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Studies on the Chemical Constituents of *Lilium henryi* BAKER

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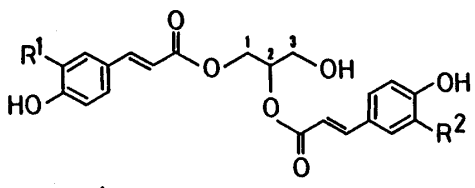
New bitter phenolic glycosides and a steroid glucoside have been isolated from the fresh bulbs of *Lilium henryi*. On the basis of spectroscopic data, chemical evidence and X-ray crystallographic analysis, their structures have been elucidated as (2*S*)-1-*O*-*p*-methoxycinnamoyl-3-*O*-β-D-glucopyranosylglycerol (methylregaloside A), (2*S*)-1-*O*-caffeoyl-3-*O*-β-D-glucopyranosylglycerol (regaloside C), 3-*O*-feruloyl-6′-*O*-(4-*O*-β-D-glucopyranosylferuloyl)sucrose, and (25*R*)-3β,26-dihydroxy-5α-cholestane-6,22-dione 3-*O*-β-D-glucopyranoside. Several known components have also been isolated and identified.

Keywords——*Lilium henryi*; Liliaceae; glycerol glucoside; phenylpropanoid glycoside; methylregaloside A; regaloside C; phenylpropanoid sucrose ester; steroid glucoside; bitter principle; X-ray analysis

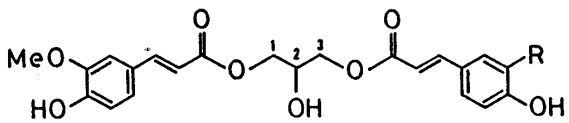
Bulbs of plants in the genus *Lilium* (Liliaceae) have been reputed in traditional Chinese medicine to be effective as a sedative, an antitussive, an anti-inflammatory or a nutrient.[1] They have also been used in folk medicine for the treatment of burns or swelling in Europe.[2] Our recent extensive survey of the chemical constituents of lily bulbs revealed the occurrence of a variety of phenolic compounds, *i.e.*, phenylpropanoid sucrose esters,[3] phenolic glycerides[4] and phenolic glycerol glucosides,[5] and an antitumor alkaloid, jatropham, and its glucoside.[6] Lilies are prone to be attacked by a considerable number of pests and diseases, and the worst disorders to which lilies are vulnerable are a number of virus diseases. However, *Lilium henryi* (Japanese name: kikanoko-yuri) is noted for its strong resistance to virus disease, and the bulbs are significantly bitter to the taste, as are those of *Lilium speciosum* var. *rubrum*[3] and *Lilium regale*.[5] In this paper, we wish to present details of the isolation and structural determination of new bitter phenolic glycosides and a steroid glucoside, in addition to some known compounds, from *Lilium henryi*.

Commercially available fresh bulbs of *Lilium henryi* were extracted with hot methanol, and the extract was treated as described in the experimental section to afford compounds **1**—**12**.

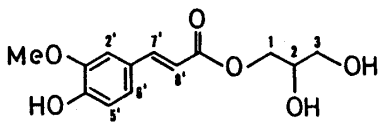
Compounds **1**—**4** were isolated from the chloroform-soluble portion and obtained as amorphous powders. The proton nuclear magnetic resonance (^{1}H-NMR) spectra and electron impact mass spectra (EI-MS) revealed that **1**—**4** were phenolic diglycerides. The structures were identified as 1,2-*O*-diferuloylglycerol (**1**), a mixture of 1-*O*-feruloyl-2-*O*-*p*-coumaroylglycerol (**2a**) and 1-*O*-*p*-coumaroyl-2-*O*-feruloylglycerol (**2b**), 1,3-*O*-diferuloylglycerol (**3**), and 1-*O*-feruloyl-3-*O*-*p*-coumaroylglycerol (**4**), respectively.[4,7] Compounds **1** and **2** were obtained as racemates which lack specific rotation and a Cotton effect in the circular dichroism (CD) spectra. To clarify the C-2 configuration of **4**, partial hydrolysis was performed. Compound **4** was treated with *ca.* 1.4% sodium methoxide at room temperature for 30 min to afford two hydrolysis products (**4a** and **4b**). Neither showed specific rotation, and **4** was



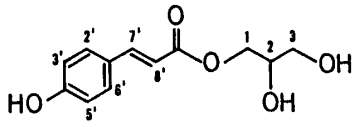
	R^1	R^2
1	OMe	OMe
2a	OMe	H
2b	H	OMe



	R
3	OMe
4	H



4a



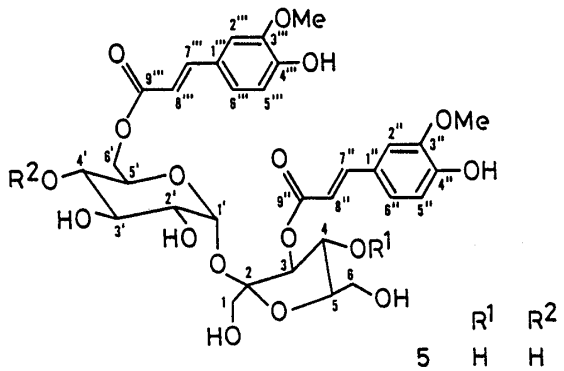
4b

Chart 1

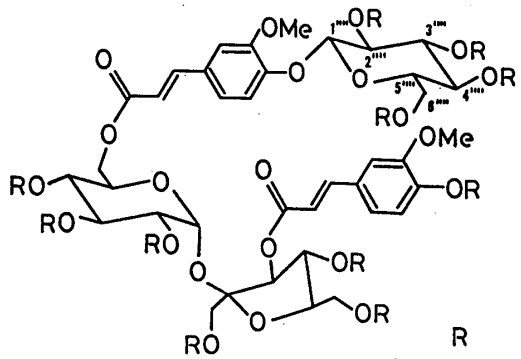
deduced to be a racemate.[8]

Compounds **5**—**7** were identified as 3,6′-*O*-diferuloylsucrose (**5**), 4-*O*-acetyl-3,6′-*O*-diferuloylsucrose (**6**) and 4′-*O*-acetyl-3,6′-*O*-diferuloylsucrose (**7**) from their spectroscopic properties and by direct comparison with authentic samples isolated previously.[3]

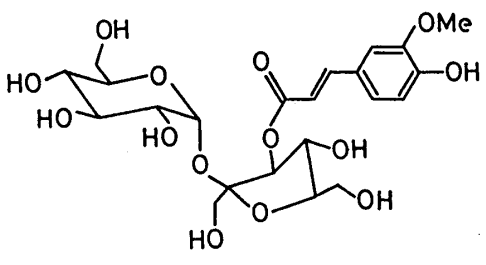
Compound **8** is a white amorphous powder. The ^{1}H-NMR and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of **8** showed signals due to sucrose and two feruloyl



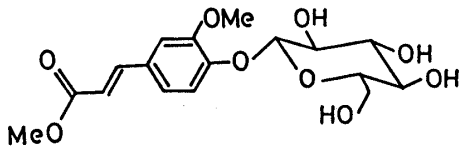
	R^1	R^2
5	H	H
6	Ac	H
7	H	Ac



	R
8	H
8a	Ac



8b



8c

Chart 2

TABLE I. ^{13}C-NMR Spectral Data for **5**, **8**, **8b**, and **8c**[a]

Carbon No.	**5**	**8**	**8b**	**8c**
Sucrose moiety				
1	65.7	65.8	65.8	
2	104.8	104.9	104.9	
3	79.5	79.7	79.9	
4	74.0	74.1	73.5[b]	
5	84.7	84.9	84.6	
6	63.3	63.5	62.8[c]	
1′	92.7	92.9	93.3	
2′	73.1	73.3	73.4[b]	
3′	75.2	75.3	75.3[d]	
4′	71.7	71.8	71.9	
5′	72.2	72.3	75.1[d]	
6′	65.0	65.3	62.3[c]	
Feruloyl moieties				
1″ 1‴	126.0 125.9	129.1 126.5	126.6	130.4
2″ 2‴	111.9 111.2	112.2 111.7	112.2	112.4
3″ 3‴	148.9 148.8	148.9[b,e]	148.8	150.8
4″ 4‴	151.5	151.1[b,e]	151.0	149.9
5″ 5‴	116.6	117.0 116.8	116.7	117.4[b]
6″ 6‴	123.8	122.9	[e]	123.4
7″ 7‴	146.3 145.7	146.3 145.1	146.2	145.9
8″ 8‴	114.9 114.4	115.9 115.0	115.2	117.0[b]
9″ 9‴	167.7 166.9	167.5 166.9	166.9	169.2
OMe	55.9	56.0	55.9	56.8
COOMe				52.1
Glucose moiety				
1⁗		101.8		102.2
2⁗		74.8		74.6
3⁗		78.5[c]		78.1[c]
4⁗		71.2		71.1
5⁗		79.0[c]		77.6[c]
6⁗		62.4		62.4

a) Spectra of **5**, **8** and **8b** were measured in C_5D_5N, and that of **8c** in CD_3OD. The spectrum of **5** was measured with a JEOL FX-100 (25.1 MHz), and others with a Bruker AM-400 (100.6 MHz). *b*—*d*) Assignments may be interchangeable in each column. *e*) Signals were unclear due to overlapping with solvent signals.

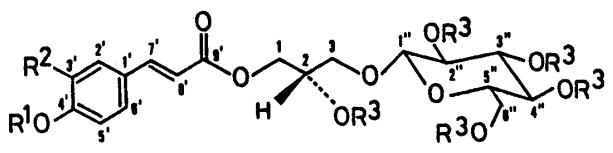
groups. In addition, the presence of one more glucose in the molecule was demonstrated by the appearance of an anomeric proton signal (δ 5.60, d, $J=7.3$ Hz) in the ^{1}H-NMR spectrum and also by characteristic ^{13}C-NMR signals (δ 101.8, 79.0, 78.5, 74.8, 71.2, 62.4). The undecaacetate (**8a**) of **8** was prepared with acetic anhydride and pyridine, and its ^{1}H-NMR spectrum confirmed the presence of ten aliphatic acetoxyl groups and an aromatic acetoxyl group. Mild treatment of **8** with 10% ammonia solution in methanol–water (2 : 1) for 30 min furnished a partial hydrolysis product, monoferuloylsucrose (**8b**), together with methyl ferulate and glucosyl methyl ferulate (**8c**). In the ^{1}H-NMR spectrum of **8b**, the signal due to sucrose H-3 was remarkably shifted downfield by 1.33 ppm compared with that of sucrose,[3] and **8b** was assigned to be 3-*O*-feruloylsucrose. The above results demonstrated that one more glucose was linked to the *p*-hydroxyl function of the feruloyl moiety, which was attached to the C-6′ hydroxyl of the sucrose moiety. Accordingly, **8** was deduced to be 3-*O*-feruloyl-6′-*O*-(4-*O*-β-D-glucopyranosylferuloyl)sucrose.

