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New Phenolic Glycerol Glucosides, Regaloside D, E, and F from the Bulbs of *Lilium* Species

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New phenolic glycerol glucosides, regalosides D and E were isolated from the fresh bulbs of *Lilium longiflorum*, and regaloside F from those of *L. lancifolium*, along with previously known compounds. Their structures were elucidated, on the basis of the spectroscopic data and chemical evidences, and by comparing them with those of known compounds, as (2*S*)-1-*O*-*p*-coumaroyl-2-*O*-*β*-D-glucopyranosylglycerol, (2*S*)-1-*O*-caffeoyl-2-*O*-*β*-D-glucopyranosyl-3-*O*-acetylglycerol, and (2*S*)-1-*O*-feruloyl-3-*O*-*β*-D-glucopyranosylglycerol, respectively.

Keywords——*Lilium longiflorum*; *Lilium lancifolium*; Liliaceae; phenolic glycerol glucoside; regaloside D; regaloside E; regaloside F; bitter principle; bulb

Plants of the genus *Lilium* have long been used both as a food and as a medicinal agent,[1] and also in certain religious rituals in Japan. In our continuous studies on the chemical ingredients of lily bulbs, we isolated and determined the structures of bitter phenolic glycosides,[2-4] an antitumor alkaloid and its glucoside,[5] phenolic glycerides,[6] and a steroid glucoside.[4] The phenolic glycosides are considered to be the main bitter principles of the bulbs of *L. speciosum* var. *rubrum*, *L. regale* and *L. henryi*. In the present work, we investigated the bulbs of *L. longiflorum* THUNB. and *L. lancifolium* THUNB. According to the Chinese herbars, both lilies have been used as medicinal material.[1,7] *L. longiflorum* is a popular lily in Japan, from the bulbs of which Nishioka isolated growth inhibitory compounds.[8,9] This paper describes the isolation of new phenolic glycerol glucosides, regaloside D and E from *L. longiflorum*, and regaloside F from *L. lancifolium*. Their structures were determined by spectroscopic and chemical means, and by comparing the data with those of known compounds. Also reported here are several known compounds.

Results

Lilium longiflorum

A methanolic extract of the fresh bulbs of *L. longiflorum* was partitioned between chloroform and water, and the water phase was extracted with *n*-butanol. Silica gel and Sephadex LH-20 column chromatographies were used for the purification of the crude extracts to provide compounds **1**–**9**.

Compounds **1**–**4** were phenolic glycerides and identified as 1, 3-*O*-diferuloylglycerol, 1-*O*-feruloyl-3-*O*-*p*-coumaroylglycerol, 1-*O*-feruloylglycerol and 1-*O*-*p*-coumaroylglycerol, respectively, by the proton nuclear magnetic resonance (^{1}H-NMR) spectra and electron impact mass spectra (EI-MS).[6,10,11] Compounds **5** and **6** were bitter phenolic glycosides, and the structures were elucidated as 3, 6′-*O*-diferuloylsucrose and 4-*O*-acetyl-3, 6′-*O*-diferuloylsucrose on the basis of the spectroscopic data and direct comparison with respective authentic samples isolated previously.[2,12,13] Compound **7** was identified as (2*S*)-1-*O*-*p*-coumaroyl-2-*O*-*β*-D-glucopyranosyl-3-*O*-acetylglycerol (regaloside B).[3]

Compound **8** was a pale-yellow amorphous powder and bitter to the taste. The infrared (IR) spectrum suggested the presence of hydroxyl group(s) (3400 cm^{-1}), a carbonyl group of *α*, *β*-unsaturated ester (1690 cm^{-1}), an alkene conjugated with an aromatic ring (1632 cm^{-1}), and an aromatic ring (1605, 1587 and 1520 cm^{-1}). The EI-MS of **8** exhibited a molecular ion peak at *m*/*z* 400 and significant fragment ion peaks at *m*/*z* 164 and 147, corresponding to *p*-coumaric acid and *p*-coumaroyl unit, respectively. The presence of *p*-coumaroyl moiety in the molecule was shown by the ultraviolet (UV) (λ_{max} 300 shoulder (sh) and 312 nm) and ^{1}H-NMR (*trans* alkene protons; δ 7.66 and 6.34, each 1H, d, J = 15.9 Hz, *p*-disubstituted aromatic protons; δ 7.47 and 6.80, each 2H, d, J = 8.6 Hz) spectra. The glucosidic linkage was easily deduced to be of *β*-orientation from the anomeric proton signal at δ 4.48 with a coupling constant, J =

