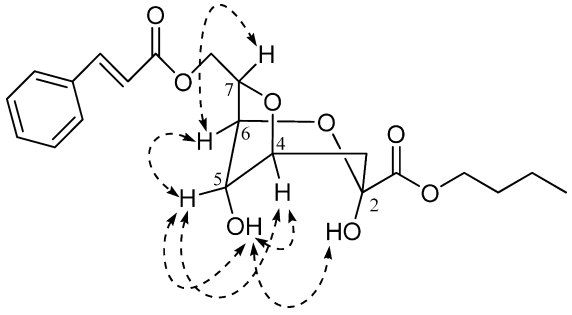

Figure 4. Key NOE correlations for **5** in DMSO-d_6.

was elucidated as shown and named decurrenside A. A literatures search on KDO-type compounds revealed that six compounds have been isolated from *Conyza canadensis*, *Smallamthus sonchifolius*, and *Erigeron breviscapus*.[7−9] This compound could be an artifact due to workup with *n*-butanol.

Compound **6** was obtained as a colorless gum. The molecular formula was assigned as $C_{18}H_{20}O_8$ by HRFABMS at m/z 365.1224 $[M + H]^+$ together with the ^{13}C NMR data. The IR spectrum showed the absorption bands due to hydroxy (3417 cm^{-1}) and carbonyl (1748, 1714 cm^{-1}) groups. The ^1H and ^{13}C NMR spectra of compound **6** were similar to those of compound **5** except for the butoxy moiety. The signals of the methoxy moiety appeared in the ^1H and ^{13}C NMR spectra of compound **6** instead of the signals of the butoxy moiety in compound **5**, indicating that compound **6** possessed a methoxy group at C-1. Just as in compound **5**, the cinnamoyl moiety had an *E* double bond. Accordingly, the structure of compound **6** was determined as shown in Figure 1 and named decurrenside B.

Compound **7** was obtained as a colorless gum. The molecular formula was determined to be $C_{18}H_{20}O_8$, the same as that of compound **6**, according to the $[M + H]^+$ ion at m/z 365.1241 in HRFABMS together with the ^{13}C NMR data. The IR spectrum showed the absorption bands due to hydroxy (3478 cm^{-1}) and carbonyl (1744, 1716 cm^{-1}) groups. The ^1H and ^{13}C NMR spectra of compound **7** were similar to those of compound **6** except for the olefinic moiety. Two olefinic proton signals at δ_H 5.98 (d, J = 12.8 Hz, H-8′) and 7.00 (d, J = 12.8 Hz, H-7′) of compound **7** indicated that **7** had a *Z* cinnamoyl substituent, instead of an *E* cinnamoyl moiety in **6**. Therefore, the structure of compound **7** was assigned as shown in Figure 1 and named decurrenside C.

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Compound **8** was obtained as a colorless gum. The molecular formula was deduced to be $C_{16}H_{18}O_8$ by HRFABMS at m/z 339.1090 $[M + H]^+$ together with the ^{13}C NMR data. The IR spectrum showed the absorption bands due to hydroxy (3487 cm^{-1}) and carbonyl (1750, 1716 cm^{-1}) groups. The ^1H and ^{13}C NMR spectra of compound **8** were similar to those of compounds **6** and **7**, except for the signals of the cinnamoyl moiety. The benzoyl moiety was observed instead of the cinnamoyl moiety in the NMR spectra of **6** and **7**. Therefore, the structure of compound **8** was elucidated as shown in Figure 1 and named decurrenside D.

Compound **9** was obtained as a colorless gum. The molecular formula was determined to be $C_{19}H_{24}O_8$ according to the $[M + H]^+$ ion at m/z 381.1563 in the HRFABMS together with the ^{13}C NMR data. The IR spectrum showed the absorption bands due to hydroxy (3474 cm^{-1}) and carbonyl (1751, 1715 cm^{-1}) groups. The ^1H and ^{13}C NMR spectra of compound **9** were similar to those of compound **8** except for the methoxy moiety. Instead of the methoxy signals in the ^1H and ^{13}C NMR spectra of compound **8**, the signals of a butoxy moiety appeared in the NMR spectrum of **9**. These indicated that compound **9** possessed a butoxy group at C-1. Therefore, the structure of compound **9** was elucidated as shown in Figure 1 and named decurrenside E. This compound, like **5**, could also be an artifact due to workup with *n*-butanol.

