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Cyclic glycolipids from glandular trichome exudates of *Cerastium glomeratum*

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ABSTRACT

Fourteen cyclic glycolipids, named glomerasides A–N, have been isolated from the glandular trichome exudate of *Cerastium glomeratum* (Caryophyllaceae). Their structures were determined by spectroscopic analysis of the glycolipids, as well as by application of the Ohrui–Akasaka method to the fatty acid methyl esters derived from the glycolipids and GCMS studies of trimethylsilyl ether derivatives of the methyl esters. The various glomerasides have a glycosidic linkage between the anomeric hydroxy group of the glucose and the C-11, C-10 or C-9 positions of the docosanoyl moiety. They also contained an ester linkage between the C-6 hydroxy group of the glucose ring and the carboxyl group of the oxygenated fatty acid to form their macrocyclic structures. The glucose moiety was optionally acetylated and/or malonylated at the C-2 or C-3 hydroxy groups. Among these compounds, the 1,6′-cyclic ester of 11(*R*)-(2-*O*-acetyl-β-D-glucopyranosyloxy)docosanoic acid (glomeraside D) was the most abundant (25%).

1. Introduction

Glandular trichomes produce secondary metabolites of diverse classes such as terpenoids, phenylpropanoids, polyketides and fatty acid derivatives (Schilmiller et al., 2008). The secondary metabolites secreted by glandular trichomes are thought to have diverse biological activities, such as protecting the aerial parts of plants against herbivores and pathogens (Duke et al., 2000; Spring, 2000). As far as glycolipid structures isolated from glandular trichome exudates are concerned, glycosyloxy-fatty acids have been reported from *Ibicella lutea* and *Proboscidea louisiana* (Martyniaceae) (Asai et al., 2010), as well as a glyceride having a glycosyloxy-fatty acyl moiety from *Cerasus yedoensis* (Rosaceae) (Asai and Fujimoto, 2011) and a series of 1,2′-cyclic ester derivatives of (β-D-glucopyranosyloxy)fatty acids (gallicasides A–H) from *Silene gallica* (Caryophyllaceae) (Asai and Fujimoto, 2010).

The characterization of the unique cyclic glycolipids from *S. gallica*, described above, is the first study to analyze secondary metabolites from glandular trichome exudates of plants belonging to the Caryophyllaceae family. These rare cyclic glycolipids structures prompted us to further investigate other Caryophyllaceous plants. To this regard, *Cerastium glomeratum* has glandular trichomes in an upper portion of the aerial part including calyxes through field research. *C. glomeratum*, a plant native to Europe, and is thought to have migrated to Japan about 100 years ago and is generally found in roadsides nowadays. This plant flowers in April and May (Shimizu, 1995). A study on fatty acids of this plant has been reported previously (Jamieson and Reid, 1971).

In this paper, the isolation and structure elucidation of fourteen cyclic glycolipids, named glomerasides A–N from the glandular trichome exudate of the plants are described. All were 1,6′-cyclic ester derivatives of (β-D-glucopyranosyloxy)dodecanoic acids.

2. Results and discussion

The exudate sample was obtained by rinsing an upper portion of the aerial part with Et_2O. The extract showed an identical TLC pattern as the sample that was obtained by gently wiping the surface of the calyxes with oil-free cotton. The extract was subjected to silica gel column chromatography to give Pools I–VI. Compounds **1**, **2** and **3** were obtained in a 28:45:27 ratio by a reversed-phase HPLC separation of Pool I. Compounds **4** and **5** were similarly obtained in a 82:18 ratio from Pool II and compounds **6**, **7** and **8** were obtained from Pool III in a 26:43:31 ratio. NMR spectroscopic analyses of Pool IV (a mixture of compounds **9** and **10**), Pool V (a mixture of compounds **11** and **12**) and Pool VI (a mixture of compounds **13m** and **14m**) indicated that all possessed malonyl groups. For example, compound **9**, the major constituent in Pool V, exhibited signals at δ 4.90 (H_2-2″) in the ^{1}H NMR and at δ 41.1 (C-2″), 166.7 (C-1″) and 170.1 (C-3″) in the ^{13}C NMR spectra. Pools IV–VI were converted to the corresponding methyl esters and then separated by HPLC. Compounds **9m** and **10m** were obtained from Pool IV in a 79:21 ratio, compounds **11m** and **12m** were obtained from Pool V in an 87:13 ratio and compounds **13m** and **14m** were obtained from Pool VI in a 75:25 ratio.

Compound **1**, named glomeraside A, showed a pseudo-molecular ion at *m*/*z* 543.3894 $[M+H]^+$ in the positive HRFABMS that corresponded to the molecular formula $C_{30}H_{54}O_8$. The IR absorption bands at 3590, 3440 and 1720 cm^{-1} suggested the presence of

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hydroxy and carbonyl groups. The ^{1}H NMR spectrum (Table 1) showed signals of seven protons assignable to a β-glucopyranosyl moiety acylated at the 3′-*O* and 6′-*O* positions [δ4.38 (*d*, *J* = 7.7 Hz, H-1′), 3.48 (*ddd*, *J* = 9.1, 7.7, 2.5 Hz, H-2′), 4.92 (*t*, *J* = 9.1 Hz, H-3′), 3.57 (*td*, *J* = 9.1, 4.8 Hz, H-4′), 3.52 (*m*, H-5′), 4.37 (*dd*, *J* = 12.1, 1.8 Hz, Ha-6′) and 4.30 (*dd*, *J* = 12.1, 4.7 Hz, Hb-6′)]. These resonances were unambiguously assigned through analysis of the H–H COSY spectrum. Furthermore, an oxymethine proton at δ 3.66 (*m*) and an acetyl methyl singlet at δ 2.18 were observed, in addition to the signals characteristic to a fatty acyl group (methyl triplet at δ 0.88, methylene protons adjacent to a carboxyl group at δ 2.37 and longer-chain methylene protons centered at δ 1.26). The ^{13}C NMR spectroscopic data (Table 2) confirmed the presence of a di-*O*-acylated glucopyranosyl moiety (ester carbonyl resonances at δ 174.35 and 172.57). It also further established that the corresponding fatty acyl group was linear (terminal methyl carbon at δ 14.13) and mono-oxygenated along the methylene chain (presence of an oxymethine carbon at δ 80.05 associated with a proton at δ 3.66). The two-ester functionalities and the glucopyranosyl moiety accounted for three of the four unsaturations of **1**, indicating the presence of an additional ring structure. The HMBC spectrum provided evidence that the acetyl group was attached to 3′-*O* of the glucosyl moiety (the acetyl methyl singlet at δ 2.18 and 3′-H at δ 4.92 were correlated with the ester carbonyl carbon at δ 172.57) and the oxymethine carbon of the fatty acyl group was linked to the sugar through a glycosidic bond (1′-H at δ 4.52 were correlated with the oxymethine carbon at δ 80.05). The 6′-*O*-fatty acyl linkage was deduced from the chemical shifts of 6′-H_2 of the glucosyl moiety. The carbon number of the oxygenated fatty acyl moiety was calculated as being C_{22} based on the molecular formula. All data indicated that compound **1** was a 1,6′-cyclic ester of (3-*O*-acetyl-β-D-glucopyranosyloxy)docosanoic acid.

However, the exact position and the absolute configuration of the oxymethine center in the docosanoyl moiety remained unknown. These issues were solved via a series of chemical transformations of **1**. Alkaline hydrolysis of compound **1**, followed by treatment with acidic conditions, gave a hydroxy-docosanoic acid that was then converted to the methyl ester **15** (EIMS *m*/*z*: 352 [M−H_2O]$^+$) (Fig. 2) by treatment with trimethylsilyldiazomethane. The EIMS spectrum of the trimethyl (TMS) ether derivative of **15**

Table 1
^{1}H NMR spectroscopic data (500 MHz, $CDCl_3$) for compounds **1**–**8** and **9m**–**14m**.[a]