Compound **9**, $C_{18}H_{24}O_{10}$ ([M^+] m/z 400, EI-MS), $[\alpha]_D$ $-17.0°$ (methanol), was concluded to be regaloside A from its physical and spectroscopic data.[5] Furthermore, the melting

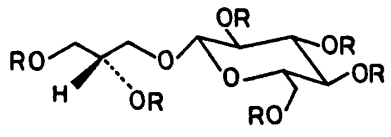
point of **9** hexaacetate (**9a**) was not depressed by admixture with authentic regaloside A hexaacetate.

Compound **10** was obtained as a colorless crystalline powder recrystallized from ethyl ether–methanol, mp 146.0—148.0 °C, $[\alpha]_D$ −13.0° (methanol). The infrared (IR) spectrum of **10** suggested the presence of hydroxyl group(s) (3550 and 3300 cm^{-1}), a carbonyl group of an α,β-unsaturated ester (1705 cm^{-1}), an alkene conjugated with an aromatic ring (1630 cm^{-1}) and an aromatic ring (1600 and 1510 cm^{-1}). The ^{1}H-NMR spectrum showed *trans* olefinic protons as AB-type signals at δ 7.68 and 6.41, J = 16.0 Hz, *p*-disubstituted aromatic protons as AA′BB′ signals at δ 7.56 and 6.96, J = 8.8 Hz and glycerol glucoside signals at 4.32—3.20 integrated for eleven protons. The configuration of the anomeric center in the glucose moiety was assigned as the β-form from its coupling constant (J = 7.8 Hz) in the ^{1}H-NMR spectrum. The EI-MS of **10** indicated a molecular ion peak at *m/z* 414, which exceeded that of regaloside A by 14 mass units, and a prominent fragment ion peak at *m/z* 161, assignable to a *p*-methoxycinnamoyl residue. The pentaacetate, prepared by acetylation with acetic anhydride and pyridine, showed five acetoxyl signals due to alcoholic acetoxyl groups in the ^{1}H-NMR spectrum. No phenolic acetoxyl group was observed. On treatment with 3% sodium methoxide, **10** liberated methyl *p*-methoxycinnamate (**10b**) and glycerol glucoside. Glycerol glucoside was converted to the corresponding hexaacetate which was assigned to be (2*R*)-1-*O*-β-D-glucopyranosylglycerol hexaacetate, that is, lilioside C hexaacetate.[5,9] From the argument presented above, **10** was concluded to be (2*S*)-1-*O*-*p*-methoxycinnamoyl-3-*O*-β-D-glucopyranosylglycerol, named methylregaloside A. The ^{13}C-NMR spectrum of **10** was in good agreement with the proposed structure.

Compound **11** was obtained as a pale-yellow amorphous powder, $[\alpha]_D$ −11.3° (methanol), with the molecular formula $C_{18}H_{24}O_{11}$. The ^{1}H-NMR spectrum was similar to that of regaloside A except for the aromatic region. The ultraviolet (UV) spectrum of **11** (methanol) showed λ_{max} at 243 (shoulder (sh)), 300 (sh) and 328 nm. Bathochromic and hyperchromic shifts of the UV maximum at 328 nm (log ε 4.15) to 376 nm (log ε 4.23) upon addition of sodium methoxide reagent as well as a dark green coloration on adding ferric chloride reagent indicated that two free vicinal phenolic hydroxyl groups were present in the molecule. On acetylation with acetic anhydride and pyridine, **11** afforded a heptaacetate (**11a**). The ^{1}H-NMR spectrum of **11a** revealed the existence of five aliphatic and two aromatic acetoxyl groups. The alkaline hydrolysis of **11** with 3% sodium methoxide in methanol yielded methyl caffeate, and glycerol glucoside, the same hydrolysis products as those of regaloside A, whose subsequent acetylation by treatment with acetic anhydride in pyridine afforded a hexaacetate, identical with lilioside C hexaacetate. Thus, **11** was determined to be (2*S*)-1-*O*-caffeoyl-3-*O*-β-D-glucopyranosylglycerol, designated as regaloside C. The assigned structure was well



	R^1	R^2	R^3
9	H	H	H
9a	Ac	H	Ac
10	Me	H	H
10a	Me	H	Ac
11	H	OH	H
11a	Ac	OAc	Ac



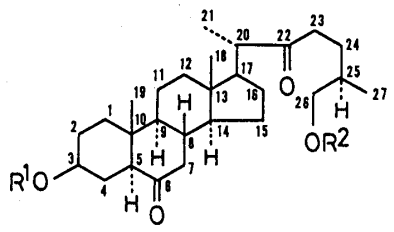
	R
lilioside C	H
lilioside C hexaacetate	Ac

Chart 3

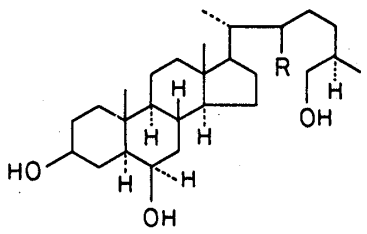
TABLE II. ^{13}C-NMR Spectral Data for **9**, **10** and **11**[a]

Carbon No.	**9**	**10**	**11**
Glycerol moiety			
1	66.7	66.8	66.7
2	69.7	69.8	69.8
3	72.0	72.0	72.0
Phenylpropanoid moiety			
1′	127.2	128.4	127.8
2′	131.2	131.0	115.0
3′	116.9	115.5	146.8
4′	161.3	163.3	149.6
5′	116.9	115.5	116.6
6′	131.2	131.0	123.0
7′	146.8	146.4	147.2
8′	115.0	116.0	115.3
9′	169.2	169.0	169.2
OMe		55.9	
Glucose moiety			
1″	104.7	104.8	104.7
2″	75.1	75.2	75.1
3″	78.0[b]	78.1[b]	78.0
4″	71.6	71.7	71.6
5″	77.9[b]	78.0[b]	78.0
6″	62.7	62.8	62.8

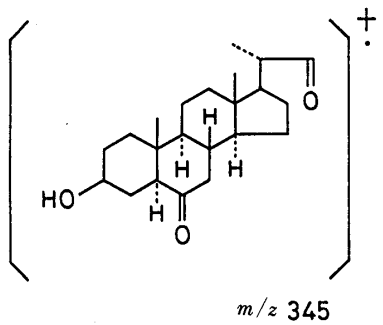
a) Spectra were measured in CD_3OD with a Bruker AM-400 (100.6 MHz). b) Assignments may be interchangeable in each column.



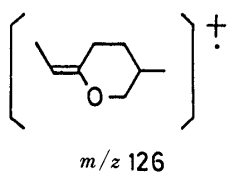
	R^1	R^2
12	Glc	H
12a	Glc(Ac)$_4$	Ac
12b	H	H
12c	Ac	Ac



	R
12d	=O
12e	OH



m/z 345



m/z 126

Chart 4

supported by the ^{13}C-NMR spectrum.

Compound **12** was obtained as colorless plates, recrystallized from isopropyl ether–methanol, mp 217.5—219.5 °C. The molecular formula, $C_{33}H_{54}O_9$ was derived from the EI-MS (*m/z* 576, $M^+ - H_2O$) and elemental analysis. The glucosidic nature of **12** was easily deduced from the ^{1}H-NMR [δ 5.03, 1H, d, J=7.7 Hz (anomeric proton); δ 4.62—3.90, total six protons] and the ^{13}C-NMR (δ 102.2, 78.6×2, 75.4, 71.9, 63.1) spectra. Furthermore, the ^{13}C-NMR spectrum showed 27 carbons, excluding the glucose carbons. Acetylation of **12** with acetic anhydride in pyridine gave the pentaacetate (**12a**), colorless needles recrystallized from *n*-hexane–ethyl ether, mp 137.5—140.5 °C. The above observations suggested that **12** is a

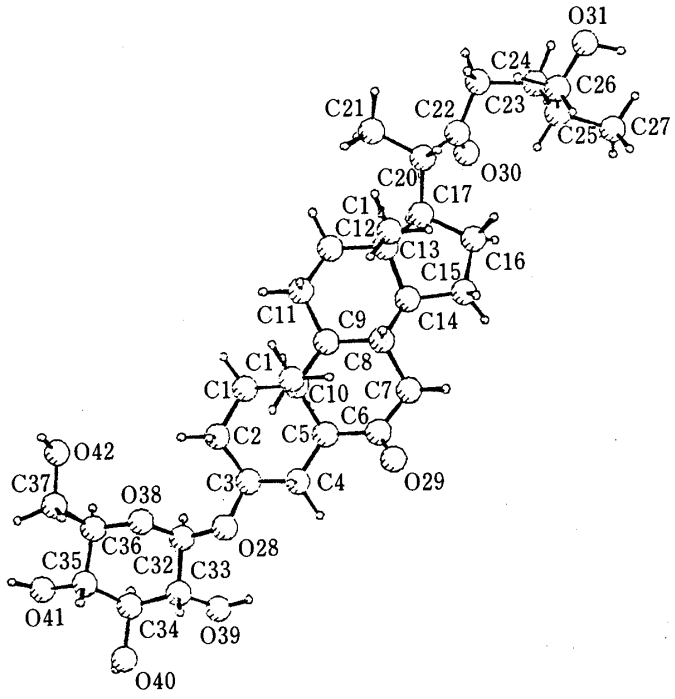


Fig. 1. Molecular Structure Drawn by the PLUTO[a] Program

a) Motherwell, W. D. S. (1972). PLUTO. A program for drawing crystal and molecular structures. Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

TABLE III. ^{13}C-NMR Spectral Data for **12** and **12b**[a]

Carbon No.	**12**	**12b**	Carbon No.	**12**	**12b**
1	39.6[b]	39.6[d]	18	13.1	13.2
2	27.1	31.3[e]	19	16.7	16.7
3	76.8	70.0	20	49.4	49.4
4	29.5	31.8[e]	21	12.3	12.3
5	52.5	52.5	22	214.0	213.8
6	209.7	210.1	23	36.8	37.1
7	46.7	46.8	24	27.8[c]	27.8[f]
8	37.8	37.9	25	36.2	36.2
9	53.8	53.9	26	67.4	67.4
10	40.9	41.0	27	17.3	17.2
11	21.7	21.7	1′	102.2	
12	27.7[c]	27.7[f]	2′	75.4	
13	43.2	43.2	3′	78.6	
14	56.5	57.0	4′	71.9	
15	24.3	24.3	5′	78.6	
16	39.9[b]	39.9[d]	6′	63.1	
17	56.1	56.1			

a) The measurements were made on a Bruker AM-400 (100.6 MHz) in C_5D_5N. *b*—*f*) Assignments may be reversed.