Compounds **5**–**9** possess a unique dioxabicyclo[3.2.1]octane skeleton. In one study, compounds having a similar skeleton were shown to have an inhibitory effect upon catecholamine secretion induced by acetylcholine, veratridine, and high $[K^+]$ in cultured bovine adrenal medullary cells.[7] We therefore believe that compounds **5**–**9** may inhibit catecholamine secretion.

EXPERIMENTAL SECTION

General Experimental Procedures. UV spectra were obtained using a Jasco V-560 ultraviolet (UV)/vis spectrophotometer (Jasco, Hachioji, Tokyo, Japan). Optical rotations were measured using a Jasco DIP-370 digital polarimeter. ^1H and ^{13}C NMR, ^1H–^1H COSY, NOESY, HSQC, and HMBC spectra were recorded in methanol-d_4 or DMSO-d_6 at room temperature with a Unity Plus 500 spectrometer (Varian, Palo Alto, CA, USA) operating at 500 MHz for ^1H and 125 MHz for ^{13}C. One-dimensional ^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-AL400 spectrometer (JEOL, Tokyo, Japan) operating at 400 MHz for ^1H and 100 MHz for ^{13}C. FAB-MS was recorded on a JMS 700N spectrometer (JEOL), and *m*-nitrobenzyl alcohol and glycerol were used as the matrix. Column chromatography was undertaken using Diaion HP20SS (Mitsubishi Chemical, Tokyo, Japan), Sephadex LH-20 (25–100 μm; GE Healthcare Bio-Science AB, Uppsala, Sweden), Cosmosil 75C_{18}-OPN (Nacalai Tesque, Inc., Kyoto, Japan), Chromatorex ODS (100–200 mesh; Fuji Silysia Chemical Ltd., Tokyo, Japan), and silica gel 60N (100–210 μm; Kanto Chemical Co., Inc., Tokyo, Japan) columns. TLC was carried out on precoated Kieselgel 60 F_{254} plates (thickness, 0.2 mm; Merck, Darmstadt, Germany). Spots were detected using UV illumination (254 nm) and by spraying plates with 2% ethanolic $FeCl_3$ or 5% H_2SO_4(aq) reagents followed by heating. Preparative HPLC was carried out on a Cosmosil 5C_{18}-AR-II (Nacalai Tesque) column (20 × 250 mm).

Plant Materials. The entire plant of *S. decurrens* was purchased in a Hong Kong (China) market as a crude drug in August 2007. It was identified by one of the authors (Z.H.J.). A voucher specimen (HKBU-0120) has been deposited in the herbarium of the School of Chinese Medicine, Hong Kong Baptist University, Hong Kong, China.

Extraction and Isolation. The entire plant of *S. decurrens* (1 kg) was extracted with 80% MeOH(aq) (6 L) three times at room temperature. The extract was concentrated *in vacuo* at 42 °C to give a brown gum (110 g). The residue was dissolved in purified H_2O (500 mL), then extracted with petroleum ether (500 mL) three times and concentrated to afford a H_2O layer and petroleum ether extract (2.72 g). The H_2O layer was extracted by EtOAc (500 mL) three times and concentrated to afford a H_2O layer and EtOAc extract (9.01 g). The H_2O layer was extracted successively with *n*-BuOH (500 mL) three times and concentrated to afford an *n*-BuOH (30 g) and H_2O extract (61.03 g).