Position	1	2	3	4	5	6	7	8
2	2.37 (*m*)	2.37 (*m*)	2.39 (*m*)	2.38 (*m*)	2.38 (*m*)	2.38 (*brt*)	2.38 (*m*)	2.38 (*m*)
3	1.65 (*m*) 1.72 (*m*)	1.66 (*m*)	1.58 (*m*) 1.72 (*m*)	1.66 (*m*) 1.72 (*m*)	1.67 (*m*)	1.63 (*m*) 1.71 (*m*)	1.66 (*m*)	1.58 (*m*) 1.73 (*m*)
4–21[b]	1.39–1.20 (*m*)	1.38–1.20 (*m*)	1.40–1.20 (*m*)	1.42–1.20 (*m*)	1.39–1.20 (*m*)	1.42–1.20 (*m*)	1.74–1.20 (*m*)	1.41–1.20 (*m*)
[c]	1.52 (*m*)	1.59-1.41 (*m*)	1.60–1.40 (*m*)	1.48 (*m*)	1.59-1.41 (*m*)	1.51 (*m*)	1.58-1.41 (*m*)	1.60–1.40 (*m*)
9/10/11	3.66 (*m*)	3.66 (*m*)	3.58 (*m*)	3.57 (*m*)	3.59 (*m*)	3.57 (*m*)	3.67 (*m*)	3.57 (*m*)
22	0.88 (*t*, 7.0)	0.88 (*t*, 6.9)	0.88 (*t*, 6.9)	0.88 (*t*, 7.0)	0.88 (*t*, 7.0)	0.88 (*t*, 7.0)	0.88 (*t*, 7.0)	0.88 (*t*, 7.0)
1′	4.38 (*d*, 7.7)	4.42 (*d*, 7.7)	4.37 (*d*, 7.8)	4.47 (*d*, 7.8)	4.50 (*d*, 7.8)	4.33 (*d*, 7.9)	4.35 (*d*, 7.7)	4.31 (*d*, 7.7)
2′	3.48 (*ddd*, 9.1, 7.7, 2.5)	3.49 (*dd*, 9.1, 7.7)	3.49 (*ddd*, 9.5, 7.8, 2.6)	4.72 (*dd*, 9.6, 7.8)	4.71 (*dd*, 9.4, 7.8)	3.35 (*dd*, 8.8, 7.9)	3.36 (*dd*, 8.8, 7.7)	3.35 (*dd*, 9.0, 7.7)
3′	4.92 (*t*, 9.1)	4.92 (*t*, 9.1)	4.90 (*t*, 9.5)	3.59 (*t*, 9.6)	3.58 (*t*, 9.4)	3.57 (*brt*, 8.8)	3.57 (*brt*, 8.8)	3.56 (*dd*, 9.6, 9.0)
4′	3.57 (*td*, 9.1, 4.8)	3.49 (*td*, 9.1, 4.8)	3.49 (*td*, 9.5, 5.1)	3.50 (*brt*, 9.6)	3.53 (*t*, 9.4)	3.48 (*m*)	3.49 (*m*)	3.42 (*brt*, 9.6)
5′	3.52 (*m*)	3.53 (*m*)	3.64 (*m*)	3.46 (*m*)	3.48 (*m*)	3.48 (*m*)	3.49 (*m*)	3.61 (*m*)
6′	4.37 (*dd*,12.1, 1.8)	4.45 (*brd*, 11.9)	4.42 (*dd*, 11.9, 1.9)	4.35 (*dd*, 12.1, 1.9)	4.43 (*dd*, 12.0, 2.0)	4.35 (*dd*, 12.0, 1.4)	4.43 (*brd*, 12.0)	4.41 (*dd*, 12.0, 2.0)
	4.30 (*dd*,12.1, 4.7)	4.19 (*dd*, 11.9, 5.3)	4.23 (*dd*, 11.9, 7.8)	4.32 (*dd*, 12.1, 4.4)	4.20 (*dd*, 12.0, 5.3)	4.33 (*dd*, 12.0, 5.4)	4.21 (*dd*, 12.0, 4.9)	4.23 (*dd*, 12.0, 7.8)
CH_3CO	2.18 (*s*)	2.18 (*s*)	2.18 (*s*)	2.12 (*s*)	2.12 (*s*)	–	–	–
2′/3′-OH	2.31 (*d*, 2.5)	2.36 (*brs*)	2.30 (*d*, 2.6)	2.99 (*brs*)	2.72 (*brs*)	2.45 (*brs*)	2.99/2.62 (*brs*)	2.98/2.50 (*brs*)
4′-OH	2.87 (*d*, 4.8)	2.91 (*d*, 4.8)	2.76 (*d*, 5.1)	2.90 (*brs*)	2.77 (*brs*)	2.88 (*brs*)	3.14 (*brs*)	2.77 (*brs*)

Position	9m	10m	11m	12m	13m	14m
2	2.38 (*m*)	2.38 (*t*, 6.4)	2.37 (*m*)	2.38 (*t*, 6.5)	2.37 (*m*)	2.38 (*t*, 6.5)
3	1.66 (*m*) 1.73 (*m*)	1.67 (*m*)	1.67 (*m*) 1.72 (*m*)	1.67 (*m*)	1.66 (*m*) 1.72 (*m*)	1.67 (*m*)
4–21[b]	1.41–1.20 (*m*)	1.38–1.20 (*m*)	1.41–1.20 (*m*)	1.38–1.20 (*m*)	1.41–1.20 (*m*)	1.39–1.20 (*m*)
[c]	1.47 (*m*)	1.58-1.39 (*m*)	1.46 (*m*)	1.58-1.39 (*m*)	1.47 (*m*)	1.58-1.39 (*m*)
9/10/11	3.57 (*m*)	3.57 (*m*)	3.57 (*m*)	3.58 (*m*)	3.57 (*m*)	3.57 (*m*)
22	0.88 (*t*, 7.0)	0.88 (*t*, 6.9)	0.88 (*t*, 6.9)	0.88 (*t*, 7.0)	0.88 (*t*, 7.0)	0.88 (*t*, 7.0)
1′	4.52 (*d*, 7.7)	4.55 (*d*, 7.4)	4.53 (*d*, 7.8)	4.56 (*d*, 7.9)	4.49 (*d*, 7.9)	4.52 (*d*, 7.9)
2′	4.97 (*dd*, 9.8, 7.7)	4.98 (*dd*, 9.7, 7.4)	4.92 (*dd*, 9.8, 7.8)	4.93 (*dd*, 9.8, 7.9)	4.81 (*dd*, 9.5, 7.9)	4.82 (*dd*, 9.3, 7.9)
3′	5.02 (*t*, 9.8)	5.01 (*t*, 9.7)	5.09 (*t*, 9.8)	5.09 (*t*, 9.8)	3.65 (*td*, 9.5, 3.1)	3.65 (*td*, 9.3, 3.0)
4′	3.64 (*td*, 9.8, 5.0)	3.64 (*td*, 9.7, 5.0)	3.70 (*td*, 9.8, 3.2)	3.71 (*td*, 9.8, 3.4)	3.57 (*t*, 9.5, 2.0)	3.59 (*td*, 9.3, 2.2)
5′	3.51 (*m*)	3.52 (*m*)	3.57 (*m*)	3.58 (*m*)	3.50 (*m*)	3.51 (*m*)
6′	4.36 (*dd*, 12.1, 2.2) 4.32 (*dd*, 12.1, 4.1)	4.45 (*dd*, 12.0, 2.0) 4.21 (*dd*, 12.0, 5.0)	4.39 (*dd*, 12.1, 1.7) 4.26 (*dd*, 12.1, 5.0)	4.40 (*dd*, 12.1, 1.7) 4.28 (*dd*, 12.1, 5.0)	4.38 (*dd*, 12.1, 1.8) 4.29 (*dd*, 12.1, 5.0)	4.46 (*dd*, 12.0, 2.0) 4.19 (*dd*, 12.0, 5.5)
CH_3CO	2.14 (*s*)	2.11 (*s*)	2.05 (*s*)	2.05 (*s*)	–	–
2″	3.35 (*s*) 3.35 (*s*)	3.36 (*s*) 3.36 (*s*)	3.49 (*d*, 16.3) 3.40 (*d*, 16.3)	3.50 (*d*, 16.3) 3.39 (*d*, 16.3)	3.47 (*d*, 16.1) 3.42 (*d*, 16.1)	3.47 (*d*, 16.2) 3.42 (*d*, 16.2)
CO_2Me	3.73 (*s*)	3.73 (*s*)	3.77 (*s*)	3.77 (*s*)	3.78 (*s*)	3.78 (*s*)
2′/3′-OH	–	–	–	–	3.41 (*d*, 3.1)	3.44 (*d*, 3.0)
4′-OH	2.81 (*d*, 5.0)	2.74 (*d*, 5.0)	3.47 (*d*, 3.2)	3.39 (*d*, 3.4)	2.74 (*d*, 2.0)	2.65 (*d*, 2.2)

[a] Multiplicity and coupling constants (*J* in Hz) are in parentheses.
[b] Methylene protons excluding those coupling to the oxymethine proton.
[c] Methylene protons (4H) coupling to the oxymethine proton.

Table 2
^{13}C NMR spectroscopic data (125 MHz, in $CDCl_3$) for **1**–**8** and **9m**–**15m**.[a]

No.	1	2	3	4	5	6	7	8	9m	10m	11m	12m	13m	14m
1	174.35	174.14	173.97	174.56	174.21	174.57	174.27	174.06	174.41	174.13	174.25	174.05	174.37	174.13
9/10/11	80.05	79.12	82.02	80.54	79.95	79.72	78.88	81.70	80.47	79.70	80.76	80.17	80.38	79.78
2–19[b]	34.53	34.37	35.26	34.57	34.40	34.62	34.43	35.34	34.45	34.28	34.51	34.40	34.45	34.33
	34.30	33.99	34.41	34.41	34.13	34.30	33.99	34.44	34.28	34.01	34.41	34.11	34.38	34.10
	34.04	33.91	34.27	34.08	33.86	34.06	33.96	34.30	34.05	33.92	34.08	33.85	34.07	33.89
	29.84	29.85	29.78	29.96	29.91	29.84	29.84	29.78	29.90	29.87	29.95	29.92	29.89	29.84
	29.65	29.67	29.70	29.71	29.72	29.65	29.68	29.69	29.68	29.69	29.68	29.70	29.73	29.73
	29.64	29.65	29.67	29.67	29.67	29.63	29.66	29.67	29.66	29.67	29.66	29.67	29.73	29.69
	29.62	29.65	29.65	29.67	29.67	29.63	29.65	29.65	29.66	29.67	29.66	29.67	29.68	29.69
	29.62	29.63	29.65	29.67	29.67	29.61	29.63	26.65	29.62	29.67	29.62	29.67	29.67	29.68
	29.59	29.61	29.61	29.62	29.64	29.60	29.61	29.62	29.34	29.65	29.34	29.64	29.64	29.65
	29.35	29.36	29.59	29.34	29.34	29.34	29.35	29.60	27.99	29.35	28.05	29.34	29.35	29.35
	27.99	27.12	29.36	29.08	27.12	28.04	27.13	29.36	27.55	27.16	27.54	27.17	28.07	27.12
	27.49	26.98	27.66	27.49	26.02	27.47	26.98	27.70	27.53	27.02	27.52	27.07	27.51	27.03
	27.35	26.48	27.27	27.28	26.70	27.30	26.52	27.31	27.27	26.60	27.34	26.70	27.33	26.65
	26.81	26.38	27.02	26.83	26.23	26.85	26.41	27.07	26.82	26.27	26.82	26.21	26.82	26.25
	25.37	25.32	25.65	25.14	25.05	25.41	25.36	25.67	25.20	25.12	25.10	25.03	25.18	25.14
	24.47	24.43	24.47	24.40	24.36	24.42	24.41	24.46	24.41	24.38	24.46	24.20	24.43	24.38
	24.27	23.86	23.23	24.21	23.80	24.27	23.94	23.31	24.13	23.77	24.23	23.76	24.21	23.78
20	31.92	31.93	31.93	31.91	31.91	31.91	31.92	31.92	31.90	31.91	31.91	31.91	31.91	31.91
21	22.69	22.70	22.70	22.68	22.67	22.68	22.68	22.69	22.68	22.68	22.68	22.68	22.68	22.68
22	14.13	14.13	14.13	14.10	14.10	14.11	14.11	14.11	14.11	14.11	14.10	14.10	14.10	14.10
1′	101.84	101.53	102.61	100.24	100.07	101.64	101.33	102.44	99.90	99.67	100.41	100.31	99.77	99.62
2′	72.20	72.27	72.21	76.75	76.01	73.62	73.31	73.31	72.32	72.34	71.27	71.32	75.77	75.86
3′	77.85	78.06	78.16	74.78	75.01	76.08	76.28	76.30	75.71	76.02	77.84	77.87	75.49	75.66
4′	69.17	69.40	70.11	70.68	70.93	69.81	70.00	70.61	69.03	69.30	68.85	69.08	69.86	70.03
5′	74.03	73.75	73.87	73.24	72.87	74.08	74.15	74.12	73.81	73.53	73.22	72.91	73.43	73.12
6′	63.29	63.07	64.02	63.35	63.08	63.34	63.21	64.15	62.99	62.78	63.23	62.99	63.3	63.12
Ac (CH_3)	21.07	21.07	21.05	20.95	20.94				20.85	20.85	20.77	20.77		
Ac (CO)	172.57	172.66	172.78	171.22	171.38				172.04	172.20	169.59	169.60		
1″									164.92	164.92	166.34	166.36	165.53	165.56
2″									41.08	41.08	41.19	41.18	41.18	41.18
3″									166.42	166.44	168.05	168.17	168.16	168.26
MeO									52.56	52.56	52.96	52.98	52.91	52.92