7.7 Hz in the ^{1}H-NMR spectrum, and also from the characteristic six carbon signals (δ 104.2, 75.0, 78.0, 71.6, 77.9 and 62.7) in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum. The above spectral properties and TLC behavior were quite similar to those of regaloside A (**13**). However, in the ^{1}H-NMR spectrum, the chemical shift of the anomeric proton of **8** was different from that of regaloside A (**8**; δ 4.48, regaloside A; δ 4.30). Compound **8** and regaloside A were, therefore, assumed to be isomeric at the glucosidation position on glycerol. When **8** was submitted to alkaline hydrolysis with sodium methoxide, **8** was cleaved to yield methyl *p*-coumarate and glycerol glucoside, which was identified as 2-*O*-β-D-glucopyranosylglycerol.[3,16] In addition, in the ^{13}C-NMR spectrum of **8**, the signal assignable to the C-2 of glycerol was shifted downfield (δ 79.5), while that of the C-3 was shifted upfield (δ 63.4) as compared with those in regaloside A (**13**) (C-2; δ 69.7, C-3; δ 72.0). On the basis of these findings, **8** was concluded to be 1-*O*-*p*-coumaroyl ester of 2-*O*-β-D-glucopyranosylglycerol. The above conclusion was finally confirmed by the fact that the spectral data of the hexaacetate (**8a**) of **8** and of regaloside B peracetate were the same.[3] Compound **8** was treated with β-glucosidase to give D-glucose and a phenolic monoglyceride, which was identical with (2*S*)-1-*O*-*p*-coumaroylglycerol (**8b**), and the specific rotation of which was the same as that of the glyceride obtained by the enzymatic hydrolysis of regaloside A (**13**).[3] Accordingly, **8** was identified as (2*S*)-1-*O*-*p*-coumaroyl-2-*O*-β-D-glucopyranosylglycerol, and designated as regaloside D.

Compound **9** was a minor component and obtained as a pale-yellow amorphous powder. The spectral data of **8** and **9** were similar. The IR spectrum of **9** indicated the presence of an ester carbonyl group (1715 cm^{-1}), and the ^{1}H-NMR spectrum showed a signal ascribable to an aliphatic acetoxyl group at δ 2.07. The occurrence of an acetoxyl group was also shown by the ^{13}C-NMR signals at δ 172.7 and 20.8. Three aromatic protons (δ 7.05, 6.96 and 6.77) ascribable to an ABC system, along with *trans* olefin signals at δ 7.59 and 6.27 (each 1H, d, J = 15.9 Hz) in the ^{1}H-NMR spectrum and the results of alkaline hydrolysis of **9** indicated that **9** possessed a caffeoyl moiety as a phenylpropanoid in it. Acetylation of **9** yielded a peracetate (**9a**), the ^{1}H-NMR spectrum of which confirmed the presence of five aliphatic acetoxyl groups and two aromatic acetoxyl groups. The ^{13}C-NMR signals of glucose and glycerol units were in good agreement with those of regaloside B (**7**). The glucose residue was determined to be attached to the C-2 position of glycerol forming β-orientation and the acetyl group to the C-3 position. The absolute configuration of the glycerol C-2 could not be determined by the same method as in regaloside B (**7**)[3] because of its low yield. However, it was presumed to be *S*, because regaloside B and D, isolated from the same sourse, had *S* configuration and the ^{13}C chemical shifts of the glycerol glucoside moiety of **9** were in good agreement with those of regaloside B (**7**). Thus, **9** was determined to be (2*S*)-1-*O*-caffeoyl-2-*O*-β-D-glucopyranosyl-3-*O*-acetylglycerol, and named regaloside E.

Lilium lancifolium

A methanolic extract of the fresh bulbs of *L. lancifolium* was treated in the same way as those of *L. longiflorum* to give compounds **3**–**5**, and **10**–**14**.