The H_2O extract (61.03 g) was again suspended in H_2O and then partitioned with *n*-BuOH. This *n*-BuOH-soluble layer was concentrated to give an extract (16.9 g). The extract (16.9 g) was subjected to Sephadex LH-20 elution with MeOH/H_2O (50:50 → 100:0) to afford three fractions (Fr. 1–3). Fr. 2 (11.09 g) was subjected to Diaion HP20SS elution with MeOH/H_2O (0:100 → 100:0) to give eight fractions (Fr. 2.1–2.8). Fr. 2.4 (1.22 g) was subjected to Cosmosil 75 C_{18}-OPN elution with MeOH/H_2O (0:1 → 100:0) to give compound **2** (701 mg). Fr. 2.5 (869.8 mg) was subjected to Chromatorex ODS elution with MeOH/H_2O (0:100 → 100:0) to give compound **1** (611 mg). Fr. 2.6 (578.9 mg) was subjected to RP-HPLC elution with MeOH/H_2O (50:5 → 100:0) to give eight fractions (Fr. 2.6.1–2.6.8). Fr. 2.6.4 (62.8 mg) and Fr. 2.6.5 (23.6 mg) were subjected to RP-HPLC elution with MeOH/H_2O (90:10 → 100:0) to give compounds **3** (4.5 mg) and **4** (5.6 mg). Fr. 2.6.6 (71.2 mg) was subjected to RP-HPLC elution with MeOH/H_2O (60:40 → 100:0) to give compound **9** (2.1 mg). Fr. 2.6.8 was subjected to RP-HPLC elution with MeOH/H_2O (50:50 → 100:0) to give compound **8** (14.3 mg). Fr. 2.7 (490.8 mg) was subjected to RP-HPLC elution with MeOH/H_2O (50:50 → 100:0) to give compounds **6** (18.8 mg) and **7** (66.6 mg).

Table 1. ^1H and ^{13}C NMR Data of 2[a]

position	δ_H (J in Hz)	δ_C
1		122.1
2		146.2
3		147.1
4	6.86, d (9.0)	119.2
5	6.90, d (9.0)	114.5
6		148.4
7		168.1
1′		126.7
2′		156.8
3′	7.22, dd (8.0, 1.0)	116.6
4′	7.31, dt (8.0 7.5, 1.5)	130.7
5′	7.05, dt (8.0, 7.5, 0.1.0)	123.5
6′	7.49, dd (8.0, 1.5)	130.8
7′	5.50, d (12.5)	63.7
	5.53, d (12.5)	
2-OCH_3	3.74, s	61.9
6-OH		
Glucose A		
1	4.74, d (7.5)	104.2
2	3.31–3.35, m	74.8
3	3.40, dd (9.0, 4.0)	77.8
4	3.31–3.35, m	71.2
5	3.31–3.35, m	78.2
6	3.64, dd (12.0, 5.5)	62.6
	3.83, dd (12.0, 2.0)	
Glucose B		
1	4.95, d (8.0)	102.8
2	3.54, dd (9.0, 7.5)	74.9
3	3.47, t (9.0)	78.0
4	3.42–3.44, m	71.3
5	3.42–3.44, m	78.2
6	3.70, dd (12.0, 5.5)	62.5
	3.88, dd (12.0, 2.0)	

[a] ^1H (500 MHz) and ^{13}C (125 MHz) NMR data in methanol-d_4.

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Table 2. ^{1}H and ^{13}C NMR Data of 5−7