[a] Signal assignments for **1**–**4**, **7**, **9m**–**11m** and **13m** were based on 2D experiments including HSQC and HMBC.
[b] Except for the oxymethine carbon.

showed intense fragment ions at *m*/*z* 257 ($[TMSOCH(CH_2)_{10}CH_3]^+$ due to C-10/C-11 cleavage) and 287 ($[CH_3OOC(CH_2)_{10}CH(OTMS)]^+$ due to C-11/C-12 cleavage) in addition to a $[M–Me]^+$ ion peak at *m*/*z* 427. The diagnostic fragment ions unequivocally established that compound **15** was methyl 11-hydroxydocosanoate. GLC analysis of the TMS ether derivative of **15** showed a single peak, indicating the absence of homologous compounds. The absolute configuration at C-11 of **15** was determined to be *R* by application of the Ohrui–Akasaka method (Ohtaki et al., 2005) (*vide infra*). Hence, the structure of glomeraside A (**1**) was determined to be the 1,6′-cyclic ester of 11(*R*)-(3-*O*-acetyl-*β*-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1.

Compounds **2** and **3**, named glomerasides B and C, respectively, had the same molecular formula as **1**. The ^{1}H NMR spectra of **2** and **3** (Table 1) resembled that of **1**, thus indicating the presence of a glucopyranosyl moiety that was esterified at the 3′-*O* and 6′-*O* positions and glycosylated at the 1′-*O* position (δ_H 3.66, δ_C 79.12 for **2** and δ_H 3.58, δ_C 82.02 for **3**) with an oxymethine carbon of a fatty acyl group, as in **1**. The HMBC spectra of **2** and **3** confirmed their 3′-*O*-acetylation, 6′-*O*-fatty acylation, and glycosidic linkage. The ^{13}C NMR spectra (Table 1) of **2** and **3** were also similar to that of **1**, but small differences were observed for most signals, compared to those of compound **1**. The resonance of the oxymethine carbon in the fatty acyl moiety displayed the largest difference (an upfield shift by 0.93 ppm for **2** and a downfield shift by 1.97 ppm for **3**, compared to that of **1**). These deviations observed in the ^{13}C spectroscopic data suggested that compounds **2** and **3** could be either a positional isomer or a stereoisomer of **1** with respect to the oxygenated position in the fatty acyl moiety. To solve this problem, compounds **2** and **3** were converted to the hydroxy fatty acid methyl esters **16** and **17**, respectively, as described for **1**. The methyl esters **16** (EIMS *m*/*z*: 352 $[M–H_2O]^+$) and **17** (EIMS *m*/*z*: 352 $[M–H_2O]^+$) (Fig. 2) were determined to be methyl 10-hydroxydocosaonoate and methyl 9-hydroxydocosanoate, respectively, on the basis of the EIMS spectra of the corresponding TMS ether derivatives (**16**-TMS *m*/*z* 427 $[M–Me]^+$, 271 ($[TMSOCH(CH_2)_{11}Me]^+$ due to C-9/C-10 cleavage), 273 ($[MeOOC(CH_2)_9CH(OTMS)]^+$ due to C-10/C-11 cleavage; **17**-TMS *m*/*z* 427 $[M–Me]^+$, 285 ($[TMSOCH(CH_2)_{12}Me]^+$ due to C-8/C-9 cleavage), 259 ($[CH_3OOC(CH_2)_7CH(OTMS)]^+$ due to C-9/C-10 cleavage). The absolute configurations at C-10 of **16** and C-9 of **17** were determined as being *R* (*vide infra*). It was therefore concluded that the structures of glomerasides B (**2**) and C (**3**) were the 1,6′-cyclic ester of 10(*R*)-(3-*O*-acetyl-*β*-D-glucopyranosyloxy)docosanoic acid and the 1,6′-cyclic ester of 9(*R*)-(3-*O*-acetyl-*β*-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1.

Compounds **1**, **2** and **3** were treated with Ac_2O and pyridine to afford the corresponding peracetates **1a**, **2a** and **3a**, respectively, which were helpful for the structure elucidation of compounds **4**–**8**. The three peracetates could not be separated by HPLC, however, with standard reversed-phase columns (ODS). However, they were effectively separated with an Inertsil ODS-P column (see Experimental).

The configuration at the oxymethine center in **15**–**17** was determined using the Ohrui–Akasaka method (Ohtaki et al., 2005). Compound **15** was thus converted into the ester derivative **15a** of (1*R*,2*R*)-2-(2,3-anthracenedicarboximide)cyclohexanecarboxylic acid ((*R*)-ACC acid) and into the (*S*)-ACC ester **15b** (Fig. 2). Compounds **16** and **17** were similarly converted into the (*R*)-ACC **16a** and (*S*)-ACC ester **16b** and (*R*)-ACC ester **17a** and (*S*)-ACC ester

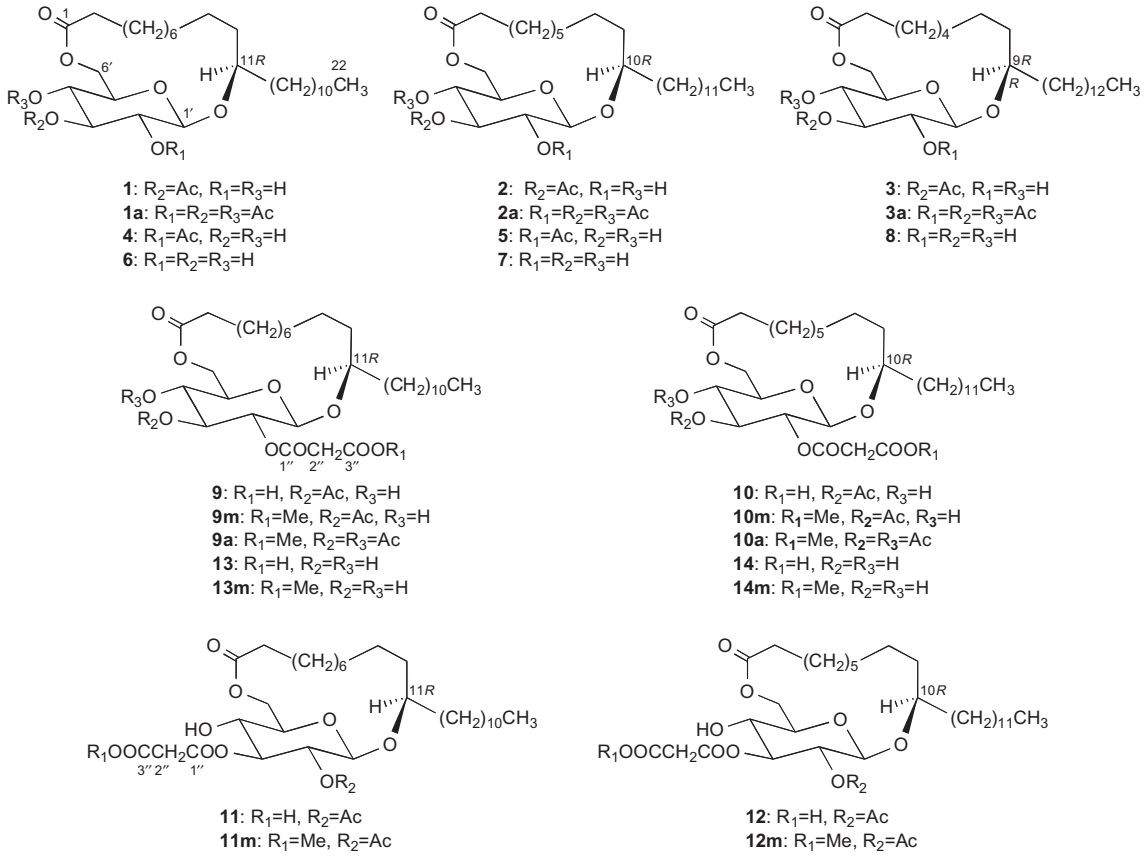

Fig. 1. Compounds **1–14** and their derivatives.