Compound **10** was isolated as a trace constituent and identified as 1-*O*-caffeoylglycerol, which was previously detected in *Ananas comosus* var. *cayenne*.[10] This compound was isolated from a Liliaceae plant for the first time. Based on their spectroscopic data and by direct comparison with commercially available authentic samples, compounds **11** and **12** were assigned to be 2′-deoxyadenosine and methyl α-D-mannopyranoside, respectively, the occurrence of which seems to be specific to *L. lancifolium* of *Lilium* plants. Compound **13** was identified as (2*S*)-1-*O*-*p*-coumaroyl-3-*O*-β-D-glucopyranosylglycerol (regaloside A).[3,4]

The ^{1}H-NMR and ^{13}C-NMR spectra of **14** resembled those of regaloside A (**13**) except the aromatic region signals caused by the phenylpropanoid moiety. The hexaacetate (**14a**) of **14** showed the signals of five aliphatic and one aromatic acetoxyl groups. Comparison of ^{13}C-NMR spectra of **14** with those of regaloside A revealed that **14** had the same glycerol substitution as regaloside A. The alkaline methanolysis of **14** with 3% sodium methoxide in methanol yielded methyl ferulate and glycerol glucoside. The latter product was subsequently acetylated to give a hexaacetate, identical with lilioside C hexaacetate (**14b**).[3,4,14] Accordingly, **14** was identified as (2*S*)-1-*O*-feruloyl-3-*O*-β-D-glucopyranosylglycerol, and designated as regaloside F.

Discussion

The bulbs of *L. lancifolium* have a bittersweet taste, while those of *L. longiflorum* a bitter taste. The bitter taste of some lily bulbs is said to be due to magnesium salts in the bulbs.[15] However, we have concluded that the bitter taste is due to the phenolic glycosides such as phenylpropanoid sucrose esters and

phenolic glycerol glucosides, that is, regalosides, and not due to inorganic salts, because only *n*-butanol soluble phases of the bulb extracts exhibit a bitter taste. The phenolic glycoside content in the bulbs of *L. longiflorum* is quite sufficient to render it bitter.

Regalosides are glycerol glucosides in which the glycerol unit is esterified with phenylpropanoid. Glucose moiety is linked to the glycerol C-2 position in regalosides B, D and E obtained from *L. longiflorum*, and to the glycerol C-3 position in regalosides A and F obtained from *L. lancifolium*: the glucoside residue links to either C-2 or C-3 of the glycerol moiety depending on the species of the original plant. Kaneda reported new glycerol glucosides, liliosides A and B from aerial parts of *L. longiflorum* and lilioside C from those of *L. lancifolium* to be characteristic constituents of the genus *Lilium*.[14,16,17] In the present investigation, no lilioside could be detected in the bulbs. However, the regalosides and liliosides from the same species were found to have corresponding structures as to the position of glucosidation. Further studies on the chemical constituents of some *Lilium* species are now being performed in our laboratory.

Experimental

All melting points were determined on a Yazawa micro melting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260–30 or JASCO A-302 spectrometer, UV spectra on a Hitachi 557 spectrometer and mass spectra on a Hitachi M-80 machine. Optical rotations were measured with a JASCO DIP-360 automatic polarimeter. ^{1}H-NMR spectra were taken with a Varian EM-390 (90 MHz) or a Bruker AM-400 (400 MHz), and ^{13}C-NMR spectra with a Bruker AM-400 (100.6 MHz) spectrometers. Chemical shifts were given in ppm (δ) relative to the internal standard TMS. The abbreviations used are as follows; s, singlet; d, doublet; dd, doublet of doublets; m, multiplet; br, broad. Column chromatographies were carried out on Fuji Davison silica gel BW-300 (200–400 mesh, Fuji Davison Co., Ltd.) and on Sephadex LH-20 (25–100 μm, Pharmacia Fine Chemicals Co., Ltd.). Thin-layer chromatography (TLC) was performed on precoated Kieselgel 60 F_{254} (0.25 mm thick, Merck), and the spots were visualized under UV light (254 nm) and by spraying 10% H_2SO_4 followed by heating. Authentic samples, 2′-deoxyadenosine and methyl α-D-mannopyranoside were purchased from Wako Pure Chemical Industries, Ltd.

Plant materials——Fresh bulbs of *L. longiflorum* were purchashed from Heiwaen Co. (Nara Prefecture in Japan), and those of *L. lancifolium* were collected in Wajima (Ishikawa prefecture in Japan).