	5[a]		6[b]		7[b]	
position	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C
1		169.2		169.6		169.6
2		104.9		104.9		104.8
3	2.25, dd (15.5, 5.0)	40.4	2.25, dd (15.5, 5.0)	40.3	2.23, dd (15.5, 5.0)	40.3
	2.31, dd (15.5, 1.0)		2.31, dd (15.5, 1.0)		2.28, dd (15.5, 1.8)	
4	4.16, br t (5.0)	65.8	4.14, t (5.0)	65.8	4.12, t (4.4)	65.8
5	4.04, t (5.0)	69.5	4.02, t (5.0)	69.5	4.00, t (4.4)	69.4
6	4.49, t (5.0)	81.0	4.48, t (5.0)	81.0	4.41, t (4.4)	80.8
7	4,43, ddd (8.5, 5.0, 2.5)	78.3	4,42, ddd (8.4, 5.0, 3.2)	78.4	4,30, ddd (8.4, 4.4, 2.8)	78.3
8	4.79, dd (12.5, 2.5)	64.7	4.78, dd (12.4, 3.2)	64.7	4.67, dd (12.4, 2.8)	64.4
	5.01, dd (12.5, 8.5)		5.01, dd (12.4, 8.4)		4.96, dd (12.4, 8.4)	
1′		135.7		135.7		136.3
2′, 6′	7.38, m	130.0	7.40, m	130.0	7.31, m	130.0
4′	7.38, m	131.5	7.40, m	131.5	7.31, m	130.9
3′, 5′	7.57, m	129.2	7.61, m	129.2	7.57, m	129.0
7′	7.70, d (16.0)	146.4	7.72, d (16.0)	146.4	7.00, d (12.8)	144.4
8′	6.53, d (16.0)	118.7	6.56, d (16.0)	118.7	5.98, d (12.8)	120.3
9′		168.4		168.4		167.7
1″	4.19, t (7.5)	66.8	3.79, s	53.2	3.78, s	53.2
2″	1.65, qui (7.5)	31.5				
3″	1.39, sext (7.5)	20.0				
4″	0.93, t (7.5)	14.0				

[a] ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data in methanol-d_4. [b] ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data in methanol-d_4.

Table 3. ^{1}H and ^{13}C NMR Data of 8 and 9

	8[a]		9[b]	
position	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C
1		169.6		169.3
2		104.9		104.9
3	2.25, dd (14.8, 5.0)	40.4	2.17, dd (15.0, 5.0)	40.4
	2.31, dd (14.8, 1.8)		2.22, dd (15.0, 1.0)	
4	4.14, t (5.0)	65.8	4.07, t (4.0)	65.9
5	4.02, t (5.0)	69.5	3.95, t (4.0)	69.5
6	4.48, t (5.0)	78.4	4.42, t (4.0)	78.5
7	4,42, ddd (8.4, 5.0, 3.2)	81.0	4.37, ddd (8.0, 4.0, 3.2)	81.0
8	4.78, dd (12.4, 3.2)	65.1	4.82, dd (12.4, 3.2)	65.1
	5.01, dd (12.4, 8.4)		5.04, dd (12.4, 8.0)	
1′		131.4		131.4
2′, 6′	8.05, dd (7.5, 1.5)	130.6	7.96, dd (7.6, 1.6)	130.6
4′	7.60, t (7.5)	134.2	7.51, t (7.6)	134.3
3′, 5′	7.47, t (7.5)	129.5	7.38, t (7.6)	129.5
7′		167.9		168.0
1″	3.79, s	53.3	4.11, t (6.4)	66.8
2″			1.57, qui (7.2, 6.4)	31.6
3″			1.32, sext (7.2)	20.1
4″			0.84, t (7.2)	14.0

[a] ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data in methanol-d_4. [b] ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data in methanol-d_4.

The *n*-BuOH extract (30 g) was subjected to silica gel elution with $CHCl_3$/MeOH/H_2O (70:30:5) to give nine fractions (A–I). Fr. H (10.3 g) was subjected to Sephadex LH-20 elution with MeOH to give four fractions (Fr. H-1−4). Fr. H-4 was subjected to Sephadex LH-20 elution with MeOH to give two fractions (Fr. H-4.1−4.2). Fr. H-4.1 (434.2 mg) was subjected to silica gel elution with $CHCl_3$/MeOH (70:30 → 60:40 → 50:50) to give three fractions (Fr. H-4.1.1−4.1.3). Fr. H-4.1.1 (87.6 mg) was subjected to Cosmosil 75 C_{18}-OPN elution with MeOH/H_2O (40:60 → 50:50 → 60:40) to give five fractions (Fr. H-4.1.1.1−4.1.1.5). Fr. H-4.1.1.5 (81.7 mg) was subjected to RP-HPLC elution with MeOH/H_2O (65:35 → 85:15) to give compound **5** (17.6 mg).