TABLE IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors

No.	Atom	x	y	z	B_{eq} (Å^2)
1	C1	534 (5)	1085 (1)	1460 (5)	3.6 (0.1)
2	C2	366 (5)	1442 (1)	1264 (5)	3.5 (0.1)
3	C3	826 (4)	1547 (1)	−550 (5)	2.9 (0.1)
4	C4	10 (4)	1384 (1)	−1970 (5)	3.3 (0.1)
5	C5	214 (4)	1028 (1)	−1771 (5)	2.7 (0.0)
6	C6	−450 (5)	835 (1)	−3206 (5)	3.4 (0.1)
7	C7	−23 (4)	494 (1)	−3209 (5)	3.2 (0.1)
8	C8	−287 (4)	341 (1)	−1416 (5)	2.7 (0.0)
9	C9	269 (4)	541 (1)	110 (5)	2.7 (0.0)
10	C10	−227 (4)	892 (1)	42 (5)	2.9 (0.1)
11	C11	−5 (5)	378 (1)	1874 (5)	3.9 (0.1)
12	C12	547 (5)	35 (1)	1932 (5)	3.8 (0.1)
13	C13	−4 (4)	−164 (1)	409 (5)	2.8 (0.1)
14	C14	351 (4)	14 (1)	−1292 (5)	2.8 (0.0)
15	C15	92 (5)	−227 (1)	−2741 (5)	3.8 (0.1)
16	C16	509 (6)	−547 (1)	−1917 (6)	4.4 (0.1)
17	C17	766 (4)	−483 (1)	76 (5)	3.2 (0.1)
18	C18	−1561 (4)	−223 (1)	596 (7)	4.1 (0.1)
19	C19	−1799 (4)	915 (1)	300 (7)	4.3 (0.1)
20	C20	402 (4)	−773 (1)	1179 (5)	3.4 (0.1)
21	C21	546 (6)	−722 (1)	3171 (6)	4.6 (0.1)
22	C22	1338 (5)	−1052 (1)	714 (6)	4.1 (0.1)
23	C23	833 (7)	−1381 (1)	1169 (7)	5.9 (0.1)
24	C24	754 (6)	−1589 (1)	−495 (10)	7.3 (0.1)
25	C25	−387 (5)	−1490 (1)	−1743 (8)	5.3 (0.1)
26	C26	−1816 (5)	−1584 (1)	−1234 (8)	5.0 (0.1)
27	C27	−89 (7)	−1620 (2)	−3606 (10)	8.6 (0.1)
28	O28	661 (3)	1881 (1)	−822 (3)	3.1 (0.0)
29	O29	−1286 (4)	942 (1)	−4219 (4)	5.1 (0.1)
30	O30	2446 (3)	−1011 (1)	62 (5)	5.0 (0.1)
31	O31	−1964 (4)	−1916 (1)	−1096 (5)	5.8 (0.1)
32	C32	1518 (4)	2072 (1)	184 (5)	2.9 (0.1)
33	C33	1900 (4)	2365 (1)	−864 (5)	3.1 (0.1)
34	C34	2693 (4)	2594 (1)	271 (5)	3.0 (0.1)
35	C35	1945 (4)	2662 (1)	1982 (5)	3.2 (0.1)
36	C36	1511 (4)	2356 (1)	2870 (5)	3.0 (0.1)
37	C37	586 (5)	2406 (1)	4438 (5)	3.9 (0.1)
38	O38	740 (3)	2165 (1)	1676 (3)	3.0 (0.0)
39	O39	2734 (3)	2274 (1)	−2294 (4)	4.4 (0.0)
40	O40	2894 (3)	2883 (1)	−668 (4)	3.9 (0.0)
41	O41	2895 (3)	2829 (1)	3064 (4)	4.2 (0.0)
42	O42	610 (3)	2121 (1)	5442 (4)	4.6 (0.0)
43	HC1	19 (5)	101 (1)	273 (6)	5.0 (1.0)
44	H′C1	164 (4)	103 (1)	137 (6)	5.0 (1.0)
45	HC2	−70 (5)	151 (1)	145 (6)	6.0 (1.0)
46	H′C2	97 (5)	157 (1)	226 (6)	6.0 (1.0)
47	HC3	191 (4)	148 (1)	−74 (5)	4.0 (1.0)
48	HC4	35 (4)	147 (1)	−326 (5)	4.0 (1.0)
49	H′C4	−106 (5)	145 (1)	−184 (6)	6.0 (1.0)
50	HC5	132 (4)	98 (1)	−186 (6)	4.0 (1.0)
51	HC7	−58 (4)	37 (1)	−422 (5)	4.0 (1.0)
52	H′C7	108 (4)	48 (1)	−351 (6)	5.0 (1.0)
53	HC8	−140 (4)	32 (1)	−124 (6)	4.0 (1.0)
54	HC9	140 (4)	55 (1)	0 (5)	3.0 (1.0)
55	HC11	40 (5)	52 (1)	293 (6)	6.0 (1.0)

TABLE IV. (continued)

No.	Atom	x	y	z	B_{eq} (Å^2)
56	H′C11	−115 (5)	37 (1)	207 (6)	6.0 (1.0)
57	HC12	30 (4)	−8 (1)	317 (6)	5.0 (1.0)
58	H′C12	169 (4)	4 (1)	184 (6)	5.0 (1.0)
59	HC14	149 (4)	4 (1)	−132 (6)	4.0 (1.0)
60	HC15	−98 (5)	−23 (1)	−316 (6)	6.0 (1.0)
61	H′C15	73 (6)	−18 (1)	−390 (8)	9.0 (2.0)
62	HC16	−32 (5)	−72 (1)	−207 (6)	6.0 (1.0)
63	H′C16	142 (6)	−64 (1)	−253 (8)	9.0 (2.0)
64	HC17	189 (4)	−45 (1)	31 (6)	5.0 (1.0)
65	HC18	−212 (4)	−1 (1)	62 (6)	4.0 (1.0)
66	H′C18	−193 (5)	−37 (1)	−47 (7)	8.0 (1.0)
67	H″C18	−178 (5)	−35 (1)	179 (7)	7.0 (1.0)
68	HC19	−216 (4)	116 (1)	22 (6)	5.0 (1.0)
69	H′C19	−235 (5)	78 (1)	−70 (7)	7.0 (1.0)
70	H″C19	−211 (5)	82 (1)	155 (7)	7.0 (1.0)
71	HC20	−69 (5)	−84 (1)	92 (6)	6.0 (1.0)
72	HC21	−8 (5)	−53 (1)	361 (7)	7.0 (1.0)
73	H′C21	26 (5)	−93 (1)	389 (7)	7.0 (1.0)
74	H″C21	162 (5)	−66 (1)	348 (7)	8.0 (1.0)
75	HC23	145 (6)	−150 (1)	213 (9)	11.0 (2.0)
76	H′C23	−25 (5)	−137 (1)	168 (6)	6.0 (1.0)
77	HC24	63 (6)	−184 (1)	−15 (8)	11.0 (2.0)
78	H′C24	177 (7)	−156 (1)	−119 (9)	13.0 (2.0)
79	HC25	−44 (5)	−123 (1)	−185 (6)	6.0 (1.0)
80	HC26	−255 (5)	−150 (1)	−216 (7)	7.0 (1.0)
81	H′C26	−205 (5)	−148 (1)	10 (7)	7.0 (1.0)
82	HC27	2 (5)	−188 (1)	−354 (7)	7.0 (1.0)
83	H′C27	−95 (5)	−156 (1)	−450 (7)	8.0 (1.0)
84	H″C27	85 (6)	−151 (1)	−411 (8)	11.0 (2.0)
85	HO31	−199 (6)	−201 (1)	−224 (8)	10.0 (2.0)
86	HC32	248 (4)	194 (1)	55 (6)	5.0 (1.0)
87	HC33	97 (5)	248 (1)	−131 (6)	5.0 (1.0)
88	HC34	370 (4)	249 (1)	55 (5)	4.0 (1.0)
89	HC35	102 (4)	280 (1)	171 (6)	5.0 (1.0)
90	HC36	242 (4)	223 (1)	332 (6)	4.0 (1.0)
91	HC37	−45 (5)	247 (1)	397 (7)	7.0 (1.0)
92	H′C37	96 (5)	261 (1)	517 (7)	6.0 (1.0)
93	HO39	224 (7)	212 (1)	−297 (9)	11.0 (2.0)
94	HO40	384 (5)	294 (1)	−63 (7)	8.0 (2.0)
95	HO41	246 (6)	291 (1)	407 (8)	9.0 (2.0)
96	HO42	−18 (6)	212 (1)	619 (8)	10.0 (2.0)

Equivalent positions:

x	y	z
$1/2-x$	$-y$	$1/2+z$
$1/2+x$	$1/2-y$	$-z$
$-x$	$1/2+y$	$1/2-z$.

steroid glucoside. When **12** was submitted to acid hydrolysis with 2.5 N sulfuric acid, it was hydrolyzed to yield a mixture of two inseparable steroids, one of which seemed to be an artifact produced under acidic conditions. On the other hand, the enzymatic hydrolysis of **12** with β-glucosidase yielded D-glucose and a steroid genin (**12b**), $C_{27}H_{44}O_4$, colorless needles recrystallized from ethyl ether–methanol, mp 157.5—160.0 °C. The IR spectrum of **12b** showed absorption bands of hydroxyl (3380 cm^{-1}) and carbonyl (1705 cm^{-1}) groups. The occurrence of the carbonyl functions was also revealed by the UV (λ_{max} 283 nm, ε 213) and