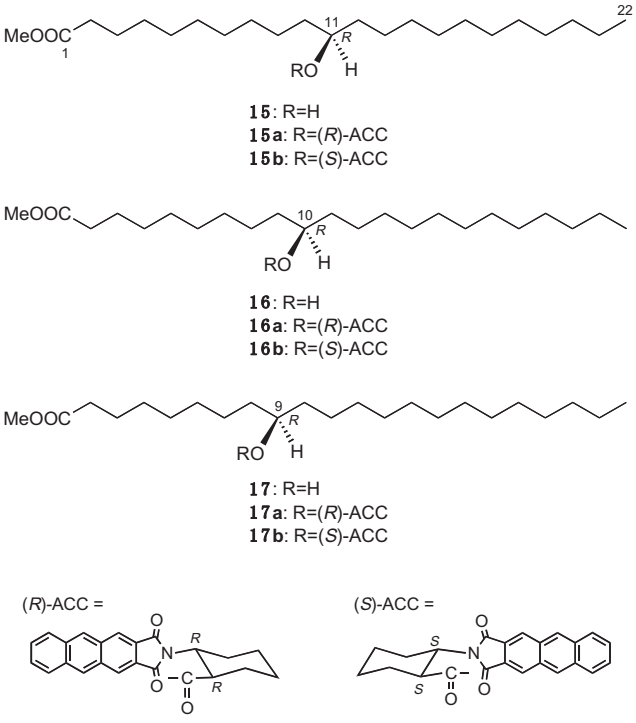

Fig. 2. Structures of the hydroxy fatty acid methyl esters **15–17** and their derivatives.

17b (Fig. 2). The chemical shifts of the key proton signals of these derivatives are listed in Table 3. The triplet resonances corresponding to H_2-2 were consistently observed at higher field in the spectra of the (*R*)-ACC esters than in those of the corresponding (*S*)-ACC esters. The $\delta_{(R)-(S)}$ values for H_2-2 of **15ab–17ab** were negative and the magnitudes of the values (−0.074, −0.058, −0.030 ppm for **17ab**, **16ab** and **15ab**, respectively) were in good agreement with those described in the paper (Ohtaki et al., 2005). The results permitted the assignments of 11*R*, 10*R* and 9*R* configurations for compounds **15**, **16** and **17**, respectively. Ohrui reported that anisotropic effect of anthracene derivative reaches protons attached to the carbon 10 bond apart from the oxymethine carbon (Ohrui, 2008). The $\delta_{(R)-(S)}$ value for the COOMe signal (10 bond apart from the oxymethine carbon) of **17ab** also showed an expected negative small $\delta_{(R)-(S)}$ value (−0.006 ppm). Careful interpretation of $\delta_{(R)-(S)}$ values in the paper of the Ohrui–Akasaka method (Ohtaki et al., 2005) indicated that the anthracene ring causes a small but unique deshielding effect on the protons attached to the carbon 12–14 bond apart from the oxymethine carbon. Thus, the signs of the $\delta_{(R)-(S)}$ values for the COOMe signal of **15a**/**b** (12 bond) and for the terminal methyl triplet signals of **17a**/**b** (13 bond) and **16a**/**b** (12 bond) were rationalized by this anomalous anisotropic effect.

The assignment was verified in the case of methyl 10-hydroxydocosanoate. Authentic samples of **16a** and **16b** with known absolute configuration at C-10 were prepared from methyl (*R*)-10-hydroxydocosanoate. This compound was synthesized by reacting undecanylmagnesium bromide with methyl (*S*)-10,11-epoxyundecanoate in the presence of CuI. The chiral epoxide was obtained by kinetic resolution of the racemic epoxide (Schaus et al., 2002). The chemical shifts of H_2-2, COOMe and H_3-22 of the derivatives were in complete agreement with those observed for **16a** and **16b**, thus confirming the 10(*R*) configuration of **16**.

Compound **4**, named glomeraside D, had the molecular formula $C_{30}H_{54}O_8$, which was identical to that of **1**. The ^{1}H NMR spectrum

Table 3
Pertinent ^{1}H NMR (500 MHz, $CDCl_3$) spectroscopic data for the ACC esters **15ab**, **16ab** and **17ab**.

Compound	CO_2Me	$\delta_{(R)-(S)}$	H_2-2	$\delta_{(R)-(S)}$	H_3-22	$\delta_{(R)-(S)}$
15	3.667 (*s*)		2.300 (*t*, *J* = 7.5 Hz)		0.887 (*t*, *J* = 7.2 Hz)	
15a	3.666 (*s*)		2.198 (*t*, *J* = 7.5 Hz)		0.867 (*t*, *J* = 7.2 Hz)	
15b	3.661 (*s*)	+0.005	2.218 (*t*, *J* = 7.5 Hz)	−0.030	0.866 (*t*, *J* = 7.2 Hz)	+0.001
16	3.667 (*s*)		2.300 (*t*, *J* = 7.5 Hz)		0.887 (*t*, *J* = 7.2 Hz)	
16a[a]	3.654 (*s*)		2.122 (*t*, *J* = 7.5 Hz)		0.877 (*t*, *J* = 7.2 Hz)	
16b[a]	3.653 (*s*)	+0.001	2.180 (*t*, *J* = 7.5 Hz)	−0.058	0.882 (*t*, *J* = 7.2 Hz)	−0.005
17	3.667 (*s*)		2.300 (*t*, *J* = 7.5 Hz)		0.887 (*t*, *J* = 7.2 Hz)	
17a	3.635 (*s*)		2.073 (*t*, *J* = 7.5 Hz)		0.882 (*t*, *J* = 7.2 Hz)	
17b	3.641 (*s*)	−0.006	2.147 (*t*, *J* = 7.5 Hz)	−0.074	0.887 (*t*, *J* = 7.2 Hz)	−0.005

[a] The ^{1}H NMR data was identical with that of synthetic authentic sample.

of **4** resembled that of **1** (Table 1). However, analysis of the H–H COSY spectrum indicated that the signals at δ 4.72 and 3.59 corresponded to H-2′ and H-3′ of the glucopyranosyl moiety, respectively. The downfield shift of H-2′ indicated a 2′-*O*-acetylation of the glucose ring in place of a 3′-*O*-acylation. This was confirmed by HMBC correlations between the acetyl methyl (δ 2.12) and H-2′ (δ 4.72) resonances and the acetyl carbonyl carbon (δ 171.22). The acetyl derivative of **4** was identified as the peracetate **1a**. Glomeraside D (**4**) was thus found to be the 1,6′-cyclic ester of 11(*R*)-(2-*O*-acetyl-β-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1.

Compounds **5**, named glomeraside E, had the same molecular formula as **1**. Analysis of the ^{1}H NMR spectrum of **5**, together with that of the H–H COSY spectrum, indicated the same acylation pattern on the β-glucopyranosyl moiety (H-2′ at δ 4.71, H-3′ at δ 4.71) as that found for compound **4** (Table 1). The ^{13}C NMR spectroscopic data of **5** (Table 2) was only slightly different from that of **4** and evidenced from the presence of the glucopyranosyl, oxygenated docosanoyl, and acetyl moieties. The acetate derivative of **5** was identified as the peracetate **2a**. Thus, glomeraside E (**5**) was determined to be the 1,6′-cyclic ester of 10(*R*)-(2-*O*-acetyl-β-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1.

Compound **6**, named glomeraside F, showed a pseudo-molecular ion at *m*/*z* 501.3804 $[M+H]^+$ in the positive HRFABMS that corresponded to the molecular formula $C_{28}H_{52}O_7$. The ^{1}H and ^{13}C NMR spectra of **6** indicated that there is no acetyl group in the molecule and that the glucopyranosyl moiety was only acylated at the 6′-*O* position (Tables 1 and 2). The oxymethine proton and carbon signals (δ_H 3.65 and δ_C δ 79.72) indicated the presence of a glycosidic linkage to an oxymethine carbon of the docosanoyl moiety. The acetate derivative of **6** was identified as the peracetate **1a**. Thus, the structure of glomeraside F (**6**) was determined to be the 1,6′-cyclic ester of 11(*R*)-(β-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1.

Compounds **7** and **8**, named glomerasides G and H, respectively, had the same molecular formula as **6**. The ^{1}H and ^{13}C NMR spectra of **7** and **8** resembled those of **6**, indicating a 1,6′-cyclic ester structure as in **6** (Tables 1 and 2). The acetate derivatives obtained from **7** and **8** were identified as the peracetates **2a** and **3a**, respectively. Thus, the structures of glomerasides G (**7**) and H (**8**) were determined to be the 1,6′-cyclic esters of 10(*R*)-(β-D-glucopyranosyloxy)docosanoic acid and 9(*R*)-(β-D-glucopyranosyloxy)docosanoic acid, respectively, as depicted in Fig. 1.