Leiocarposide [3-β-D-glucopyranosyloxy-2-methoxy-6-hydroxybenzoic acid 2′-β-D-glucopyranosyloxy benzyl ester] (1): colorless powder; $[\alpha]^{28.5}_D$ −95.1 (*c* 0.2, MeOH); IR ν_{max} cm^{-1} 3400, 1700; UV λ_{max} (MeOH) nm (log ε) 276 (4.336), 216 (4.142); HRFABMS *m*/*z* 615.1951 (calcd for $C_{27}H_{35}O_{16}$, 615.1925); FABMS *m*/*z* 637[M + Na]$^+$, 615[M + H]$^+$; mp 187−189 °C (dec); ^{1}H NMR (500 MHz, methanol-d_4) δ 3.25−3.27 (2H, m, GlcA-4, 5), 3.30−3.31 (1H, m, GlcA-2), 3.33−3.35 (1H, m, GlcA-3), 3.38−3.40 (2H, m, GlcB-4, 5), 3.43 (1H, t, J = 8.8 Hz, GlcB-3), 3.50 (1H, t, J = 8.8, 7.6 Hz, GlcB-2), 3.61−3.66 (2H, m, GlcA, B-6), 3.74 (3H, s, 2-OCH$_3$), 3.76 (1H, dd, J = 12.4, 2 Hz, GlcA-6), 3.84 (1H, dd, J = 12.4, 2 Hz, GlcB-6), 4.74 (1H, d, J = 7.6 Hz, GlcA-1), 4.92 (1H, d, J = 7.6 Hz, GlcB-1), 5.45 (1H, d, J = 12.8 Hz, H-7′), 5.50 (1H, d, J = 12.8 Hz, H-7′), 6.56 (1H, d, J = 9.2 Hz, H-5), 7.01 (1H, dt, J = 7.6, 7.2, 1 Hz, H-5′), 7.19 (1H, dd, J = 7.6, 1 Hz, H-3′), 7.23 (1H, d, J = 9.2 Hz, H-4), 7.28 (1H, dt, J = 7.6, 7.2, 1.6 Hz, H-4′), 7.44 (1H, dd, J = 7.6, 1.6 Hz, H-6′); ^{13}C NMR (125 MHz, methanol-d_4) δ 62.8 (2-OCH$_3$), 62.4 (GlcB-6), 62.5 (GlcA-6), 63.8 (C-7′), 71.3 (GlcA-4, B-4), 74.9 (GlcB-2), 75.0 (GlcA-2), 77.9 (GlcB-3), 78.0 (GlcA-3), 78.1 (GlcB-5), 78,2 (GlcA-5), 102.6 (GlcB-1), 103.8 (GlcA-1), 112.7 (C-5), 114.6 (C-1), 116.6 (C-3′), 123.4 (C-5′), 124.3 (C-4), 126.6 (C-1′), 130.8 (C-4′, 6′), 144.7 (C-3), 150.5 (C-2), 154.7 (C-6), 156.9 (C-2′), 169.4 (C-7).

Isoleiocarposide [6-β-D-glucopyranosyloxy-2-methoxy-3-hydroxybenzoic acid 2′-β-D-glucopyranosyloxy benzyl ester] (2): colorless powder; $[\alpha]^{28.0}_D$ −40.5 (*c* 0.2, MeOH); IR ν_{max} cm^{-1} 3423, 1700; UV λ_{max} (MeOH) nm (log ε) 276 (4.336), 216 (4.142); HRFABMS *m*/*z* 615.1951 (calcd for $C_{27}H_{35}O_{16}$, 615.1925); FABMS *m*/*z* 637[M + Na]$^+$, 615[M + H]$^+$; mp 130−135 °C (dec); ^{1}H and ^{13}C NMR data (methanol-d_4) see Table 1; ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.12−3.18 (2H, m, GlcA-4, 5), 3.21−3.28 (2H, m, GlcA-2, 3), 3.30−3.36 (2H, m, GlcB-4, 5), 3.42−3.48 (2H, m, GlcB-2, 3), 3.64−3.68 (2H, m, GlcA, B-6), 3.69 (3H, s, 2-OCH$_3$), 4.75 (1H, d, J = 7.5 Hz, GlcA-1), 4.85 (1H, d, J = 7.5 Hz, GlcB-1), 5.34 (1H, d, J = 14.0 Hz, H-7′), 5.44 (1H, d, J = 14.0 Hz, H-7′), 6.80 (1H, d, J = 9.0 Hz, H-4), 6.85 (1H, d, J = 9.0 Hz, H-5), 7.02 (1H, dt, J = 8.0, 7.5, 1.0 Hz, H-5′), 7.12 (1H, dd, J = 8.0, 1.0 Hz, H-3′), 7.27 (1H, dt, J = 8.0, 7.5, 1.5 Hz, H-4′), 7.46 (1H, dd, J = 8.0, 1.5 Hz, H-6′), 9.38 (1H, s, 6-OH); ^{13}C NMR (125 MHz, DMSO-d_6) δ 60.7 (2-OCH$_3$, GlcA, B-6), 61.7