TABLE V. Temperature Factors

No.	Atom	$U(ij)$'s are multiplied by 10^3					
		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
1	C1	72 (3)	43 (2)	23 (2)	−5 (2)	−1 (2)	0 (2)
2	C2	62 (3)	41 (2)	29 (2)	−4 (2)	6 (2)	−4 (2)
3	C3	42 (2)	39 (2)	29 (2)	−2 (2)	2 (2)	0 (2)
4	C4	52 (2)	42 (2)	31 (2)	−3 (2)	−4 (2)	1 (2)
5	C5	38 (2)	42 (2)	24 (2)	−1 (2)	−1 (2)	−1 (2)
6	C6	53 (2)	49 (2)	27 (2)	−6 (2)	−4 (2)	2 (2)
7	C7	51 (2)	45 (2)	25 (2)	−3 (2)	−1 (2)	0 (2)
8	C8	36 (2)	40 (2)	25 (2)	−3 (2)	0 (2)	0 (2)
9	C9	40 (2)	41 (2)	23 (2)	−1 (2)	1 (2)	−1 (1)
10	C10	41 (2)	41 (2)	28 (2)	−1 (2)	6 (2)	1 (2)
11	C11	80 (3)	42 (2)	27 (2)	−2 (2)	7 (2)	0 (2)
12	C12	75 (3)	43 (2)	27 (2)	−2 (2)	−3 (2)	2 (2)
13	C13	36 (2)	42 (2)	30 (2)	1 (2)	1 (2)	1 (2)
14	C14	40 (2)	41 (2)	26 (2)	1 (2)	1 (2)	−1 (2)
15	C15	69 (3)	45 (2)	32 (2)	2 (2)	−8 (2)	−6 (2)
16	C16	82 (3)	48 (2)	36 (2)	10 (3)	−8 (3)	−6 (2)
17	C17	43 (2)	41 (2)	37 (2)	3 (2)	−2 (2)	−1 (2)
18	C18	37 (2)	57 (3)	63 (3)	2 (2)	12 (2)	10 (2)
19	C19	43 (2)	49 (2)	69 (3)	2 (2)	19 (3)	−1 (2)
20	C20	45 (2)	44 (2)	42 (2)	−1 (2)	−5 (2)	1 (2)
21	C21	77 (3)	56 (3)	40 (2)	0 (3)	−2 (3)	6 (2)
22	C22	63 (3)	47 (2)	45 (2)	4 (2)	−22 (2)	−2 (2)
23	C23	113 (5)	48 (3)	64 (3)	7 (3)	−20 (4)	8 (3)
24	C24	80 (4)	55 (3)	141 (6)	8 (3)	−31 (5)	−4 (4)
25	C25	65 (3)	43 (2)	94 (4)	−2 (2)	−24 (3)	2 (3)
26	C26	63 (3)	50 (3)	76 (4)	11 (2)	−3 (3)	0 (3)
27	C27	97 (5)	128 (6)	101 (5)	−24 (5)	32 (5)	−18 (5)
28	O28	49 (2)	37 (1)	34 (1)	−5 (1)	−6 (1)	1 (1)
29	O29	88 (2)	56 (2)	50 (2)	2 (2)	−35 (2)	1 (2)
30	O30	55 (2)	63 (2)	73 (2)	11 (2)	−5 (2)	−6 (2)
31	O31	103 (3)	68 (2)	51 (2)	−10 (2)	−7 (2)	8 (2)
32	C32	37 (2)	45 (2)	29 (2)	−3 (2)	4 (2)	0 (2)
33	C33	37 (2)	49 (2)	32 (2)	−4 (2)	3 (2)	6 (2)
34	C34	37 (2)	39 (2)	39 (2)	−4 (2)	−3 (2)	8 (2)
35	C35	38 (2)	42 (2)	41 (2)	−4 (2)	−5 (2)	−2 (2)
36	C36	41 (2)	45 (2)	29 (2)	−4 (2)	−1 (2)	−2 (2)
37	C37	57 (3)	55 (2)	36 (2)	−1 (2)	7 (2)	−4 (2)
38	O38	42 (1)	46 (1)	27 (1)	−7 (1)	6 (1)	−2 (1)
39	O39	55 (2)	78 (2)	34 (2)	−14 (2)	13 (2)	−4 (2)
40	O40	44 (2)	48 (2)	55 (2)	−9 (1)	−5 (2)	18 (1)
41	O41	51 (2)	61 (2)	49 (2)	−14 (2)	−3 (2)	−13 (2)
42	O42	66 (2)	72 (2)	36 (2)	−11 (2)	5 (2)	6 (2)

^{13}C-NMR (δ 213.8 and 210.1) spectra. The ^{1}H-NMR spectrum ($CDCl_3$) showed signals due to tertiary methyl groups at δ 0.69 (18-CH_3) and 0.76 (19-CH_3), two secondary methyl groups at δ 1.10 (21-CH_3) and 0.91 (27-CH_3), a hydroxymethyl group at δ 3.43, and a hydroxymethine group at δ 3.58. These results suggested that **12b** has a cholestane skeleton with two hydroxyl and two carbonyl groups. Treatment of **12b** with acetic anhydride in pyridine gave a diacetate (**12c**). The ^{1}H-NMR spectrum showed two new acetoxyl signals at δ 2.06 and 2.03, while the methylene and methine signals were shifted to δ 3.93, 3.88 and 4.67, respectively. The methylene and methine signals were assignable to C-26 protons and the 3α-proton. In the ^{13}C-NMR spectrum of **12b**, the signal attributable to the C-3 position was

TABLE V. (continued)

No.	Atom	$U(ij)$'s are multiplied by 10^2 U_{11}	No.	Atom	U_{11}
43	HC1	7 (1)	70	H″C19	9 (2)
44	H′C1	7 (1)	71	HC20	8 (2)
45	HC2	7 (1)	72	HC21	8 (2)
46	H′C2	8 (2)	73	H′C21	9 (2)
47	HC3	4 (1)	74	H″C21	10 (2)
48	HC4	5 (1)	75	HC23	14 (3)
49	H′C4	7 (1)	76	H′C23	8 (2)
50	HC5	5 (1)	77	HC24	14 (2)
51	HC7	5 (1)	78	H′C24	16 (3)
52	H′C7	6 (1)	79	HC25	8 (2)
53	HC8	5 (1)	80	HC26	9 (2)
54	HC9	4 (1)	81	H′C26	9 (2)
55	HC11	8 (2)	82	HC27	9 (2)
56	H′C11	8 (2)	83	H′C27	10 (2)
57	HC12	6 (1)	84	H″C27	14 (2)
58	H′C12	6 (1)	85	HO31	13 (2)
59	HC14	6 (1)	86	HC32	6 (1)
60	HC15	7 (1)	87	HC33	7 (1)
61	H′C15	11 (2)	88	HC34	5 (1)
62	HC16	7 (2)	89	HC35	6 (1)
63	H′C16	11 (2)	90	HC36	6 (1)
64	HC17	6 (1)	91	HC37	9 (2)
65	HC18	6 (1)	92	H′C37	8 (2)
66	H′C18	10 (2)	93	HO39	14 (2)
67	H″C18	9 (2)	94	HO40	11 (2)
68	HC19	7 (1)	95	HO41	11 (2)
69	H′C19	9 (2)	96	HO42	13 (2)

Temperature factor T is in the form of

$$T=\exp(-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)).$$

remarkably shifted to upper field by 6.8 ppm, whereas the signals due to C-2 and C-4 were shifted to lower field as compared with those of **12**. Therefore, the glucose moiety was linked to the C-3 hydroxyl position on the genin, not the C-26 hydroxyl position. From the fragment ion peaks at m/z 345 and 126 in the EI-MS, it is deduced that one carbonyl group is located at C-22.[10] Reduction of **12b** with sodium borohydride gave two reduced compounds, triol (**12d**) and tetraol (**12e**) steroids. The signal assignable to 19-CH_3 of **12d** was shifted downfield by *ca.* 0.3 ppm compared with that of **12b** in the ^{1}H-NMR spectrum (CD_3OD). Therefore, a 1,3-diaxial relationship between 19-CH_3 and the new hydroxyl group in **12d** is expected. In addition, considering the ^{13}C-NMR spectral data of **12b**, another carbonyl group was concluded to be located at the C-6 position. The above spectral data and chemical properties of **12b** were essentially identical with those of a steroid sapogenin (**13**) isolated from the aerial parts of *Fritillaria thunbergii*.[10a] However, from differences in melting point (**12b**, 157.5—160.0 °C; **13**, 135—138 °C) and specific rotation (**12b**, −16.3°; **13**, −34.0°), **12b** was assumed to be a C-25 epimer of **13**; the literature does not mention the C-25 absolute configuration. The CD spectrum of **12b** exhibited a negative Cotton effect at 292 nm ($[\theta]=-6048$), and that of **12d** (C-22 keto-steroid) a weak, negative Cotton effect at 290 nm ($[\theta]=-174$). The application of the octant rule indicated that **12b** had a usual steroid skeleton. In addition, the results of the X-ray crystallographic analysis of **12** bearing D-glucose as a sugar moiety gave unequivocal evidence for the C-25 configuration shown in Fig. 1. Thus, the structure of **12** was

TABLE VI. Bond Lengths (Å)

Atom 1		Atom 2	Length (STD)	Atom 1		Atom 2	Length (STD)
C1	–	C2	1.526 (5)	C1	–	HC1	1.07 (5)
C1	–	C10	1.551 (5)	C1	–	H′C1	1.11 (4)
C2	–	C3	1.527 (5)	C2	–	HC2	1.09 (5)
C3	–	C4	1.516 (5)	C2	–	H′C2	1.10 (5)
C3	–	O28	1.436 (4)	C3	–	HC3	1.10 (4)
C4	–	C5	1.524 (5)	C4	–	HC4	1.10 (4)
C5	–	C6	1.517 (5)	C4	–	H′C4	1.08 (4)
C5	–	C10	1.565 (5)	C5	–	HC5	1.10 (4)
C6	–	C7	1.501 (6)	C7	–	HC7	1.09 (4)
C6	–	O29	1.215 (5)	C7	–	H′C7	1.11 (4)
C7	–	C8	1.541 (5)	C8	–	HC8	1.10 (4)
C8	–	C9	1.543 (5)	C9	–	HC9	1.11 (4)
C8	–	C14	1.520 (5)	C11	–	HC11	1.07 (5)
C9	–	C10	1.560 (5)	C11	–	H′C11	1.13 (5)
C9	–	C11	1.541 (5)	C12	–	HC12	1.08 (4)
C10	–	C19	1.552 (6)	C12	–	H′C12	1.12 (4)
C11	–	C12	1.548 (6)	C14	–	HC14	1.12 (4)
C12	–	C13	1.537 (5)	C15	–	HC15	1.10 (5)
C13	–	C14	1.544 (5)	C15	–	H′C15	1.11 (6)
C13	–	C17	1.567 (5)	C16	–	HC16	1.10 (5)
C13	–	C18	1.548 (6)	C16	–	H′C16	1.09 (6)
C14	–	C15	1.527 (5)	C17	–	HC17	1.12 (4)
C15	–	C16	1.549 (6)	C18	–	HC18	1.07 (4)
C16	–	C17	1.571 (6)	C18	–	H′C18	1.08 (5)
C17	–	C20	1.530 (6)	C18	–	H″C18	1.09 (5)
C20	–	C21	1.548 (6)	C19	–	HC19	1.08 (4)
C20	–	C22	1.537 (6)	C19	–	H′C19	1.10 (5)
C22	–	C23	1.517 (7)	C19	–	H″C19	1.09 (5)
C22	–	O30	1.205 (6)	C20	–	HC20	1.12 (5)
C23	–	C24	1.550 (9)	C21	–	HC21	1.08 (5)
C24	–	C25	1.528 (9)	C21	–	H′C21	1.09 (5)
C25	–	C26	1.503 (7)	C21	–	H″C21	1.11 (5)
C25	–	C27	1.558 (9)	C23	–	HC23	1.08 (6)
C26	–	O31	1.416 (6)	C23	–	H′C23	1.13 (5)
O28	–	C32	1.396 (5)	C24	–	HC24	1.09 (6)
C32	–	C33	1.521 (5)	C24	–	H′C24	1.14 (7)
C32	–	O38	1.428 (5)	C25	–	HC25	1.09 (4)
C33	–	C34	1.516 (5)	C26	–	HC26	1.07 (5)
C33	–	O39	1.418 (5)	C26	–	H′C26	1.13 (5)
C34	–	C35	1.529 (6)	C27	–	HC27	1.10 (5)
C34	–	O40	1.433 (5)	C27	–	H′C27	1.11 (5)
C35	–	C36	1.522 (6)	C27	–	H″C27	1.09 (6)
C35	–	O41	1.431 (5)	O31	–	HO31	0.96 (6)
C36	–	C37	1.518 (6)	C32	–	HC32	1.12 (4)
C36	–	O38	1.435 (5)	C33	–	HC33	1.09 (4)
C37	–	O42	1.428 (5)	C34	–	HC34	1.10 (4)
				C35	–	HC35	1.11 (4)
				C36	–	HC36	1.09 (4)
				C37	–	HC37	1.10 (5)
				C37	–	H′C37	1.10 (4)
				O39	–	HO39	0.96 (6)
				O40	–	HO40	0.95 (5)
				O41	–	HO41	0.95 (6)
				O42	–	HO42	0.96 (6)

STD: The standard deviation.