Compound **9m** showed a pseudo-molecular ion at *m*/*z* 643.4080 $[M+H]^+$ in the positive HRFABMS that corresponded to the molecular formula $C_{34}H_{58}O_{11}$. The ^{1}H NMR spectrum of **9m** presented seven proton signals that correspond to a 2,3,6-tri-*O*-acyl-β-glucopyranosyl moiety [δ 4.52 (*d*, *J* = 7.7 Hz, H-1′), 4.97 (*dd*, *J* = 9.8, 7.7 Hz, H-2′), 5.02 (*dd*, *J* = 9.8 Hz, H-3′), 3.64 (*td*, *J* = 9.8, 5.0 Hz, H-4′), 3.51 (*m*, H-5′), 4.36 (*dd*, *J* = 12.1, 2.2 Hz, H_a-6′) and 4.32 (*dd*, *J* = 12.1, 4.1 Hz, H_b-6′)], an oxygenated fatty acid moiety (δ 3.57) and an acetyl methyl singlet (δ 2.14). In addition, resonances corresponding to a malonate methyl ester were observed at δ 3.35 (*s*, 2H) and δ 3.73 (*s*, 3H) (Table 1). The ^{13}C NMR spectrum exhibited 34 signals among which four resonances were assigned to the malonate methyl ester (δ 166.42, 164.92, 52.56 and 41.08) (Table 2). The HMBC spectrum gave evidence for the 2′-*O*-malonylation (H-2′ at δ 4.97 and H_2-2″ at δ 3.35 were correlated with the malonate C-1″ at δ 164.92) and the 3′-*O*-acetylation (the acetyl methyl singlet at δ 2.14 and 3′-H at δ 5.02 were correlated with the ester carbonyl carbon at δ 172.04). The remaining ester linkage was therefore located at 6′-*O*-position. A glycosidic bond with an oxygenated carbon in the fatty acyl moiety was also determined by the HMBC correlation between H′-1 (δ 4.52) and the oxymethine carbon (δ 80.47). The hydroxy fatty acid methyl ester that was obtained from **9m** was identified as methyl 11(*R*)-hydroxydocosanoate (**15**). The ^{1}H NMR spectrum of the (*R*)-ACC ester of the methyl ester was superimposable to that of **15**. Thus, compound **9** was determined to be the 1,6′-cyclic ester of 11(*R*)-(3-*O*-acetyl-2-*O*-malonyl-β-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1. It was named glomeraside I.

Compound **10m** had the same molecular formula as **9m**. The ^{1}H and ^{13}C NMR spectroscopic data indicated that the β-glucopyranosyl moiety was acylated at the 2′-*O*, 3′-*O* and 6′-*O* positions, similarly to **9m** (Tables 1 and 2). HMBC correlations indicated that the acetyl, malonyl and fatty acyl groups were located at the same position as in compound **10m**. The hydroxy fatty acid methyl ester obtained from **10m** was identified as methyl 10(*R*)-hydroxydocosanoate (**16**). The ^{1}H NMR spectrum of the (*R*)-ACC ester of the methyl ester was superimposable to that of **16**. Compound **10** was thus determined to be the 1,6′-cyclic ester of 10(*R*)-(3-*O*-acetyl-2-*O*-malonyl-β-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1. It was named glomeraside J. Compounds **9m** and **10m** were converted into the peracetates **9a** and **10a**, respectively, to help elucidate the structures of **13** and **14** (*vide infra*).

Compound **11m** had the same molecular formula as **9m**. The ^{1}H NMR spectroscopic data resembled that of **9m**, thus indicating the presence of a β-glucopyranosyl moiety that was acylated at the 2′-*O*, 3′-*O* and 6′-*O* positions (H-2′ at δ 4.92, H-3′ at δ 5.09 and H-6′ at δ 4.40/4.28) with acetyl, malonyl and fatty acyl groups and glycosylated at the 1′-*O* position with an oxymethine carbon of a fatty acyl group. The ^{13}C NMR spectroscopic data was similar to that of compound **9m**. However, the signals of the ester carbonyl groups showed small but distinct differences when compared to those of **9m** and **10m** (Table 2). The differences were found to be due to the interchange of the acyl groups at the 2′-*O* and 3′-*O* positions in compound **11m**, compared to compounds **9m** and **10m**. The HMBC spectrum of **11m** established the 2′-*O*-acetyation (the acetyl methyl singlet at δ 2.05 and H-2′ at δ 4.92 were correlated with the acetyl carbonyl carbon at δ 169.59) and the 3′-*O*-malonylation (H-3′ at δ 5.09 and H_2-3″ at 3.49/3.40 were correlated with the malonate C-1″ at δ 166.34). The hydroxy fatty acid methyl ester obtained

from **11m** was identified as methyl 11(*R*)-hydroxydocosanoate (**15**). Hence, compound **11** was determined to be the 1,6′-cyclic ester of 11(*R*)-(2-*O*-acetyl-3-*O*-malonyl-*β*-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1. It was named glomeraside K.

Compound **12m** had the same molecular formula as **9m**. The ^{1}H and ^{13}C NMR spectroscopic data indicated that **12m** had the same acylation pattern on the glucose ring as in compound **11m** (Tables 1 and 2). The hydroxy fatty acid methyl ester obtained from **12m** was identified as methyl 10(*R*)-hydroxydocosanoate (**16**). Thus, compound **12** was determined to be the 1,6′-cyclic ester of 10(*R*)-(2-*O*-acetyl-3-*O*-malonyl-*β*-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1. It was named glomeraside L.

Compound **13m** showed a pseudo-molecular ion at *m*/*z* 601.3933 $[M+H]^+$ in the positive HRFABMS that corresponded to the molecular formula $C_{32}H_{56}O_{10}$. The ^{1}H NMR spectrum had seven signals that corresponded to a 2,6-di-*O*-acyl-*β*-glucopyranosyl moiety (δ 4.81 for H-2′ and δ 4.38/4.29 for H_2-6′), in addition to signals for a malonate methyl ester [δ 3.78 (*s*, 3H) and 3.42 (*d*, *J* = 16.1 Hz)/3.47 (*d*, *J* = 16.1 Hz)] and an oxygenated fatty acyl group (δ 3.57) (Table 1). The 2′-*O*-malonylation was confirmed by HMBC correlations between H-2′ and H_2-2″ and the malonate C-1″ at δ 165.53. These NMR spectroscopic data, together with the fact that acetylation of **13m** furnished the peracetate **9a** allowed us to assign the structure of compound **13** as the 1,6′-cyclic ester of 11(*R*)-(2-*O*-malonyl-*β*-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1. It was named glomeraside M.

Compound **14m** had the same molecular formula as **13m**. The ^{1}H and ^{13}C NMR spectra of **13m** indicated 2′-*O*-malonylation (H-2′ at δ 4.82) and the 6′-*O*-fatty acylation (H_2-6′ at δ 4.46/4.19) on a *β*-glucopyranosyl moiety. These spectroscopic data and the fact that acetylation of **14m** furnished **10a** established that compound **14m** was the 1,6′-cyclic ester of 10(*R*)-(2-*O*-malonyl-*β*-D-glucopyranosyloxy)docosanoic acid, as depicted in Fig. 1. Compound **14** was named glomeraside N.

3. Concluding remarks

A glandular trichome exudate of *C. glomeratum* specifically contained the 14 new macrocyclic glycolipids (compounds **1**–**14**). The relative abundance of these constituents is summarized in Table 4. Glomeraside D (**4**) was the most abundant constituent (25%), followed by glomeraside G (**7**) (16%). The glomerasides were found to be unique 1,6′-cyclic esters with 19-, 18- or 17-membered ring. The oxygenation position in the docosanoyl moiety varied from C-9 to C-11, whereas the absolute configurations at the oxymethine centers were consistently *R*.

This is the first report that presents evidence of the presence of 1,6′-cyclic esters of glycosyloxy-fatty acids in the plants. The structures of glomerasides were in sharp contrast with those of gallicasides isolated from *S. gallica*, which were 1,2′-cyclic esters of (*β*-D-glucopyranosyloxy)fatty acids (Asai and Fujimoto, 2010). 1,2′-Cyclic esters of 5-(*β*-D-xylopyranosyloxy)fatty acids were, however, reported from the aerial part of *Stellaria dichotoma* (Caryophyllaceae) (Ganenko et al., 2001). The 1,2′-cyclic esters is also likely to be of glandular trichome origin, since *S. dichotoma* is known to be rich in glandular trichomes. These findings thus suggest that cyclic glycolipids are specific in glandular trichome exudates of the Caryophyllaceae family and are interesting from a chemotaxonomic point of view. Our present and previous findings also suggest that glandular trichomes have a unique capacity to introduce a hydroxy group at various positions in fatty acids and to form a glycosidic bond with the introduced hydroxy group. Examples of glycosyloxy-fatty acids have been reported in glandular trichome exudates of *I. lutea* and *P. louisiana* (Martyniaceae) (Asai et al., 2010). It appears that glandular trichomes of Caryophyllaceous plants can further convert glycosyloxy-fatty acids to macrocyclic compounds via an intramolecular lactonization. The initial hydroxylation step is reminiscent of the action of a cytochrome P450 enzyme that is associated with the formation of a hydroxy fatty acid as one of the components of cutin polyester lipids (Li-Beisson et al., 2009). Resin glycosides, most of which have a macrocyclic ring across disaccharides, are reported from the Convolvulaceae family (Pereda-Miranda et al., 2010). Investigation of secondary metabolites of glandular trichome exudates may help understand the relationships between chemical structures of glycolipids and the genera of Caryophyllaceae. Such studies are currently in progress in our laboratory.

Table 4
Relative abundance of glomerasides in the glandular trichome exudate.

Compound	Relative abundance (%)[a]
Glomeraside A (**1**)	3.7
Glomeraside B (**2**)	5.9
Glomeraside C (**3**)	3.7
Glomeraside D (**4**)	24.8
Glomeraside E (**5**)	5.4
Glomeraside F (**6**)	9.6
Glomeraside G (**7**)	16.1
Glomeraside H (**8**)	11.7
Glomeraside I (**9**)	3.7
Glomeraside J (**10**)	1.0
Glomeraside K (**11**)	8.9
Glomeraside L (**12**)	1.3
Glomeraside M (**13**)	3.1
Glomeraside N (**14**)	1.1

[a] The remainder (19.2% of the whole extract) of the exudate constituents was exclusively a mixture of wax (hydrocarbons) that was not included in the % calculation.