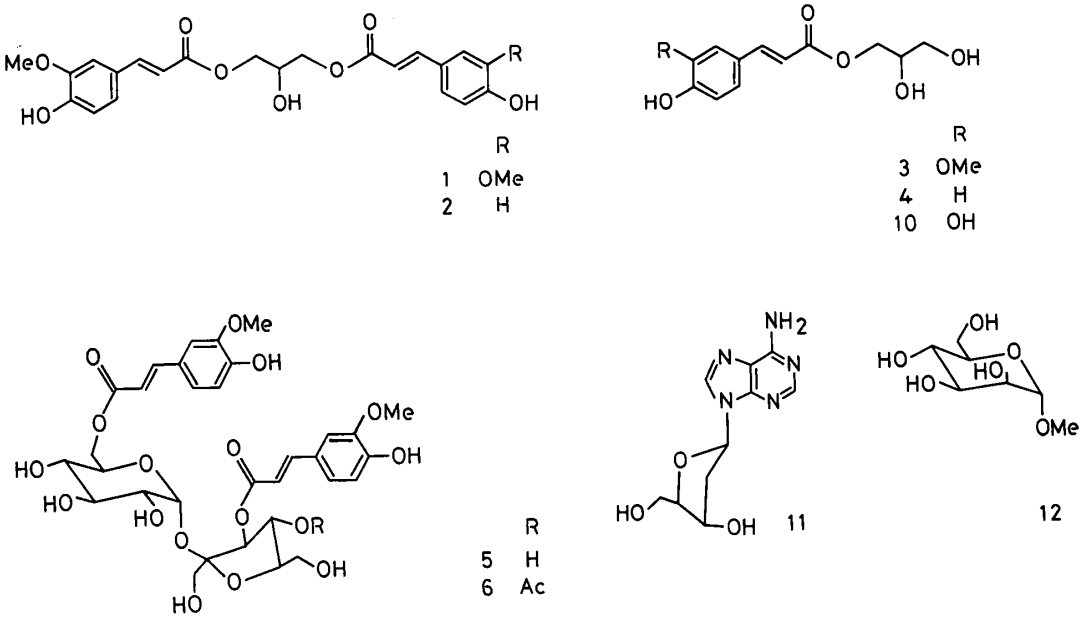
Extraction and isolation——Fresh dormant bulbs of *L. longiflorum* (2.8 kg) were cut into pieces and extracted with hot MeOH. The MeOH extract was concentrated to a small volume under reduced pressure. The crude residue was suspended in H_2O and extracted with $CHCl_3$ and then with *n*-BuOH. After concentration, each fraction was subjected to column chromatography on silica gel with $CHCl_3$–EtOAc, $CHCl_3$–acetone and $CHCl_3$–MeOH solvent systems for the $CHCl_3$ soluble phase, and with $CHCl_3$–MeOH, $CHCl_3$–MeOH–H_2O, EtOAc–acetone, EtOAc–MeOH, EtOAc–MeOH–H_2O, Et_2O–MeOH and Et_2O–MeOH–H_2O systems for the *n*-BuOH soluble phase. Sephadex LH-20 column chromatography with MeOH was also used for the purification. Compounds **1** and **2** were obtained from $CHCl_3$ soluble portion and **3**–**9** from *n*-BuOH soluble portion. Yields; **1** (38.9 mg), **2** (12.8 mg), **3** (6.3 mg), **4** (6.0 mg), **5** (459 mg), **6** (293 mg), **7** (153 mg), **8** (209 mg), and **9** (6.2 mg).

Fresh dormant bulbs of *L. lancifolium* (5.0 kg) were treated as in the case of those of *L. longiflorum* to yield **3**–**5** and **10**–**14**, which were isolated from the *n*-BuOH soluble phase. Yields; **3** (84.3 mg), **4** (26.6 mg), **5** (1.04 g), **10** (2.1 mg), **11** (9.7 mg), **12** (1.00 g), **13** (7.4 mg), and **14** (42.7 mg).