TABLE VII. Bond Angles (°)

Atom 1	Atom 2	Atom 3	Angle (STD)	Atom 1	Atom 2	Atom 3	Angle (STD)
C2	C1	C10	113.7 (3)	C16	C15	C14	104.0 (3)
C3	C2	C1	110.2 (3)	C17	C16	C15	106.7 (4)
C4	C3	C2	111.5 (3)	C20	C17	C13	119.2 (3)
C4	C3	O28	106.5 (3)	C20	C17	C16	111.3 (3)
C2	C3	O28	112.6 (3)	C13	C17	C16	103.3 (3)
C5	C4	C3	108.0 (3)	C21	C20	C17	114.4 (3)
C6	C5	C4	113.8 (3)	C21	C20	C22	106.4 (3)
C6	C5	C10	109.1 (3)	C17	C20	C22	110.5 (3)
C4	C5	C10	114.6 (3)	C23	C22	C20	117.3 (4)
C7	C6	C5	113.6 (3)	C23	C22	O30	121.3 (4)
C7	C6	O29	123.0 (4)	C20	C22	O30	121.3 (4)
C5	C6	O29	123.3 (4)	C24	C23	C22	110.3 (5)
C8	C7	C6	110.8 (3)	C25	C24	C23	113.3 (5)
C9	C8	C7	112.7 (3)	C26	C25	C24	116.2 (5)
C9	C8	C14	108.0 (3)	C26	C25	C27	108.5 (5)
C7	C8	C14	111.7 (3)	C24	C25	C27	109.9 (5)
C10	C9	C8	112.8 (3)	O31	C26	C25	112.2 (4)
C10	C9	C11	113.5 (3)	C32	O28	C3	115.0 (3)
C8	C9	C11	111.0 (3)	C33	C32	O28	109.1 (3)
C19	C10	C1	110.6 (3)	C33	C32	O38	109.2 (3)
C19	C10	C5	111.2 (3)	O28	C32	O38	106.4 (3)
C19	C10	C9	111.4 (3)	C34	C33	C32	110.1 (3)
C1	C10	C5	107.2 (3)	C34	C33	O39	108.8 (3)
C1	C10	C9	109.2 (3)	C32	C33	O39	109.2 (3)
C5	C10	C9	107.1 (3)	C35	C34	C33	111.6 (3)
C12	C11	C9	112.6 (3)	C35	C34	O40	109.6 (3)
C13	C12	C11	111.7 (3)	C33	C34	O40	109.2 (3)
C14	C13	C12	107.2 (3)	C36	C35	C34	110.8 (3)
C14	C13	C17	100.0 (3)	C36	C35	O41	110.0 (3)
C14	C13	C18	112.1 (3)	C34	C35	O41	106.3 (3)
C12	C13	C17	115.4 (3)	C37	C36	C35	113.7 (3)
C12	C13	C18	111.3 (3)	C37	C36	O38	105.6 (3)
C17	C13	C18	110.4 (3)	C35	C36	O38	109.9 (3)
C15	C14	C8	119.5 (3)	O42	C37	C36	107.5 (3)
C15	C14	C13	104.7 (3)	C32	O38	C36	112.7 (3)
C8	C14	C13	113.8 (3)				

assigned as (25*R*)-3β,26-dihydroxy-5α-cholestane-6,22-dione 3-*O*-β-D-glucopyranoside, and the C-25 configuration of the compound from *Fritillaria thunbergii* seems to be *S*.

Compounds **8**, **10**—**12** are new natural compounds, and **5**—**12** have a bitter taste. It is considered that **5**, **9** and **11**, which were obtained in good yields, make the main contribution to the bitter taste of the bulbs of *Lilium henryi*. The occurrence of the hydroxycinnamic acid conjugates with sucrose, such as **5**—**8**, is limited to several groups of higher plants. The conjugates have been found to occur in Polygonaceae,[11] Polygalaceae[12] and Brassicaceae[13] plants, and most predominantly in Liliaceae.[3,14] 26-Hydroxycholesterol or a derivative carrying an oxygen function at C-22 is considered to be a precursor in the biosynthesis of C_{27} steroidal alkaloids,[10b,15] which are widely distributed in Liliaceae and Solanaceae plants[16] as two types of compounds, one derived from a 25*R* precursor, and the other from 25*S*. In this investigation, we could not detect a steroidal alkaloid in the bulbs, but the isolation of **12** whose 25-geminal-dimethyl was stereospecifically oxidized is of interest from the viewpoint of chemotaxonomy. Further chemical examination of other lilies is under way, and in parallel with this, various biological tests of the compounds isolated in this research are in progress.

Experimental

All melting points were determined on a Yazawa micro melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 or a JASCO DIP-360 automatic polarimeter. UV spectra were measured on a Hitachi 557 spectrometer, and CD spectra on a JASCO J-500C spectropolarimeter. IR spectra were recorded with a Hitachi 260-30 or a Perkin-Elmer 1710 FT-IR instrument. MS were obtained on a Hitachi M-80 machine. ^{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 JEOL FX-100 (25.1 MHz) or a Bruker AM-400 (100.6 MHz) spectrometer respectively. Chemical shifts are expressed in δ (ppm) values with tetramethylsilane as an internal standard, and 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 preparative TLC on precoated Kieselgel 60 F_{254} (0.5 mm thick, Merck), and spots were detected by UV irradiation of the plates at 254 nm and by spraying 10% H_2SO_4 followed by heating.

Isolation——The dormant fresh bulbs of *Lilium henryi* Baker (7.2 kg) purchased from Sakata-shubyo Co., Ltd., Kanagawa prefecture, Japan, were cut into pieces and extracted with hot MeOH (60 l), and the extract was concentrated under reduced pressure. The crude residue, a dark viscous syrup, was suspended in H_2O, and extracted with $CHCl_3$ and then with *n*-BuOH. Each fraction was concentrated to a small volume under reduced pressure and subjected to column chromatography on silica gel with various solvent systems and on Sephadex LH-20 with $CHCl_3$ or MeOH as the eluent to provide compounds **1**—**12**. Purification of the compounds was carried out by preparative TLC. Compounds **1**—**4** were obtained from the $CHCl_3$-soluble portion and **5**—**12** from the *n*-BuOH-soluble portion.

1,2-*O*-Diferuloylglycerol (1)——A white amrophous powder (14.6 mg), $[\alpha]_D^{23}$ $\pm 0°$ ($c=0.29$, $CHCl_3$). The CD spectrum measured in EtOH showed no Cotton effect.

A Mixture of 1-*O*-Feruloyl-2-*O*-*p*-coumaroylglycerol (2a) and 1-*O*-*p*-Coumaroyl-2-*O*-feruloylglycerol (2b)——A pale-yellow amorphous powder (84.0 mg), $[\alpha]_D^{25}$ $\pm 0°$ ($c=0.49$, acetone). The CD spectrum measured in EtOH showed no Cotton effect.

1,3-*O*-Diferuloylglycerol (3)——A white amorphous powder (117 mg).

1-*O*-Feruloyl-3-*O*-*p*-coumaroylglycerol (4)——A pale-yellow amorphous powder (521 mg), $[\alpha]_D^{25}$ $\pm 0°$ ($c=0.54$, acetone).

Mild Methanolysis of 4——A MeOH–acetone (3 : 1) solution (4 ml) of **4** (150 mg) was treated with 3% NaOMe in MeOH (3.5 ml), and the mixture was left standing at room temperature for 30 min. The reaction mixture, after being diluted with MeOH, was passed through a cation exchange resin (Amberlite IR-120B) and the eluate was concentrated to give a residue, which was subjected to silica gel column chromatography (solvent $CHCl_3$–MeOH (19 : 1)), yielding methyl ferulate, methyl *p*-coumarate, 1-*O*-feruloylglycerol (**4a**) (15.2 mg) and 1-*O*-*p*-coumaroylglycerol (**4b**) (13.2 mg). Methyl ferulate and methyl *p*-coumarate were identified by TLC (solvent $CHCl_3$–EtOAc (5 : 1), methyl ferulate; *Rf* 0.71, methyl *p*-coumarate; *Rf* 0.63). 1-*O*-Feruloylglycerol (**4a**); a pale-yellow viscous syrup, TLC; *Rf* 0.55 (solvent $CHCl_3$–MeOH (8 : 1), $[\alpha]_D^{26}$ $\pm 0°$ ($c=0.48$, MeOH). ^{1}H-NMR (CD_3OD) δ: 7.63 (1H, d, $J=16.0$ Hz, H-7′), 7.19—6.73 (3H, H-2′, -5′, -6′), 6.36 (1H, d, $J=16.0$ Hz, H-8′), 4.19 (2H, m, H-1), 3.85 (3H, s, OMe), 3.77 (1H, m, H-2), 3.57 (2H, d, $J=5.5$ Hz, H-3). 1-*O*-*p*-Coumaroylglycerol (**4b**); a white amorphous powder, TLC; *Rf* 0.50 (solvent $CHCl_3$–MeOH (8 : 1), $[\alpha]_D^{29}$ $\pm 0°$ ($c=0.95$, MeOH). ^{1}H-NMR (CD_3OD) δ: 7.65 (1H, d, $J=16.0$ Hz, H-7′), 7.45 (2H, d, $J=9.0$ Hz, H-2′, -6′), 6.81 (2H, d, $J=9.0$ Hz, H-3′, -5′), 6.35 (1H, d, $J=16.0$ Hz, H-8′), 4.22 (2H, m, H-1), 3.83 (1H, m, H-2), 3.59 (2H, d, $J=5.5$ Hz, H-3).

3,6′-*O*-Diferuloylsucrose (5)——A white amorphous powder (1.04 g).

4-*O*-Acetyl-3,6′-*O*-diferuloylsucrose (6)——A white amorphous powder (140 mg).

4′-*O*-Acetyl-3,6′-*O*-diferuloylsucrose (7)——A white amorphous powder (234 mg).