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(C-7′), 69.7 (GlcA, B-4), 73.3 (GlcA, B-2), 76.6 (GlcB-3), 76.8 (GlcA-3), 77.1 (GlcA, B-5), 100.9 (GlcB-1), 101.3 (GlcA-1), 111.5 (C-5), 114.6 (C-3′), 117.8 (C-4), 120.0 (C-1), 121.8 (C-5′), 125.1 (C-1′), 128.0 (C-4′), 128.9 (C-6′), 144.3 (C-2), 144.9 (C-3), 146.4 (C-6), 154.6 (C-2′), 165.2 (C-7).

Decurrenside A [(*E*)-butyl-7-{(cinnamoyloxy)methyl}-3,8-dihydroxy-2,6- dioxabicyclo[3.2.1]octane-3-carboxylate] (5): colorless powder; $[\alpha]^{21.7}_{D}$ −2.9 (*c* 0.1, MeOH); IR ν_{max} cm^{-1} 3410, 1754, 1712; UV λ_{max} (MeOH) nm (log ε) 276 (4.336), 216 (4.142); HRFABMS *m*/*z* 407.1721 (calcd for $C_{21}H_{27}O_8$, 407.1706); FABMS *m*/*z* 429[M + Na]$^+$, 407[M + H]$^+$; mp 95−97 °C (dec); ^{1}H and ^{13}C NMR data (methanol-d_4) see Table 2; ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.88 (3H, t, *J* = 7.5 Hz, H-4″), 1.32 (2H, sext, *J* = 7.5 Hz, H-3″), 1.58 (2H, qui, *J* = 7.5, 6.5 Hz, H-2″), 2.12 (2H, m, H-3), 3.88 (1H, br s, H-5), 4.00 (1H, br s, H-4), 4.12 (2H, td, *J* = 6.5, 2.0 Hz, H-1″), 4.26 (1H, ddd, *J* = 8.5, 4.0, 2.5 Hz, H-7), 4.49 (1H, t, *J* = 4.0 Hz, H-6), 4.63 (1H, dd, *J* = 12.5, 2.5 Hz, H-8), 4.78 (1H, d, *J* = 3.5 Hz, 5-OH), 5.01 (1H, dd, *J* = 12.5, 8.5 Hz, H-8), 5.21 (1H, br s, 2-OH), 6.66 (1H, d, *J* = 16.0 Hz, H-8′), 7.42 (3H, m, H-2′, 4′, 6′), 7.65 (1H, d, *J* = 16.0 Hz, H-7′), 7.72 (2H, m, H-3′, 5′); ^{13}C NMR (125 MHz, DMSO-d_6) δ 13.4 (C-4″), 18.4 (C-3″), 29.9 (C-2″), 39.6 (C-3), 63.5 (C-4), 63.6 (C-8), 64.8 (C-1″), 67.8 (C-5), 76.2 (C-6), 78.9 (C-7), 103.1 (C-2), 118.0 (C-8′), 128.3 (C-3′, 5′), 128.9 (C-2′, 6′), 130.4 (C-4′), 134.0 (C-1′), 144.5 (C-7′), 166.1 (C-9′), 167.2 (C-1).