4. Experimental

4.1. General experimental procedures

The apparatus and conditions used for the experiments are described in our previous paper (Asai and Fujimoto, 2010), unless otherwise cited. HPLC was performed using an ODS column (Shimadzu Shim-Pack CLC-ODS, 15 cm × 4.6 mm i.d.) under isocratic solvent conditions, unless otherwise stated.

4.2. Plant material

C. glomeratum (Caryophyllaceae) were collected in May 2010 in Kawasaki city in the Kanagawa prefecture. The plant was identified by Prof. S. Kohshima (Department of Biological Sciences, Graduate School of Bioscience and Biotechnology, Tokyo Institute of Technology). A voucher specimen (CMS22–02) was deposited in the Department of Chemistry and Materials Science of the Tokyo Institute of Technology.

4.3. Extraction and isolation

Fresh upper aerial parts of *C. glomeratum* (fresh wt. 400 g) were briefly (ca. 10 s) rinsed in a beaker containing Et_2O (1.5 L), and the Et_2O solution was filtered and concentrated to dryness under reduced pressure. The residue (788 mg) was subjected to silica gel (80 g) column chromatography (CC). The column was eluted with a discontinuous gradient of hexane–EtOAc (10:1 → 0:1, total volume 1.4 L) and EtOAc–MeOH (50:1 → 3:1, total volume 450 mL). The fractions (50 mL each, a total of 36 fractions) were combined to give a non-polar fraction (152 mg, frs. 1–7, eluted with hexane–EtOAc, 10:1 → 1:1, the major substance was identified as a

mixture of hydrocarbons) and six pools (I–VI) according to the TLC profile: Pool I (70 mg, frs. 18–20, a mixture of **1**, **2** and **3**, eluted with hexane–EtOAc, 1:1), Pool II (159 mg, a mixture of **4** and **5,** frs. 21–22, eluted with hexane–EtOAc, 1:2), Pool III/IV (222 mg, frs. 23–27, eluted with hexane–EtOAc, 1:2), Pool V (54 mg, a mixture of **11** and **12**, frs. 28–33, eluted with EtOAc-MeOH, 5:1) and Pool VI (22 mg, a mixture of **13** and **14,** frs. 34–36, eluted with EtOAc–MeOH, 5:1 → 3:1). The Pool III/IV was further separated by silica gel CC with increasing polarity of hexane-EtOAc to give Pool III (195 mg, a mixture of **6**, **7** and **8**, eluted with hexane–EtOAc, 1:2) and Pool IV (23 mg, a mixture of **9** and **10**, eluted with EtOAc). A portion of Pool I (26 mg) was further separated by HPLC (MeOH–H_2O, 20:1; flow rate, 1.0 mL/min) to afford **1** (6.8 mg), **2** (11.1 mg) and **3** (6.8 mg) at 12.4, 12.8 and 13.3 min, respectively. A portion of Pool II (10 mg) was further separated by HPLC (MeOH–H_2O, 20:1; flow rate, 1.0 mL/min) to afford **4** (7.8 mg) and **5** (1.7 mg) at 13.9 and 14.7 min, respectively. A portion of Pool III (18 mg) was further separated by HPLC (MeOH–H_2O, 20:1; flow rate, 1.0 mL/min, UV detection at 215 nm) to afford **6** (3.6 mg), **7** (6.0 mg) and **8** (4.4 mg) at 12.4, 12.8and 13.4 min, respectively.

A portion of Pool IV (12 mg) in Et_2O (100 μL) and MeOH (40 μL) was treated with $TMSCH_2N_2$ in hexane (0.6 M solution, 40 μL) at room temperature for 30 min. Removal of the solvent by flushing with N_2, followed by purification by silica gel CC (eluted with hexane–EtOAc 2:1), yielded a mixture of methyl esters **9m** and **10m** (11 mg). A portion of Pool V (10 mg) was similarly converted to a mixture of methyl esters **11m** and **12m** (9.0 mg). A portion of Pool VI (14 mg) was dissolved in EtOAc (200 μL) and ethereal CH_2N_2 was added until a yellow color persisted. Removal of the solvent by flushing with N_2 followed by purification by silica gel CC (eluted with hexane–EtOAc 1:1) yielded a mixture of methyl esters **13m** and **14m** (11 mg). An aliquot (10 mg) of these was separated by HPLC (MeOH–H_2O, 20:1; flow rate, 1.0 mL/min) to afford **9m** (7.4 mg) and **10m** (1.8 mg) at 13.4 and 14.0 min, respectively. The mixture of the methyl esters **11m** and **12m** (17 mg) was separated by HPLC (MeOH–H_2O, 20:1; flow rate, 1.0 mL/min) to afford **11m** (12 mg) and **12m** (1.8 mg) at 15.3 and 15.9 min, respectively. The mixture of the methyl esters **13m** and **14m** (10 mg) was separated by HPLC (MeOH–H_2O, 20:1; flow rate, 1.0 mL/min) to afford **13m** (5.7 mg) and **14m** (2.0 mg) at 11.8 and 12.3 min, respectively.

4.4. Glomeraside A (*1*)

Colorless oil; (+)-HRFABMS *m/z*: 543.3894 $[M+H]^+$ (calcd for $C_{30}H_{55}O_8$, 543.3897); $[\alpha]_D^{25}$ – 9.2 (*c* = 0.60, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3590, 3440, 2930, 2860, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **1** (3.0 mg) was hydrolyzed as described in our previous paper (Asai and Fujimoto, 2010) to give glucose and a hydroxy-fatty acid. Glucose was identified by TLC and GC–MS as described in our previous paper (Asai and Fujimoto, 2010; Asai et al., 2009). Treatment of the hydroxy-fatty acid with ethereal CH_2N_2 gave, after PTLC purification (hexane–EtOAc, 6:1), methyl 11(*R*)-hydroxydocosanoate **15** (1.3 mg). Amorphous; EIMS *m/z*: 352 ($[M–H_2O]^+$, 1), 339 ($[M–MeO]^+$, 2), 320 ($[M–H_2O–MeO]^+$, 10), 215 (C-11/C-12 cleavage, 42), 186 (45), 183 (215–MeOH, 42), 143 (23), 87 (42); ^1H NMR ($CDCl_3$) *δ*: 3.67 (*s*, OMe), 3.59 (*m*, H-11), 2.30 (*t*, *J* = 7.6 Hz, H_2-2), 1.65-1.25 (*m*), 0.88 (*t*, *J* = 7.8 Hz, H_3-22).

A portion of **15** was converted to the corresponding TMS ether as described previously (Asai and Fujimoto, 2010) and analyzed by GLC and EIMS. EIMS of TMS derivative of **15**: *m/z* 427 ($[M–Me]^+$, 9), 411 ($[M–MeO]^+$, 10), 395 (28), 287 (C-11/C-12 cleavage, 100), 257 (C-10/C-11 cleavage, 100), 129 (31), 73 (65), 57 (36).

Compound **1** (2.2 mg) was treated with Ac_2O (20 μL) and pyridine (40 μL) at room temperature overnight. Removal of the solvent by flushing with N_2 and purification of the crude product by PTLC (hexane–EtOAc, 3:1) gave the peracetyl derivative **1a** (2.5 mg): Colorless oil; $[\alpha]_D^{25}$ – 1.0 (*c* = 0.22, $CHCl_3$); IR ($CHCl_3$) ν_{max} 2930, 2860, 1720 cm^{-1}; (+)-HRFABMS *m/z*: 649.3950 $[M+Na]^+$ (calcd for $C_{34}H_{58}O_{10}Na$, 649.3928); ^1H NMR *δ*: 0.88 (*t*, *J* = 6.9 Hz, H_3-22), 1.52-1.20 (*m*), 1.63 (*m*, Ha-3), 1.75 (*m*, Hb-3), 2.00 (*s*, Ac), 2.02 (*s*, Ac), 2.03 (*s*, Ac), 2.32 (*ddd*, *J* = 11.7, 9.4, 4.5 Hz, Ha-2), 2.43 (*ddd*, *J* = 11.7, 8.0, 4.5 Hz, Hb-2), 3.56 (*m*, H-11), 3.69 (*m*, H-5′), 4.09 (*dd*, *J* = 12.3, 4.6 Hz, Ha-6′), 4.15 (*dd*, *J* = 12.3, 1.9 Hz, Hb-6′), 4.53 (*d*, *J* = 8.0 Hz, H-1′), 4.98 (*dd*, *J* = 9.7, 8.0 Hz, H-2′), 5.10 (*t*, *J* = 9.7 Hz, H-4′), 5.20 (*t*, *J* = 9.7 Hz, H-3′), ^{13}C NMR *δ*: 14.11, 20.63, 20.65, 20.68, 22.68, 24.33, 24.35, 25.09, 26.88, 27.29, 27.52, 27.64, 28.14, 29.34, 29.61, 29.65 (x2), 29.68, 29.93, 31.90, 34.12, 34.44, 34.60, 62.22, 68.28, 71.46, 71.77, 73.14, 80.85, 100.34, 169.28, 169.31, 170.43, 173.94.