Compounds **1**, **2**, **3**, **4** and **10** were phenolic glycerols and identified by the EI-MS and ^{1}H-NMR spectra and by the direct TLC comparison with respective authentic samples. Compounds **5** and **6** were phenylpropanoid sucrose esters and identified by the IR and ^{1}H-NMR spectra and by the direct TLC comparison with respective authentic samples. Compounds **7** (regaloside B) and **13** (regaloside A) were known phenylpropanoid glycerol glucosides and identified by the IR, EI-MS and ^{1}H-NMR spectra, and by the direct TLC comparison with authentic samples. Compound **11** was identified as 2′-deoxyadenosine by the specific rotation, EI-MS, IR and ^{1}H-NMR spectra, and by the direct TLC comparison with an authentic sample. Compound **12** was identified as methyl α-D-mannopyranoside by the specific rotation, IR, ^{1}H- and ^{13}C-NMR spectra, and by the direct TLC comparison with an authentic sample.

(2*S*)-1-*O*-*p*-Coumaroyl-2-*O*-β-D-glucopyranosylglycerol (regaloside D) (8)——A pale-yellow amorphous powder, $[\alpha]_D^{20}$ –26.8° (*c* = 0.80, MeOH). UV λ_{max}^{MeOH} nm (log ε): 225 (4.52), 300 sh (4.71), 312 (4.76). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2900 (CH), 1690 (C = O), 1632 (CH = CH), 1605, 1587, 1520 (aromatic ring), 1445, 1330, 1265, 1203, 1170, 1075, 1030, 832. EI-MS *m*/*z* (%): 400.1296 [M]$^+$ (0.7, Calcd for $C_{18}H_{24}O_{16}$: 400.1369), 249 (4), 239 (4), 238 (5), 221 (11), 164 (17), 147 (100), 119 (10), 103 (30). ^{1}H-NMR (CD_3OD) δ: 7.66 (1H, d, *J* = 15.9 Hz, H-7′), 7.47 (2H, d, *J* = 8.6 Hz, H-2′, -6′), 6.80 (2H, d, *J* = 8.6 Hz, H-3′, -5′), 6.34 (1H, d, *J* = 15.9 Hz, H-8′), 4.48 (1H, d, *J* = 7.7 Hz, H-1″), 4.36 (1H, dd, *J* = 11.6, 4.9 Hz, H-1a), 4.30 (1H, dd, *J* = 11.6, 5.8 Hz, H-1b), 4.05 (1H, m, H-2), 3.87 (1H, dd, *J* = 11.9, 1.5 Hz, H-6″a), 3.72 (2H, d, *J* = 5.0 Hz, H-3), 3.66 (1H, m, H-6″b), 3.41–3.27 (H-3″, -4″, -5″), 3.22 (1H, dd, *J* = 9.0, 7.7 Hz, H-2″). ^{13}C-NMR spectrum; TABLE I.

Alkaline hydrolysis of regaloside D (8)——Compound **8** (17.5 mg) was treated with 3% NaOMe–MeOH at room temperature for 2 h. After dilution with MeOH, the reaction solution was neutralized with a cation exchange regin



	R
1	OMe
2	H

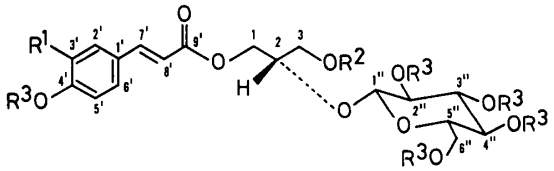
	R
3	OMe
4	H
10	OH

	R
5	H
6	Ac

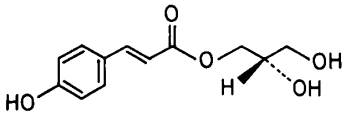
11

12

Chart 1.

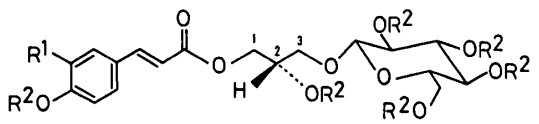


	R^1	R^2	R^3
7	H	Ac	H
8	H	H	H
8a	H	Ac	Ac
9	OH	Ac	H
9a	OAc	Ac	Ac

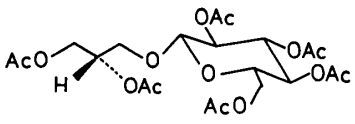


8b

Chart 2.



	R^1	R^2
13	H	H
14	OMe	H
14a	OMe	Ac



14b

Chart 3.