3-*O*-Feruloyl-6′-*O*-(4-*O*-β-D-glucopyranosylferuloyl)sucrose (8)——A white amorphous powder (71.0 mg), $[\alpha]_D^{29}$ $-68.0°$ ($c=1.60$, MeOH). UV λ_{max}^{MeOH} nm (log ε): 234 (4.35), 300 sh (4.49), 322 (4.56). EI-MS *m/z* (%): 338 (3.8), 302 (2.8), 236 (2.3), 194 (100), 177 (78), 150 (54), 135 (25). IR ν_{max}^{KBr} cm^{-1}: 3415 (OH), 2926 (CH), 1703 (C=O), 1631 (C=C), 1600, 1514 (aromatic ring), 1261, 1164, 1072, 812. ^{1}H-NMR (C_5D_5N–CD_3OD (4 : 1)) δ: 8.01, 7.87 (each 1H, d, $J=15.9$ Hz, H-7″, -7‴), 7.48—7.06 (6H, H-2″, -2‴, -5″, -5‴, -6″, -6‴), 6.82, 6.63 (each 1H, d, $J=15.9$ Hz, H-8″, -8‴), 6.32 (1H, d, $J=7.9$ Hz, H-3), 6.09 (1H, d, $J=3.7$ Hz, H-1′), 5.60 (1H, d, $J=7.3$ Hz, H-1⁗), 5.25 (1H, dd, $J=$ 7.9, 7.9, H-4), 5.20 (1H, dd, $J=11.7$, 1.4 Hz, H-6′a), 4.96 (1H, ddd, $J=9.6$, 6.7, 1.4 Hz, H-5′), 4.79 (1H, dd, $J=11.7$, 6.7 Hz, H-6′b), 4.66 (1H, m, H-5), 4.57—4.01 (11H, H-1, -6, -3′, -2⁗—6⁗), 4.05 (1H, dd, $J=9.6$, 3.7 Hz, H-2′), 3.98 (1H, dd, $J=9.6$, 9.6 Hz, H-4′), 3.87, 3.79 (each 3H, s, OMe ×2). ^{13}C-NMR spectrum: Table I.

Acetylation of 8——A solution of **8** (15.4 mg) in Ac_2O–pyridine was allowed to stand at room temperature overnight. After addition of H_2O, the solution was extracted twice with $CHCl_3$. The organic layer was evaporated to dryness and the crude product was chromatographed on silica gel (solvent $CHCl_3$–EtOAc (5 : 1)) to give a white amorphous powder, 19.0 mg (**8a**). EI-MS *m/z* (%): 273 (11), 220 (16), 205 (58), 167 (33), 149 (100). IR ν_{max}^{KBr} cm^{-1}: 2962 (CH), 1756 (C=O), 1638 (C=O), 1601, 1511 (aromatic ring), 1422, 1371, 1229, 1162, 1038, 906. ^{1}H-NMR ($CDCl_3$) δ: 7.72, 7.60 (each 1H, d, $J=15.9$ Hz, H-7″, -7‴), 7.29—7.03 (6H, H-2″, -2‴, -5″, -5‴, -6″, -6‴), 6.49, 6.41 (each

1H, d, J=15.9 Hz, H-8″, -8‴), 5.71 (1H, d, J=3.6 Hz, H-1′), 5.60 (1H, d, J=6.1 Hz, H-3), 5.48 (1H, dd, J=6.1, 6.1 Hz, H-4), 5.46 (1H, dd, J=9.7, 9.7 Hz, H-3′), 5.31—4.99 (4H, H-1⁗—4⁗), 5.08 (1H, dd, J=9.7, 9.7 Hz, H-4′), 4.95 (1H, dd, J=9.7, 3.6 Hz, H-2′), 4.44—4.14 (10H, H-1, -5, -6, -5′, -6′, -6‴), 3.90, 3.86 (each 3H, s, OMe ×2), 3.81 (1H, m, H-5⁗), 2.32 (3H, s, arom. OAc), 2.12, 2.11, 2.10, 2.08×3, 2.04×2, 1.97, 1.88 (each 3H, s, OAc ×10).

Mild Hydrolysis of 8——Compound **8** (40 mg) in 10% NH_3 in MeOH–H_2O (2 : 1) was kept at room temperature for 30 min. The reaction solution was evaporated to dryness under reduced pressure and the crude product was chromatographed on silica gel using $CHCl_3$–MeOH–H_2O (3 : 1 : 0.1) to provide methyl ferulate (3.0 mg), 3-*O*-feruloylsucrose (**8b**) (4.1 mg), and glucosyl methyl ferulate (**8c**) (5.4 mg). 3-*O*-Feruloylsucrose (**8b**); a white amorphous powder. UV ν_{max}^{MeOH} nm (log ε): 238 (4.12), 302 (4.15), 328 (4.30), UV $\lambda_{max}^{MeOH+NaOMe}$ nm: 302 sh, 312, 383. IR ν_{max}^{KBr} cm^{-1}: 3415 (OH), 2927 (CH), 1704 (C=O), 1631 (C=C), 1599, 1516 (aromatic ring), 1429, 1383, 1263, 1161, 1128, 1051. ^{1}H-NMR (C_5D_5N–CD_3OD (4 : 1)) δ: 7.99 (1H, d, J=15.9 Hz, H-7″), 7.32 (1H, d, J=1.8 Hz, H-2″), 7.24 (1H, dd, J=8.1, 1.8 Hz, H-6″), 7.06 (1H, dd, J=8.1 Hz, H-5″), 6.62 (1H, d, J=15.9 Hz, H-8″), 6.27 (1H, d, J=7.8 Hz, H-3), 6.03 (1H, d, J=3.7 Hz, H-1′), 5.17 (1H, dd, J=7.8, 7.8 Hz, H-4), 4.68 (1H, ddd, J=9.5, 3.1, 2.5 Hz, H-5′), 4.53 (1H, ddd, J=7.8, 5.3, 4.7 Hz, H-5), 4.49 (1H, dd, J=9.5, 9.5 Hz, H-3′), 4.44 (1H, dd, J=11.8, 2.5 Hz, H-6′a), 4.35 (1H, dd, J=12.3, 5.3 Hz, H-6a), 4.30 (1H, dd, J=12.3, 4.7 Hz, H-6b), 4.25 (1H, dd, J=11.8, 3.1 Hz, H-6′b), 4.21 (1H, d, J=12.1 Hz, H-1a), 4.15 (1H, d, J=12.1 Hz, H-1b), 4.12 (1H, dd, J=9.5, 9.5 Hz, H-4′), 4.01 (1H, dd, J=9.5, 3.7 Hz, H-2′), 3.84 (3H, s, OMe). ^{13}C-NMR spectrum: Table I. Glucosyl methyl ferulate (**8c**); a white amorphous powder. UV λ_{max}^{MeOH} nm (log ε): 233 (4.29), 293 (4.40), 318 (4.40). EI-MS m/z (%): 371 (M^++H), 209 (38), 208 (100), 177 (48), 145 (13). IR ν_{max}^{KBr} cm^{-1}: 3456, 3320 (OH), 1713 (C=O), 1638 (C=C), 1602, 1580, 1513 (aromatic ring), 1434, 1351, 1311, 1265, 1196, 1170, 1137, 1093, 1025. ^{1}H-NMR (CD_3OD) δ: 7.63 (1H, d, J=16.0 Hz, H-7‴), 7.22 (1H, d, J=1.3 Hz, H-2‴), 7.16 (2H, H-5‴, -6‴, overlapping), 6.42 (1H, d, J=16.0 Hz, H-8‴), 4.96 (1H, d, J=7.4 Hz, H-1⁗), 3.91 (3H, s, OMe), 3.88 (1H, dd, J=12.0, 2.0 Hz, H-6⁗a), 3.78 (3H, s, COOMe), 3.71 (1H, dd, J=12.0, 5.1 Hz, H-6⁗b), 3.54 (1H, dd, J=8.9, 7.4 Hz, H-2⁗), 3.49 (1H, dd, J=8.9, 8.9 Hz, H-3⁗), 3.42 (2H, H-4⁗, -5⁗, overlapping). ^{13}C-NMR spectrum: Table I.

(2*S*)-1-*O*-*p*-Coumaroyl-3-*O*-β-D-glucopyranosylglycerol (Regaloside A) (9)——A pale-yellow amorphous powder (35.5 g), $[\alpha]_D^{25}$ −17.0° (c=1.00, MeOH).

Acetylation of 9——Upon acetylation of **9** (100 mg) with Ac_2O–pyridine, 130 mg of the peracetate (**9a**) was obtained as colorless needles (EtOH), mp 138.0—141.0 °C, undepressed by admixture with authentic regaloside A hexaacetate.

(2*S*)-1-*O*-*p*-Methoxycinnamoyl-3-*O*-β-D-glucopyranosylglycerol (Methylregaloside A) (10)——A colorless crysalline powder (84.0 mg) (Et_2O–MeOH), mp 146.0—148.0 °C, $[\alpha]_D^{22}$ −13.0° (c=0.20, MeOH). UV λ_{max}^{MeOH} nm (log ε): 224 (4.12), 300 sh (4.38), 308 (4.40). EI-MS m/z (%): 414 (M^+, 0.4), 263 (1.6), 252 (1), 235 (1.5), 205 (1.8), 178 (7), 163 (17), 161 (23), 145 (22), 121 (19), 103 (100). IR ν_{max}^{KBr} cm^{-1}: 3550, 3300 (OH), 2950, 2900 (CH), 1705 (C=O), 1630 (C=C), 1600, 1510 (aromatic ring), 1320, 1250, 1180, 1160, 1115, 1100, 1080, 1060, 1040, 1000, 980, 820. ^{1}H-NMR (CD_3OD) δ: 7.68 (1H, d, J=16.0 Hz, H-7′), 7.56 (2H, d, J=8.8 Hz, H-2′, -6′), 6.96 (2H, d, J=8.8 Hz, H-3′, -5′), 6.41 (1H, d, J=16.0 Hz, H-8′), 4.30 (1H, d, J=7.8 Hz, H-1″), 4.29 (1H, dd, J=11.5, 4.5 Hz, H-1a), 4.24 (1H, dd, J=11.5, 6.2 Hz, H-1b), 4.07 (1H, m, H-2), 3.96 (1H, dd, J=10.5, 5.2 Hz, H-3a), 3.87 (1H, dd, J=11.9, 1.2 Hz, H-6″a), 3.83 (3H, s, OMe), 3.71 (1H, dd, J=10.5, 4.7 Hz, H-3b), 3.67 (1H, br dd, J=11.9, 5.4 Hz, H-6″b), 3.39—3.26 (H-3″—5″), 3.22 (1H, dd, J=9.0, 7.8 Hz, H-2″). ^{13}C-NMR spectrum: Table II.