4.5. Glomeraside B (*2*)

Colorless oil; (+)-HRFABMS *m/z*: 543.3919 $[M+H]^+$ (calcd for $C_{30}H_{55}O_8$, 543.3897); $[\alpha]_D^{25}$ – 6.3 (*c* = 1.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3590, 3440, 2930, 2860, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Methyl 10(*R*)-hydroxydocosanoate **16** (0.8 mg) was obtained from **2** (2.0 mg) in the same manner as described for **1**. EIMS *m/z*: 352 ($[M–H_2O]^+$, 1), 339 ($[M–MeO]^+$, 2), 320 ($[M–H_2O–MeO]^+$, 10), 201 (C-10/C-11 cleavage, 53), 172 (46), 169 (201–MeOH) (100), 143 (14), 87 (42), 55 (24); ^1H NMR ($CDCl_3$) *δ*: 3.67 (*s*, OMe), 3.59 (*m*, H-10), 2.30 (*t*, *J* = 7.6 Hz, H_2-2), 1.65-1.25 (*m*), 0.88 (*t*, *J* = 6.7 Hz, H_3-22). A portion of **16** (0.1 mg) was converted into the corresponding TMS ether in the same manner as that described for **15** and was analyzed by GLC and EIMS. EIMS of the TMS derivative of **16**: *m/z* 427 ($[M–Me]^+$, 9), 411 ($[M–MeO]^+$, 10), 395 (28), 287 (C-11/C-12 cleavage, 100), 257 (C-10/C-11 cleavage, 100), 129 (31), 73 (65), 57 (36).

Compound **2** (2.2 mg) was converted to the corresponding acetate **2a** (2.4 mg) following the procedure described for compound **1**: Colorless oil; $[\alpha]_D^{25}$ – 5.0 (*c* = 0.24, $CHCl_3$); IR ($CHCl_3$) ν_{max} 2930, 2860, 1720 cm^{-1}; (+)-HRFABMS *m/z*: 649.3906 $[M+Na]^+$ (calcd for $C_{34}H_{58}O_{10}Na$, 649.3928); ^1H NMR ($CDCl_3$) *δ*: 0.88 (*t*, *J* = 6.9 Hz, H_3-22), 1.49-1.20 (*m*), 1.65 (*m*, Ha-3), 1.71 (*m*, Hb-3), 2.01 (*s*, Ac), 2.03 (*s*, Ac (x2)), 2.37 (*m*), 3.58 (*m*, H-10), 3.69 (*m*, H-5′), 3.97 (*dd*, *J* = 12.1, 5.5 Hz, Ha-6′), 4.23 (*dd*, *J* = 12.1, 1.9 Hz, Hb-6′), 4.57 (*d*, *J* = 8.0 Hz, H-1′), 4.98 (*dd*, *J* = 9.7, 8.0 Hz, H-2′), 5.07 (*t*, *J* = 9.7 Hz, H-4′), 5.21 (*t*, *J* = 9.7 Hz, H-3′); ^{13}C NMR *δ*:14.13, 20.66 (x2), 20.70, 22.69, 23.66, 24.37, 25.05, 26.21, 26.59, 27.00, 27.09, 29.36, 29.65, 29.67 (x3), 29.71, 29.90, 31.92, 33.82, 34.01, 34.36, 62.28, 68.59, 71.26, 71.83, 73.18, 80.20, 100.24, 169.30, 169.37, 170.45, 173.91.

4.6. Glomeraside C (*3*)

Colorless oil; (+)-HRFABMS *m/z*: 543.3807 $[M+H]^+$ (calcd for $C_{30}H_{55}O_8$, 543.3897); $[\alpha]_D^{25}$ 0 (*c* = 0.68, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3590, 3440, 2930, 2860, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Methyl 9(*R*)-hydroxydocosanoate **17** (0.8 mg) was obtained from **3** (2.0 mg) in the same manner as that described for **1**. **17**: EIMS *m/z*: 352 ($[M–H_2O]^+$, 1), 339 ($[M–MeO]^+$, 2), 320 ($[M–H_2O–MeO]^+$, 10), 187 (C-9/C-10 cleavage, 45), 158 (45), 155 (188–MeOH, 100), 87 (30), 55 (20); ^1H NMR ($CDCl_3$) *δ*: 3.67 (*s*, OMe), 3.59 (*m*, H-9), 2.30 (*t*, *J* = 7.6 Hz, H_2-2), 1.65-1.25 (*m*), 0.88 (*t*, *J* = 7.8 Hz, H_3-22). A portion of the methyl ester **17** was converted to the corresponding TMS ether in the same manner as described for **15** and analyzed by GLC and EIMS. EIMS of the TMS derivative of **17**: *m/z* 427 ($[M–Me]^+$, 9), 411 ($[M–MeO]^+$, 12), 395 (12), 285 (C-8/C-9 cleavage, 100), 259 (C-9/C-10 cleavage, 100), 129 (28), 73 (55), 57 (53).

Compound **3** (3.0 mg) was converted into the corresponding acetate **3a** (2.1 mg) following the procedure described for compound **1**. Colorless oil; $[\alpha]_D^{25}$ – 18.1 (*c* = 0.21, $CHCl_3$); IR ($CHCl_3$) ν_{max} 2930, 2860, 1720 cm^{-1}; (+)-HRFABMS *m/z*: 649.3953 $[M+Na]^+$ (calcd for $C_{34}H_{58}O_{10}Na$, 649.3928); ^1H NMR δ: 0.88 (*t*, *J* = 6.9 Hz, H_3-22), 1.50-1.20 (*m*), 1.60 (*m*, Ha-3), 1.70 (*m*, Hb-3), 2.00 (*s*, Ac), 2.03 (*s*, Ac), 2.04 (*s*, Ac), 2.39 (*t*, *J* = 6.0 Hz, H_2-2), 3.50 (*m*, H-9), 3.79 (*m*, H-5′), 4.08 (*dd*, *J* = 12.1, 7.2 Hz, Ha-6′), 4.12 (*dd*, *J* = 12.1, 2.6 Hz, Hb-6′), 4.54 (*d*, *J* = 8.0 Hz, H-1′), 4.95 (*t*, *J* = 9.8 Hz, H-4′), 4.96 (*dd*, *J* = 9.8, 8.0 Hz, H-2′), 5.21 (*t*, *J* = 9.8 Hz, H-3′); ^{13}C NMR δ: 14.11, 20.63 (x2), 20.68, 22.68, 23.25, 24.42, 25.38, 26.90, 27.17, 27.54, 29.35, 29.65 (x4), 29.68 (x2), 29.87, 31.91, 34.25 (x2), 35.24, 63.21, 69.01, 71.54, 71.85, 72.99, 82.57, 100.86, 169.19, 169.46, 170.37, 173.77.

4.7. Glomeraside D (*4*)

Colorless oil; (+)-HRFABMS *m/z*: 543.3881 $[M+H]^+$ (calcd for $C_{30}H_{55}O_8$, 543.3897); $[\alpha]_D^{25}$ – 26.1 (*c* = 1.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3590, 3440, 2930, 2860, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **4** (2.0 mg) was converted into the peracetate (2.1 mg) in the same manner as described for **1**. The peracetate was identified as **2a** by ^1H and ^{13}C NMR, FABMS and HPLC. HPLC identification of the peracetate with **1a** was carried out as follows. The peracetates **1a**, **2a** and **3a** could not be separated using routine ODS columns (with either MeOH–H_2O or CH_3CN–H_2O as the elution solvents), but were separated with an Inertsil ODS-P column (GL Science Inc., 4.6 × 15 cm, solvent CH_3CN, flow rate 0.8 L/min, UV detection at 215 nm). The retention times for **1a**, **2a** and **3a** were 9.43, 10.05 and 10.80 min, respectively.

4.8. Glomeraside E (*5*)

Colorless oil; (+)-HRFABMS *m/z*: 543.3901 $[M+H]^+$ (calcd for $C_{30}H_{55}O_8$, 543.3897); $[\alpha]_D^{25}$ – 21.3 (*c* = 0.15, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3590, 3440, 2930, 2860, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **5** (1.7 mg) was converted into the corresponding peracetate (1.8 mg) in the same manner as described for **1**. The peracetate was identified as **2a** by ^1H and ^{13}C NMR, FABMS and HPLC.

4.9. Glomeraside F (*6*)

Colorless oil; (+)-HRFABMS *m/z*: 501.3804 $[M+H]^+$ (calcd for $C_{28}H_{53}O_7$, 501.3791); $[\alpha]_D^{25}$ – 27.8 (*c* = 0.36, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3590, 3440, 2930, 2860, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **6** (1.8 mg) was converted into the corresponding peracetate (2.0 mg) in the same manner as described for **1**. The peracetate was identified as **1a** by ^1H and ^{13}C NMR, FABMS and HPLC.

4.10. Glomeraside G (*7*)

Colorless oil; (+)-HRFABMS *m/z*: 501.3825 $[M+H]^+$ (calcd for $C_{28}H_{53}O_7$, 501.3791); $[\alpha]_D^{25}$ – 25.5 (*c* = 0.60, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3590, 3440, 2930, 2860, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **7** (2.1 mg) was converted into the corresponding peracetate (2.2 mg) in the same manner as described for **1**. The peracetate was identified as **2a** by ^1H and ^{13}C NMR, FABMS and HPLC.

4.11. Glomeraside H (*8*)

Colorless oil; (+)-HRFABMS *m/z*: 501.3782 $[M+H]^+$ (calcd for $C_{28}H_{53}O_7$, 501.3791); $[\alpha]_D^{25}$ – 16.0 (*c* = 0.44, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3590, 3440, 2930, 2860, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **8** (2.2 mg) was converted to the corresponding peracetate (2.2 mg) in the same manner as described for **1**. The peracetate was identified as **3a** by ^1H and ^{13}C NMR, FABMS and HPLC.

4.12. Glomeraside I methyl ester (*9m*)

Colorless oil; (+)-HRFABMS *m/z*: 643.4080 $[M+H]^+$ (calcd for $C_{34}H_{59}O_{11}$, 643.4057); $[\alpha]_D^{25}$ – 17.2 (*c* = 0.29, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3500, 2930, 2860, 1760, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **9m** (3.0 mg) was converted into a hydroxy fatty acid methyl ester (1.1 mg) that was identified as methyl 11(*R*)-hydroxydocosanoate **15** by TLC, EIMS of the TMS ether derivative and ^1H NMR of the (*R*)-ACC ester.