(Amberlite IR-120B) and the solution was concentrated to give a residue, which was subjected to silica gel column chromatography with $CHCl_3$–MeOH (2:1), yielding methyl *p*-coumarate (7.4 mg) and 2-*O*-*β*-D-glucopyranosylglycerol (8.6 mg). Methyl *p*-coumarate was identified by the TLC comparison with an authentic sample (*Rf* 0.64, $CHCl_3$–MeOH (10:1)), and the glycerol glucoside by the IR and ^{1}H-NMR spectra, and by the TLC comparison with an authentic sample (*Rf* 0.54, MeOH–acetone–H_2O (8: 12: 1)).[3,16]

Acetylation of regaloside D (8)——To a pyridine solution of **8** (15.0 mg) was added Ac_2O and it was left standing overnight. After the addition of H_2O and the removal of the solvent under reduced pressure, the crude product was chromatographed on silica gel with *n*-hexane–acetone (2:1) to give a pure acetate (**8a**) (17.0 mg). The EI-MS, IR and ^{1}H-NMR spectra were in good agreement with those of regaloside B peracetate.[3]

Enzymatic hydrolysis of regaloside D (8)——A mixture of **8** (38.4 mg) and *β*-glucosidase (Tokyo Kasei Co., Ltd.) in AcOH–NaOAc buffer (pH 5) was incubated at room temperature for 24 h. The reaction mixture was diluted with H_2O and extracted with EtOAc (10 ml × 2). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated off to dryness. The crude residue was purified by silica gel column chromatography with $CHCl_3$–MeOH (19:1) to afford (2*S*)-1-*O*-*p*-coumaroylglycerol (15.0 mg), which was identified by the specific rotation, IR and ^{1}H-NMR spectra.[3] From the H_2O layer, D-glucose was detected by TLC (*Rf* 0.65, MeOH–acetone–H_2O (4:5:1), *Rf* 0.34, *n*-BuOH–AcOH–H_2O (3:1:1)).

(2*S*)-1-*O*-Caffeoyl-2-*O*-*β*-D-glucopyranosyl-3-*O*-acetylglycerol (Regaloside E) (9)——A pale-yellow amorphous powder, $[\alpha]_D^{20}$ − 22.4° (*c* = 0.08, MeOH). UV λ_{max}^{MeOH} nm (log *ε*): 242 sh (4.52), 300 sh (4.62), 327 (4.74). IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 2960, 2920 (CH), 1715 (C = O), 1630 (CH = CH), 1600, 1520 (aromatic ring), 1450, 1375, 1260, 1160, 1075, 1040, 805. ^{1}H-NMR (CD_3OD) *δ*: 7.59 (1H, d, *J* = 15.9 Hz, H-7′), 7.05 (1H, d, *J* = 2.0 Hz, H-2′), 6.96 (1H, dd, *J* = 8.2, 2.0 Hz, H-6′), 6.77 (1H, d, *J* = 8.2 Hz, H-5′), 6.27 (1H, d, *J* = 15.9 Hz), 4.48 (1H, d, *J* = 7.8 Hz, H-1″), 4.42–4.16 (5H, H-1, -2, -3), 3.86 (1H, dd, *J* = 12.0, 1.6 Hz, H-6″a), 3.67 (1H, m, H-6′b), 3.41–3.26 (H-3″, -4″, -5″), 3.20 (1H, dd, *J* = 9.0, 7.8 Hz, H-2″), 2.07 (3H, s, Ac). ^{13}C-NMR spectrum; Table I.

Alkaline hydrolysis of regaloside E (9)——Compound **9** (1.0 mg) was treated with 3% NaOMe–MeOH at room tem-

Table I. ^{13}C-NMR Spectral Data for **7**, **8**, **9**, **13** and **14**[a]