Acetylation of 10——A pyridine solution of **10** (10.0 mg) was treated with Ac_2O and the mixture was left standing overnight. After addition of H_2O and solvent removal under reduced pressure, the crude product was subjected to column chromatography using *n*-hexane–acetone (2 : 1) to give a pure acetate (**10a**) (12.1 mg) as a white amorphous powder. EI-MS m/z (%): 624 (M^+, 31), 331 (5), 322 (12), 278 (27), 277 (100), 178 (10), 170 (16), 161 (95), 145 (16). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3005 (CH), 1750, 1710 (C=O), 1625 (C=C), 1600, 1505 (aromatic ring), 1360, 1210, 1160, 1030. ^{1}H-NMR ($CDCl_3$) δ: 7.64 (1H, d, J=16.0 Hz, H-7′), 7.49 (2H, d, J=8.8 Hz, H-2′, -6′), 6.91 (2H, d, J=8.8 Hz, H-3′, -5′), 6.30 (1H, d, J=16.0 Hz, H-8′), 5.26 (1H, m, H-2), 5.21 (1H, dd, J=9.6, 9.6 Hz, H-3″), 5.09 (1H, dd, J=9.6, 9.6 Hz, H-4″), 5.00 (1H, dd, J=9.6, 7.9 Hz, H-2″), 4.56 (1H, d, J=7.9 Hz, H-1″), 4.39 (1H. dd, J=12.0, 3.7 Hz, H-1a), 4.29 (1H, dd, J=12.0, 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, 5.2 Hz, H-3a), 3.84 (3H, s, OMe), 3.75 (1H, dd, J=10.9, 5.5 Hz, H-3b), 3.71 (1H, ddd, J=9.6, 4.7, 2.3 Hz, H-5″), 2.09 ×2, 2.06, 2.02, 2.01 (each 3H, s, OAc ×5).

Alkaline Methanolysis Followed by Acetylation of 10——Compound **10** (30.0 mg) was treated with 3% NaOMe–MeOH at room temperature for 2 h. The reaction solution was neutralized with a cation exchange resin (Amberlite IR-120B) and the solution was concentrated to give a residue, which was subjected to Sephadex LH-20 column chromatography with MeOH as the eluent, yielding methyl *p*-methoxycinnamate (**10b**) (7.8 mg) and glycerol glucoside. Compound **10b**; colorless plates (*n*-hexane–acetone), mp 79.0—83.5 °C. IR ν_{max}^{KBr} cm^{-1}: 2945 (CH), 1710 (C=O), 1630 (C=C), 1600, 1505 (aromatic ring), 1430, 1330, 1300, 1285, 1250, 1200, 1190, 1170, 1020, 1010, 980, 840, 820. ^{1}H-NMR ($CDCl_3$) δ: 7.65 (1H, d, J=16.0 Hz, H-7′), 7.48 (2H, d, J=8.7 Hz, H-2′, -6′), 6.91 (2H, d, J=8.7 Hz, H-3′, -5′), 6.31 (1H, d, J=16.0 Hz, H-8′), 3.84 (3H, s, arom. OMe), 3.79 (3H, s, COOMe). Glycerol glucoside was acetylated with Ac_2O–pyridine to give a crude acetate. Purification of the acetate was carried out by using silica gel column chromatography with *n*-hexane–acetone (3 : 1) and *n*-hexane–EtOAc (1 : 2) to afford a pure acetate

(12.6 mg), colorless needles (*n*-hexane–Et_2O), mp 110.5—111.5 °C, $[\alpha]_D^{23}$ −7.9° (c=0.56, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 5.20 (1H, dd, J=9.5, 9.5 Hz, H-3′′), 5.18 (1H, m, H-2), 5.08 (1H, dd, J=9.5, 9.5 Hz, H-4′′), 4.98 (1H, dd, J=9.5, 7.9 Hz, H-2′′), 4.53 (1H, d, J=7.9 Hz, H-1′′), 4.30 (1H, dd, J=12.0, 3.6 Hz, H-1a), 4.25 (1H, dd, J=12.3, 4.8 Hz, H-6′′a), 4.14 (1H, dd, J=12.3, 2.5 Hz, H-6′′b), 4.13 (1H, dd, J=12.0, 6.2 Hz, H-1b), 3.95 (1H, dd, J=11.0, 5.1 Hz, H-3a), 3.70 (1H, ddd, J=9.5, 4.8, 2.5 Hz, H-5′′), 3.69 (1H, J=11.0, 5.4 Hz, H-3b), 2.10, 2.07, 2.06 ×2, 2.03, 2.01 (each 3H, s, OAc ×6).

(2*S*)-1-*O*-Caffeoyl-3-*O*-β-D-glucopyranosylglycerol (Regaloside C) (11)——A pale-yellow amorphous powder (1.05 g), $[\alpha]_D^{27}$ −11.3° (c=0.62, MeOH). UV λ_{max}^{MeOH} nm (log ε): 243 sh (3.92), 300 sh (4.04), 328 (4.15). UV $\lambda_{max}^{MeOH+NaOMe}$ nm: 263, 310, 376. EI-MS m/z (%): 416 (M^+, 2.5), 255 (7), 177 (9), 163 (63), 145 (100), 127 (32). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 2930 (CH), 1695 (C=O), 1630 (C=C), 1600, 1515 (aromatic ring), 1445, 1380, 1260, 1160, 1070, 1030, 810. ^{1}H-NMR (CD_3OD) δ: 7.58 (1H, d, J=15.9 Hz, H-7′), 7.05 (1H, d, J=2.0 Hz, H-2′), 6.95 (1H, dd, J=8.2, 2.0 Hz, H-6′), 6.78 (1H, d, J=8.2 Hz, H-5′), 6.29 (1H, d, J=15.9, H-8′), 4.30 (1H, d, J=7.7 Hz, H-1′′), 4.28 (1H, dd, J=11.4, 4.5 Hz, H-1a), 4.23 (1H, dd, J=11.4, 6.2 Hz, H-1b), 4.06 (1H, m, H-2), 3.96 (1H, dd, J=10.5, 5.2 Hz, H-3a), 3.87 (1H, dd, J=11.8, 1.4 Hz, H-6′′a), 3.71 (1H, dd, J=10.5, 4.6 Hz, H-3b), 3.67 (1H, br dd, J=11.8, 5.2 Hz, H-6′′b), 3.40—3.27 (H-3′′—5′′), 3.22 (1H, dd, J=9.0, 7.7 Hz, H-2′′). ^{13}C-NMR spectrum: Table II.

Acetylation of 11——Compound **11** (13.0 mg) was acetylated with Ac_2O–pyridine. The crude product was chromatographed over silica gel using *n*-hexane–acetone (2:1) to provide a pure acetate (**11a**) (16.0 mg) as a white amorphous powder. EI-MS m/z (%): 710 (M^+, 0.4), 668 (2.4), 626 (6.8), 465 (2.1), 464 (2.9), 447 (1.1), 363 (20), 331 (78), 321 (20), 271 (18), 205 (21), 169 (100), 163 (31), 162 (32), 145 (41), 117 (18), 109 (51). IR ν_{max}^{KBr} cm^{-1}: 2960 (CH), 1750 (C=O), 1635 (C=C), 1500 (aromatic ring), 1425, 1370, 1320, 1220, 1170, 1105, 1035, 900. ^{1}H-NMR ($CDCl_3$) δ: 7.62 (1H, d, J=16.0 Hz, H-7′), 7.41 (1H, dd, J=8.4, 2.0 Hz, H-6′), 7.37 (1H, d, J=2.0 Hz, H-2′), 7.23 (1H, d, J=8.4 Hz, H-5′), 6.37 (1H, d, J=16.0 Hz, H-8′), 5.25 (1H, m, H-2), 5.21 (1H, dd, J=9.5, 9.5 Hz, H-3′′), 5.08 (1H, dd, J=9.5, 9.5 Hz, H-4′′), 4.99 (1H, dd, J=9.5, 7.9 Hz, H-2′′), 4.55 (1H, d, J=7.9 Hz, H-1′′), 4.40 (1H, dd, J=12.1, 3.6 Hz, H-1a), 4.29 (1H, dd, J=12.1, 6.0 Hz, H-1b), 4.26 (1H, dd, J=12.3, 4.7 Hz, H-6′′a), 4.14 (1H, dd, J=12.3, 2.4 Hz, H-6′′b), 3.99 (1H, dd, J=10.9, 5.1 Hz, H-3a), 3.73 (1H, dd, J=10.9, 5.6 Hz, H-3b), 3.70 (1H, ddd, J=9.5, 4.7, 2.4 Hz, H-5′′), 2.31, 2.30 (each 3H, s, arom. OAc ×2), 2.09, 2.08, 2.06, 2.02, 2.00 (each 3H, s, OAc ×5).

Alkaline Methanolysis Followed by Acetylation of 11——Compound **11** (14.0 mg) was hydrolyzed with 3% NaOMe–MeOH, and the crude hydrolysate was chromatographed on silica gel using $CHCl_3$–MeOH (2:1) to give methyl caffeate and glycerol glucoside. Glycerol glucoside was acetylated with Ac_2O–pyridine to afford a hexaacetate (6.6 mg), which was identified as lilioside C hexaacetate.

(25*R*)-3β,26-Dihydroxy-5α-cholestane-6,22-dione 3-*O*-β-D-Glucopyranoside (12)——Colorless plates (530 mg) (isopropyl ether–MeOH), mp 217.5—219.5 °C, $[\alpha]_D^{25}$ −41.9° (c=0.85, EtOH). *Anal.* Calcd for $C_{33}H_{54}O_9$: C, 66.64; H, 9.15. Found: C, 66.46; H, 9.12. UV λ_{max}^{MeOH} nm (ε): 269 (129), 275 (132), 282 (197). CD (c=0.0034, MeOH) $[\theta]^{20}$ (nm): −6653 (291) (negative maximum). EI-MS m/z (%): 576 ($M^+ - H_2O$, 8), 571 (11), 461 (15), 433 (12), 416 (30), 415 (100), 398 (18), 397 (53), 392 (33), 317 (14), 299 (17), 283 (16), 271 (13), 253 (14). IR ν_{max}^{KBr} cm^{-1}: 3470, 3380 (OH), 2950, 2900, 2870, 2850 (CH), 1705 (C=O), 1445, 1385, 1365, 1355, 1340, 1250, 1110, 1100, 1075, 1060, 1030, 1015, 985, 975. ^{1}H-NMR (C_5D_5N) δ: 5.03 (1H, d, J=7.7 Hz, H-1′), 4.59 (1H, dd, J=11.7, 2.1 Hz, H-6′a), 4.39 (1H, dd, J=11.7, 5.6 Hz, H-6′b), 4.27 (1H, dd, J=8.7, 8.7 Hz, H-3′), 4.22 (1H, dd, J=8.7, 8.7 Hz, H-4′), 4.03 (1H, dd, J=8.7, 7.7 Hz, H-2′), 4.01—3.90 (2H, H-3, -5′, overlapping), 3.75 (1H, dd, J=10.5, 6.0 Hz, H-26a), 3.70 (1H, dd, J=10.5, 6.0 Hz, H-26b), 2.72—2.50 (3H, H-20, -23), 2.37 (1H, br d, J=12.6 Hz, H-5), 2.30 (1H, dd, J=13.1, 4.5 Hz, H-7 equatorial), 1.96 (1H, dd, J=13.1, 12.8 Hz, H-7 axial), 1.08 (3H, d, J=6.9 Hz, H-21), 1.07 (3H, d, J=6.7 Hz, H-27), 0.62 (3H, s, H-19), 0.56 (3H, s, H-18). ^{13}C-NMR spectrum: Table III.