Compound **9m** (2.5 mg) was converted into the corresponding peracetate **9a** (2.6 mg) in the same manner as described for **1**. **9a**: Colorless oil; (+)-HRFABMS *m/z*: 685.4143 $[M+H]^+$ (calcd for $C_{36}H_{61}O_{12}$, 685.4163); $[\alpha]_D^{25}$ – 5.9 (*c* = 0.34, $CHCl_3$); IR ($CHCl_3$) ν_{max} 2930, 2860, 1750 cm^{-1}; ^1H NMR δ: 0.88 (*t*, *J* = 7.0 Hz, H_3-22), 1.50-1.20 (*m*), 1.63 (*m*, H_a-3), 1.76 (*m*, H_b-3), 2.02 (*s*, Ac), 2.04 (*s*, Ac), 2.32 (*ddd*, *J* = 14.5, 9.0, 4.0 Hz, Ha-2), 2.43 (*ddd*, *J* = 14.5, 8.0, 4.5 Hz, Hb-2), 3.34 (*s*, H-2″), 3.56 (*m*, H-11), 3.69 (*m*, H-5′), 3.72 (*s*, OMe), 4.09 (*dd*, *J* = 12.0, 4.5 Hz, Ha-6′), 4.16 (*dd*, *J* = 12.0, 2.0 Hz, Hb-6′), 4.54 (*d*, *J* = 8.0 Hz, H-1′), 5.03 (*dd*, *J* = 9.5, 8.0 Hz, H-2′), 5.10 (*t*, *J* = 9.5 Hz, H-4′), 5.23 (*t*, *J* = 9.5 Hz, H-3′); ^{13}C NMR δ: 14.10, 20.60, 20.62, 22.68, 24.34 (x2), 25.20, 26.89, 27.32, 27.53, 27.66, 28.14, 29.35, 29.62, 29.67 (x3), 29.89, 31.90, 34.09, 34.38, 34.53, 41.08, 52.55, 62.16, 68.37, 71.56, 72.43, 72.61, 80.76, 99.99, 164.73, 166.29, 169.31, 170.44, 173.90.

4.13. Glomeraside J methyl ester (*10m*)

Colorless oil; (+)-HRFABMS *m/z*: 643.4030 $[M+H]^+$ (calcd for $C_{34}H_{59}O_{11}$, 643.4057); $[\alpha]_D^{25}$ – 13.3 (*c* = 0.07, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3500, 2930, 2860, 1760, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **10m** (1.7 mg) was converted into the corresponding peracetate **10a** (1.7 mg) in the same manner as described for **1**. **10a**: Colorless oil; (+)-HRFABMS *m/z*: 685.4176 $[M+H]^+$ (calcd for $C_{36}H_{61}O_{12}$, 685.4163); $[\alpha]_D^{25}$ 0 (*c* = 0.15, $CHCl_3$); IR ($CHCl_3$) ν_{max} 2930, 2860, 1750 cm^{-1}; ^1H NMR δ: 0.88 (*t*, *J* = 7.0 Hz, H_3-22), 1.49-1.20 (*m*), 1.65 (*m*, H_a-3), 1.70 (*m*, H_b-3), 2.03 (*s*, Ac), 2.04 (*s*, Ac), 2.36 (*m*, H_2-2), 3.34 (*s*, H-2″), 3.59 (*m*, H-10), 3.69 (*m*, H-5′), 3.72 (*s*, OMe), 3.97 (*dd*, *J* = 12.0, 5.5 Hz, Ha-6′), 4.24 (*dd*, *J* = 12.0, 2.0 Hz, Hb-6′), 4.57 (*d*, *J* = 8.0 Hz, H-1′), 5.03 (*dd*, *J* = 9.5, 8.0 Hz, H-2′), 5.07 (*t*, *J* = 9.5 Hz, H-4′), 5.23 (*t*, *J* = 9.5 Hz, H-3′); ^{13}C NMR δ: 14.11, 20.62 (x2), 22.68, 23.67, 24.37, 25.14, 26.27, 26.58, 27.00, 27.11, 29.35, 29.65, 29.67, 29.68 (x3), 29.86, 31.92, 33.85, 33.96, 34.29, 41.08, 52.56, 62.19, 68.66, 71.33, 72.47, 72.65, 80.00, 99.82, 164.74, 166.31, 169.36, 170.46, 173.87.

Compound **10a** (1.6 mg) was converted into a hydroxy fatty acid methyl ester (0.4 mg) that was identified as methyl 10(*R*)-hydroxydocosanoate **16** by TLC, EIMS of the TMS ether derivative and ^1H NMR of the (*R*)-ACC ester.

4.14. Glomeraside K methyl ester (*11m*)

Colorless oil; (+)-HRFABMS *m/z*: 643.4069 $[M+H]^+$ (calcd for $C_{34}H_{59}O_{11}$, 643.4057); $[\alpha]_D^{25}$ – 24.7 (*c* = 0.60, $CHCl_3$); IR ($CHCl_3$) ν_{max}

3500, 2930, 2860, 1760, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

Compound **11m** (3.0 mg) was converted into a hydroxy-fatty acid methyl ester (1.1 mg) that was identified as 11(*R*)-hydroxydocosanoate **15** by TLC, EIMS of TMS ether derivative and ^1H NMR of the (*R*)-ACC ester.

4.15. Glomeraside L methyl ester (*12m*)

Colorless oil; (+)-HRFABMS *m/z*: 643.4086 $[M+H]^+$ (calcd for $C_{34}H_{59}O_{11}$, 643.4057); $[\alpha]_D^{25}$ – 36.7 (*c* = 0.03, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3500, 2930, 2860, 1760, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2. Compound **12m** (1.7 mg) was converted into a hydroxy fatty acid methyl ester (0.5 mg) that was identified as methyl 10(*R*)-hydroxydocosanoate **16** by TLC, EIMS of the TMS ether derivative and ^1H NMR of the (*R*)-ACC ester.

4.16. Glomeraside M methyl ester (*13m*)

Colorless oil; (+)-HRFABMS *m/z*: 601.3933 $[M+H]^+$ (calcd for $C_{32}H_{57}O_{10}$, 601.3952); $[\alpha]_D^{25}$ – 16.9 (*c* = 0.38, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3580, 3500, 2930, 2860, 1760, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **13m** (2.0 mg) was converted into the corresponding peracetate (1.7 mg) in the same manner as described for **1**. The peracetate was identified as **9a** by ^1H and ^{13}C NMR, FABMS and HPLC. HPLC identification of the peracetate with **9a** was carried out as follows. The peracetates **9a** and **10a** were separated using an Inertsil ODS-P column (conditions: CH_3CN–H_2O 40:1, at a flow rate of 0.8 L/min, UV detection at 215 nm). The retention times for **9a** and **10a** were 9.95 and 10.52 min, respectively.

4.17. Glomeraside N methyl ester (*14m*)

Colorless oil; (+)-HRFABMS *m/z*: 601.3941 $[M + H]^+$ (calcd for $C_{32}H_{57}O_{10}$, 601.3952); $[\alpha]_D^{25}$ – 11.1 (*c* = 0.17, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3580, 3500, 2930, 2860, 1760, 1720 cm^{-1}; for ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2, respectively.

Compound **14m** (2.0 mg) was converted to the corresponding acetate (1.7 mg) in the same manner as described for **1**. The peracetate was identified as **10a** by ^1H and ^{13}C NMR, FABMS and HPLC.

4.18. Determination of the configuration at the oxymethine center of the methyl 11-, 10-, and 9-hydroxydocosanoates *15*, *16* and *17*

The methyl ester **15** (0.5 mg) was treated with (*R*)-ACC acid (3 mg), EDC (6 mg) and dimethylaminopyridine (0.5 mg) in CH_3CN (50 μL)-toluene (50 μL) for two days at room temperature. After removal of the solvent by flushing with N_2, the product was purified by p-TLC (developing solvent: $CHCl_3$–hexane, 1:3) to yield the oily (*R*)-ACC derivative **15b** in good yield. Reaction of **15** with the (*S*)-ACC acid instead of (*R*)-ACC acid gave the (*S*)-ACC derivative **15c**. Compounds **16** and **17** were similarly converted into the corresponding derivatives **16b** and **16c**, and **17b** and **17c**. **16b**: (+)-FABMS *m/z*: 726 $[M+H]^+$; ^1H NMR δ: 8.62 (2H, *s*), 8.47 (2H, *s*), 8.08 ((2H, *m*), 7.61 (2H, *m*), 4.73 (1H, *m*), 4.48 (1H, *td*, 12.0, 3.5 Hz), 3.67 (3H, *s*, OCH_3), 3.56 (1H, *td*, 12.0, 3.5 Hz), 2.20 (2H, *t*, *J* = 7.5 Hz, H_2-2), 2.18 (1H, *m*), 1.87 (2H, *m*), 1.50-0.84 (5H, *m*), 0.867 (3H, *t*, *J* = 7.2 Hz). The chemical shifts of the key ^1H signals of these derivatives are summarized in Table 3.

Stereochemically defined methyl 10(*R*)-hydroxydocosanoate **16**, $[\alpha]_D^{25}$ – 0.2 (*c* = 2.8, $CHCl_3$), was synthesized by reacting (*S*)-10,11-epoxyundecanoic acid methyl ester with undecanylmagnesium bromide in the presence of CuI according to a published protocol (Ohtaki et al., 2005). The (*S*)-epoxide was obtained by kinetic resolution of the racemic epoxide according to a published method (Schaus et al., 2002), which was prepared by *m*-CPBA treatment of methyl undec-10-enoate.

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