Carbon No.	7	8	9	13	14
Glycerol moiety					
1	65.1	64.8	65.2	66.7	66.7
2	76.1	79.5	76.2	69.7	69.8
3	64.4	63.4	64.5	72.0	72.0
Ac	172.7		172.7		
	20.8		20.8		
Phenylpropanoid moiety					
1′	127.1	127.2	127.8	127.2	127.8
2′	131.3	131.2	114.8	131.2	111.9
3′	116.9	116.9	146.9	116.9	150.7
4′	161.3	161.3	149.8	161.3	149.4
5′	116.9	116.9	116.6	116.9	116.6
6′	131.3	131.2	123.1	131.2	124.1
7′	147.1	147.0	147.5	146.8	147.1
8′	114.8	115.0	115.3	115.0	115.4
9′	168.9	169.1	169.0	169.2	169.2
OMe					56.6
Glucose moiety					
1″	104.4	104.2	104.5	104.7	104.7
2″	75.0	75.0	75.1	75.1	75.1
3″	78.0[b]	78.0[c]	78.1	78.0[d]	78.0[e]
4″	71.5	71.6	71.6	71.6	71.6
5″	77.9[b]	77.9[c]	78.1	77.9[d]	77.9[e]
6″	62.8	62.7	62.9	62.7	62.8

[a] The measurements were made on a Bruker AM-400 (100.6 MHz) in CD_3OD. Chemical shifts were given in ppm relative to the internal standard TMS.

[b]–[e]: Assignments may be reversed.

perature for 1 h. Methyl caffeate and glycerol glucoside were detected on TLC plates. Methyl caffeate; $Rf = 0.17$ ($CHCl_3$–acetone = 15:1). Glycerol glucoside; $Rf = 0.54$ (MeOH–acetone–H_2O = 8:12:1).

Acetylation of regaloside E (9)——Compound **9** (5.1 mg) was acetylated with Ac_2O in pyridine to give a peracetate, which was purified by silica gel column chromatography with *n*-hexane–acetone (1:1) to provide a colorless amorphous powder (**9a**) (7.2 mg). IR$\nu_{max}^{CHCl_3}$ cm^{-1}: 3030, 2960 (CH), 1760 (C = O), 1640 (CH = CH), 1605, 1510 (aromatic ring), 1425, 1372, 1220, 1180, 1115, 1040, 905, 728. EI-MS *m/z* (%): 710 $[M]^+$ (0.5), 668 $[M - CH_3CO + H]^+$ (1.2), 640 (6.3), 626 (7.2), 507 (0.4), 409 (0.9), 363 (36), 331 (87), 278 (21), 205 (24), 169 (100), 163 (45), 162 (25), 145 (23), 134 (22), 109 (47). ^{1}H-NMR ($CDCl_3$) δ: 7.66 (1H, d, J = 16.0 Hz, H-7′), 7.44 (1H, dd, J = 8.4, 2.0 Hz, H-6′), 7.39 (1H, d, J = 2.0 Hz, H-5′), 7.25 (1H, d, J = 8.4 Hz, H-5′), 6.37 (1H, d, J = 16.0 Hz, H-8′), 5.22 (1H, dd, J = 9.5, 9.5 Hz, H-3″), 5.08 (1H, dd, J = 9.5, 9.5 Hz, H-4″), 5.01 (1H, dd, J = 9.5, 8.0 Hz, H-2″), 4.70 (1H, d, J = 8.0 Hz, H-1″), 4.37–4.10 (7H, H-1, -2, -3, -6″), 3.72 (1H, m, H-5″), 2.31, 2.30 (each 3H, s, arom. Ac), 2.09, 2.08, 2.02, 2.00, 1.99 (each 3H, s, Ac).

(2*S*)-1-*O*-Feruloyl-3-*O*-β-D-glucopyranosylglycerol (regaloside F) (14)——A pale-yellow amorphous powder, $[\alpha]_D^{26}$ − 9.1° (*c* = 0.22, MeOH), UVλ_{max}^{MeOH} nm (log ε): 236 (4.17), 301 sh (4.23), 325 (4.38). IRν_{max}^{KBr} cm^{-1}: 3400 (OH), 2940, 2880 (CH), 1700 (C = O), 1630 (CH = CH), 1600, 1520 (aromatic ring), 1430, 1275, 1160, 1075, 1035. EI-MS *m/z* (%): 430 $[M]^+$ (4), 279 (7), 268 (25), 251 (7), 194 (19), 177 (80), 163 (15), 145 (28), 121 (18), 103 (100). ^{1}H-NMR (CD_3OD) δ: 7.65 (1H, d, J = 15.9 Hz, H-7′), 7.19 (1H, d, J = 1.8 Hz, H-2′), 7.08 (1H, dd, J = 8.2, 1.8 Hz, H-6′), 6.81 (1H, d, J = 8.2 Hz, H-5′), 6.38 (1H, d, J = 15.9 Hz, H-8′), 4.30 (1H, d, J = 7.7 Hz, H-1″), 4.29 (1H, dd, J = 11.5, 4.5 Hz, H-1a), 4.24 (1H, dd, J = 11.5, 6.1 Hz, H-1b), 4.07 (1H, m, H-2), 3.96 (1H, dd, J = 10.5, 5.2 Hz, H-3a), 3.89 (3H, s, OMe), 3.87 (1H, dd, J = 11.6, 1.2 Hz, H-6″a), 3.71 (1H, dd, J = 10.5, 4.7 Hz, H-3b), 3.66 (1H, m, H-6″ b), 3.39–3.26 (H-3″, -4″, -5″), 3.22 (1H, dd, J = 9.0, 7.7 Hz, H-2″). ^{13}C-NMR spectrum: Table I.