Acetylation of 12——Compound **12** (25.0 mg) was acetylated with Ac_2O–pyridine and the crude product was chromatographed on silica gel using *n*-hexane–acetone (2:1) to yield a pure acetate (**12a**) (29.0 mg), colorless needles (*n*-hexane–Et_2O), mp 137.5—140.5 °C. EI-MS m/z (%): 803 ($M^+ - H$), 745 (1.5), 517 (1), 457 (90), 456 (27), 397 (100), 331 (22), 300 (20), 271 (13), 242 (26), 200 (20), 169 (56), 115 (100). IR ν_{max}^{KBr} cm^{-1}: 2940 (CH), 1745, 1700 (C=O), 1360, 1225, 1030. ^{1}H-NMR ($CDCl_3$) δ: 5.18 (1H, dd, J=9.5, 9.5 Hz, H-3′), 5.08 (1H, dd, J=9.5, 9.5 Hz, H-4′), 4.96 (1H, dd, J=9.5, 8.0 Hz, H-2′), 4.61 (1H, d, J=8.0 Hz, H-1′), 4.25 (1H, dd, J=12.2, 4.7 Hz, H-6′a), 4.12 (1H, dd, J=12.2, 2.5 Hz, H-6′b), 3.93 (1H, dd, J=10.9, 6.0 Hz, H-26a), 3.88 (1H, dd, J=10.9, 6.4 Hz, H-26b), 3.66 (1H, dd, J=9.5, 4.7, 2.5 Hz, H-5′), 3.56 (1H, m, H-3), 2.56—2.35 (3H, H-20, -23), 2.31 (1H, dd, J=13.3, 4.3 Hz, H-7 equatorial), 2.14 (1H, br d, J=12.6 Hz, H-5), 2.08, 2.07, 2.06, 2.02, 2.00 (each 3H, s, OAc ×5), 1.10 (3H, d, J=6.9 Hz, H-21), 0.94 (3H, d, J=6.7 Hz, H-27), 0.74 (3H, s, H-19), 0.69 (3H, s, H-18).

Acid Hydrolysis of 12——Compound **12** (120 mg) was hydrolyzed with 2.5 N H_2SO_4 in 50% EtOH on a boiling water bath for 2 h. The reaction mixture was diluted with H_2O and extracted with EtOAc. The EtOAc extract was washed with H_2O and concentrated to dryness under reduced pressure. The crude residue was purified by silica gel column chromatography using $CHCl_3$–acetone (4:1) to afford the hydrolysate (48.0 mg). The ^{1}H- and ^{13}C-NMR spectra measured in $CDCl_3$ indicated that the product was a mixture of two steroidal sapogenins. Efforts to separate the mixture were unsuccessful.

Enzymatic Hydrolysis of 12——A mixture of **12** (100 mg) and β-glucosidase (Tokyo Kasei Co., Ltd.) in AcOH–NaOAc buffer (pH 5) was incubated at 37 °C for 24 h, then H_2O was added and the whole was extracted with EtOAc.

The EtOAc-soluble portion, after removal of the solvent under reduced pressure, was chromatographed on silica gel using $CHCl_3$–acetone (4 : 1) to yield a pure sapogenin (**12b**) (39.0 mg), colorless needles (Et_2O–MeOH), mp 157.5—160.0 °C. The H_2O-soluble phase was subjected to silica gel column chromatography using $CHCl_3$–MeOH (2 : 1) to yield a white amorphous powder (13.9 mg), $[\alpha]_D^{20}$ +57.6° ($c=0.28$, H_2O). The *Rf* value on TLC (*Rf*=0.46, *n*-BuOH–AcOH–H_2O (2 : 1 : 1)) was consistant with that of an authentic sample. Compound **12b**; $[\alpha]_D^{22}$ −16.3° ($c=0.60$, MeOH). UV λ_{max}^{MeOH} nm (ε): 283 (213). CD ($c=0.0014$, MeOH) $[\theta]^{20}$ (nm): −6048 (292) (negative maximum). EI-MS *m/z* (%): 414.3119 (M^+-H_2O, 8, Calcd for $C_{27}H_{42}O_3$: 414.3136), 345 (12), 317 (27), 299 (15), 281 (8), 177 (33), 126 (100), 115 (57), 97 (77), 69 (80). IR ν_{max}^{KBr} cm^{-1}: 3380 (OH), 2950, 2875 (CH), 1705 (C=O), 1440, 1380, 1360, 1050, 1015, 990, 960. ^{1}H-NMR (CD_3OD) δ: 3.50 (1H, br m, H-3), 3.39 (1H, dd, $J=10.7$, 5.9 Hz, H-26a), 3.34 (1H, dd, $J=10.7$, 6.2 Hz, H-26b), 2.65—2.45 (3H, H-20, -23), 2.37 (1H, br dd, $J=12.6$, 2.4 Hz, H-5), 2.20 (1H, dd, $J=13.2$, 4.9 Hz, H-7 equatorial), 2.10 (1H, ddd, $J=13.2$, 13.2, 1.0 Hz, H-7 axial), 1.10 (3H, d, $J=6.9$ Hz, H-21), 0.90 (3H, d, $J=6.7$ Hz, H-27), 0.75 (3H, s, H-18 or H-19), 0.74 (3H, s, H-18 or H-19). ^{1}H-NMR ($CDCl_3$) δ: 3.58 (1H, m, H-3), 3.43 (2H, d, $J=5.8$ Hz, H-26), 2.58—2.40 (3H, H-20, -23), 2.30 (1H, dd, $J=13.2$, 4.5 Hz, H-7 equatorial), 2.22 (1H, br dd, $J=12.5$, 2.6 Hz, H-5), 1.96 (1H, br dd, $J=13.2$, 13.2 Hz, H-7 axial), 1.10 (3H, d, $J=6.9$ Hz, H-21), 0.91 (3H, d, $J=6.7$ Hz, H-27), 0.76 (3H, s, H-19), 0.69 (3H, s, H-18). ^{13}C-NMR spectrum: Table III.

Acetylation of 12b——Compound **12b** (15.0 mg) was acetylated with Ac_2O–pyridine to give the corresponding diacetate, which was purified by silica gel column chromatography with *n*-hexane–EtOAc (5 : 2) to yield a white amorphous powder (**12c**) (17.4 mg). EI-MS *m/z* (%): 516 (M^+, 0.5), 457 (2.9), 456 (55), 387 (6), 327 (2.2), 299 (27), 177 (29), 126 (22), 115 (100). IR ν_{max}^{KBr} cm^{-1}: 2950, 2870 (CH), 1735, 1705 (27), 1370, 1350, 1250, 1230, 1040, 1020, 1005, 985. ^{1}H-NMR ($CDCl_3$) δ: 4.67 (1H, m, H-3), 3.93 (1H, dd, $J=10.8$, 6.0 Hz, H-26a), 3.88 (1H, dd, $J=10.8$, 6.4 Hz, H-26b), 2.57—2.36 (3H, H-20, -23), 2.31 (1H, dd, $J=13.2$, 4.5 Hz, H-7 equatorial), 2.27 (1H, br dd, $J=12.8$, 2.8 Hz, H-5), 2.06, 2.03 (each 3H, s, OAc ×2), 1.10 (3H, d, $J=6.9$ Hz, H-21), 0.94 (3H, d, $J=6.7$ Hz, H-27), 0.77 (3H, s, H-19), 0.69 (3H, s, H-18).

Reduction of 12 by $NaBH_4$——A mixture of **12** (30.0 mg) dissolved in MeOH with $NaBH_4$ (10.0 mg) was allowed to stand at room temperature for 1 h. Purification of the EtOAc extract from the reaction mixture was carried out by silica gel column chromatography to give two products, **12d** (9.5 mg) (triol steroid) and **12e** (18.2 mg) (tetraol steroid). Compound **12d**; a white amorphous powder. UV λ_{max}^{MeOH} nm (ε): 295 (141). CD ($c=0.0023$, MeOH) $[\theta]^{20}$ (nm): 174 (290). EI-MS *m/z* (%): 435 (M^++H, 5), 417 (M^+ −OH, 6), 416 (M^+-H_2O, 10), 347 (12), 318 (9), 302 (28), 301 (85), 283 (22), 213 (12), 144 (23), 126 (91), 114 (55), 97 (76), 95 (62), 81 (47), 69 (100). IR ν_{max}^{KBr} cm^{-1}: 3421 (OH), 2931 (CH), 1711 (C=O), 1458, 1385, 1262, 1040, 804. ^{1}H-NMR (CD_3OD) δ: 3.73 (1H, br, H-6), 3.55 (1H, m, H-3), 3.40 (1H, dd, $J=11.2$, 5.9 Hz, H-26a), 3.34 (1H, dd, $J=11.2$, 6.2 Hz, H-26b), 2.65—2.45 (3H, H-20, -23), 1.10 (3H, d, $J=6.9$ Hz, H-21), 1.03 (3H, s, H-19), 0.90 (3H, d, $J=6.7$ Hz, H-27), 0.76 (3H, s, H-18). Compound **12e**; a white amorphous powder. EI-MS *m/z* (%): 419 (M^+ −OH), 418 (M^+-H_2O), 401 (M^++H−$2H_2O$, 0.5), 400 (M^+-2H_2O, 0.3), 349 (0.7), 331 (2), 319 (0.9), 318 (0.9), 313 (1.3), 302 (0.9), 229 (5), 117 (35), 99 (100), 81 (28). IR ν_{max}^{KBr} cm^{-1}: 3387 (OH), 2933, 2865 (CH), 1458, 1381, 1261, 1040, 803. The ^{1}H-NMR spectrum measured in CD_3OD indicated that **12e** was a mixture of two isomers.

X-Ray Analysis of 12——Crystals of **12** were grown in a mixed solution of isopropyl ether and MeOH as colorless plates. An X-ray specimen with approximate dimensions 0.4×0.5×0.2 mm was cut from the crystal and mounted on a Philips PW 1100 diffractometer. The setting angles of twelve reflections ($\theta=13°$—49°) and the intensity data were collected using CuK_α radiation monochromated by a graphite plate. The crystal data: $C_{33}H_{54}O_9$, $M_r=594.8$. Orthorhombic, space group $P2_12_12_1$, $Z=4$. Lattice constants; $a=9.771(7)$, $b=42.29(3)$, $c=7.664(4)$ Å, $U=3167$ Å^3. Crystal density (calculated, $D_{calc}=1.247$ g/cm^3, μ for Cu$K_\alpha=6.9$ cm^{-1}. Intensities of 3785 reflections were measured in the 2θ range of 6° through 156°, of which 3536 were taken as above the 2σ (*I*) level and used for the subsequent analysis. The crystal structure was determined by the direct method and refined by block-diagonal-matrix least-squares calculations. The final *R* value was 0.053 for 3536 reflections including 54 hydrogen atoms which were located on the difference electron density map and refined assuming isotropic thermal vibrations.

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