Decurrenside B [(*E*)-methyl-7-{(cinnamoyloxy)methyl}-3,8-dihydroxy-2,6-dioxabicyclo[3.2.1]octane-3-carboxylate] (6): colorless gum; $[\alpha]^{22.7}_{D}$ −3.1 (*c* 0.1, MeOH); IR ν_{max} cm^{-1} 3417, 1748, 1714; UV λ_{max} (MeOH) nm (log ε) 276 (4.117), 216 (3.985), 204 (4.003); HRFABMS *m*/*z* 365.1224 (calcd for $C_{18}H_{21}O_8$, 365.1236); FABMS *m*/*z* 387[M + Na]$^+$, 365[M + H]$^+$; ^{1}H and ^{13}C NMR data (methanol-d_4) see Table 2.

Decurrenside C [(*Z*)-methyl-7-{(cinnamoyloxy)methyl}-3,8-dihydroxy-2,6- dioxabicyclo[3.2.1]octane-3-carboxylate] (7): colorless gum; $[\alpha]^{25.8}_{D}$ −10.3 (*c* 0.2, MeOH); IR ν_{max} cm^{-1} 3478, 1744, 1716; UV λ_{max} (MeOH) nm (log ε) 272 (3.926), 204 (4.071), 201 (4.088); HRFABMS *m*/*z* 365.1241 (calcd for $C_{18}H_{21}O_8$, 365.1237); FABMS *m*/*z* 387[M + Na]$^+$, 365[M + H]$^+$; ^{1}H and ^{13}C NMR data (methanol-d_4) see Table 2.

Decurrenside D [methyl-7-{(benzoyloxy)methyl}-3,8-dihydroxy-2,6-dioxabicyclo[3.2.1]octane-3-carboxylate] (8): colorless gum; $[\alpha]^{19.0}_{D}$ −11.7 (*c* 0.1, MeOH); IR ν_{max} cm^{-1} 3487, 1750, 1716; UV λ_{max} (MeOH) nm (log ε) 229 (3.921), 202 (3.800); HRFABMS *m*/*z* 339.1090 (calcd for $C_{16}H_{19}O_8$, 339.1080); FABMS *m*/*z* 361[M + Na]$^+$, 339[M + H]$^+$; ^{1}H and ^{13}C NMR data (methanol-d_4) see Table 3.

Decurrenside E [butyl-7-{(benzoyloxy)methyl}-3,8-dihydroxy-2,6-dioxabicyclo[3.2.1]octane-3-carboxylate] (9): colorless gum; $[\alpha]^{27.8}_{D}$ −1.9 (*c* 0.08, MeOH); IR ν_{max} cm^{-1} 3474, 1751, 1715; UV λ_{max} (MeOH) nm (log ε) 273 (2.973), 229 (3.994); HRFABMS *m*/*z* 381.1563 (calcd for $C_{19}H_{25}O_8$, 381.1550); FABMS *m*/*z* 403[M + Na]$^+$, 381[M + H]$^+$; ^{1}H and ^{13}C NMR data (methanol-d_4) see Table 3.

Determination of Aldose Configuration. A solution of **1** (10 mg) in 1 M H_2SO_4 (1 mL) was heated at 100 °C in a screw-capped vial for 48 h. The mixture was neutralized by addition of Amberlite IRA400 (OH^- form) and filtered. The filtrate was dried *in vacuo*, then dissolved in 1 mL of pyridine containing L-cysteine methyl ester (10 mg/mL), and reacted at 60 °C for 1 h. To this mixture was added a solution (0.5 mL) of *o*-tolyl isothiocyanate in pyridine (20 mg/mL), and the solution heated at 60 °C for 1 h. The reaction mixture was directly analyzed by HPLC [Cosmosil 5C_{18} AR II (250 × 4.6 mm i.d., Nacalai Tesque Inc.); 25% CH_3CN in 50 mM H_3PO_4; flow rate, 0.8 mL/min; detection, 250 nm]. The retention time (t_R) of the peak at 17.00 min coincided with that of D-glucose.

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