Acetylation of regaloside F (14)——Compound **14** (6.0 mg) was acetylated with Ac_2O in pyridine. The crude product was chromatographed over silica gel with $CHCl_3$–EtOAc (4:1) to give a pure acetate (**14a**) (6.3 mg) as a colorless amorphous powder. IR$\nu_{max}^{CHCl_3}$ cm^{-1}: 3020, 2930, 2860 (CH), 1755 (C = O), 1638 (CH = CH), 1600, 1510 (aromatic ring), 1465, 1418, 1370, 1220, 1170, 1155, 1125, 1037, 980, 905. EI-MS *m/z* (%): 682 $[M]^+$ (0.5), 640 $[M - CH_3CO + H]^+$ (26), 337 (13), 335 (41), 331 (27), 293 (19), 219 (18), 177 (59), 169 (100), 109 (46). ^{1}H-NMR ($CDCl_3$) δ: 7.64 (1H, d, J = 15.9 Hz, H-7′), 7.15–7.04 (3H, H-2′, -5′, -6′), 6.38 (1H, d, J = 15.9 Hz, H-8′), 5.27 (1H, m, H-2), 5.21 (1H, dd, J = 9.5, 9.5 Hz, H-3″), 5.09 (1H, dd, J = 9.5, 9.5 Hz, H-4″), 5.00 (1H, dd, J = 9.5, 7.8 Hz, H-2″), 4.56 (1H, d, J = 7.8 Hz, H-1″), 4.40 (1H, dd, J = 12.1, 3.7 Hz, H-1a), 4.31 (1H, dd, J = 12.1, 6.0 Hz, H-1b), 4.26 (1H, dd, J = 12.3, 4.7 Hz, H-6″a), 4.15 (1H, dd, J = 12.3, 2.3 Hz, H-6″b), 4.00 (1H, dd, J = 10.9, 5.1 Hz, H-3a), 3.88 (3H, s, OMe), 3.74 (1H, dd, J = 10.9, 5.5 Hz, H-3b), 3.71 (1H, ddd, J = 9.5, 4.7, 2.3 Hz, H-5″), 2.32 (3H, s, arom. Ac), 2.09 × 2, 2.07, 2.02, 2.01 (each 3H, s, Ac).

Alkaline hydrolysis followed by acetylation of regaloside F (14)——Compound **14** (24.4 mg) was hydrolized with 3% NaOMe—MeOH at room temperature for 2 h. After neutralization with a cation exchange resin (Amberlite IR-120B) and removal of the solvent, the crude hydrolysate was added to H_2O and extracted with EtOAc. Methyl ferulate was detected in the EtOAc layer, and identified by TLC ($Rf = 0.15$, *n*-hexane–acetone = 4:1). The H_2O layer was concentrated and the residue was, without further purification, acetylated with Ac_2O in pyridine at room temperature overnight. After usual work-up and chromatography on silica-gel with *n*-hexane–acetone (3:1), glycerol glucoside hexaacetate was obtained (11.7 mg). Colorless needles (*n*-hexane–Et_2O), mp 109.5–110.0°C, $[\alpha]_D^{27}$ − 6.8° (*c* = 0.25, $CHCl_3$), identified as lilioside C hexaacetate (**14b**) by the ^{1}H-NMR spectrum and the above physical data.[3,4,14]

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