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# Studies on the Constituents of Asclepiadaceae Plants. LV.[1] The Structures of Three New Glycosides, Glaucoside-H, -I, and -J from the Chinese Drug "Pai-ch'ien," *Cynanchum glaucescens* HAND-MAZZ

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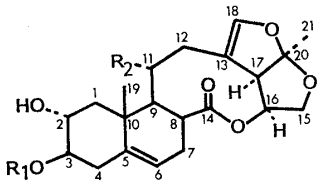
The glycosides of the Chinese crude drug "Pai-ch'ien" ("Bai-qian") were further investigated. Column chromatography of the polar portion of the crude glycosides of this drug gave three new glycosides named glaucoside-H (**1**), -I (**2**), and -J (**3**), and their structures were characterized on the bases of spectroscopic evidence and hydrolytic degradative studies. The structure of a new disaccharide named glaucobiose (**12**), formed by hydrolyses of **1**, **2**, and **3**, was also characterized as 4-*O*-*β*-D-glucopyranosyl-L-cymaropyranose. Compounds **1** and **2** were found to correspond to 4‴-*O*-*β*-D-glucopyranosyl derivatives of glaucoside-C (**4**) and glaucoside-B (**5**) previously reported, respectively. Compound **3** is a glycoside having glaucogenin-B as the aglycone, and its sugar moiety corresponds to that of the 4‴-*O*-*β*-D-glucopyranosyl derivative of glaucoside-D (**7**) previously reported.

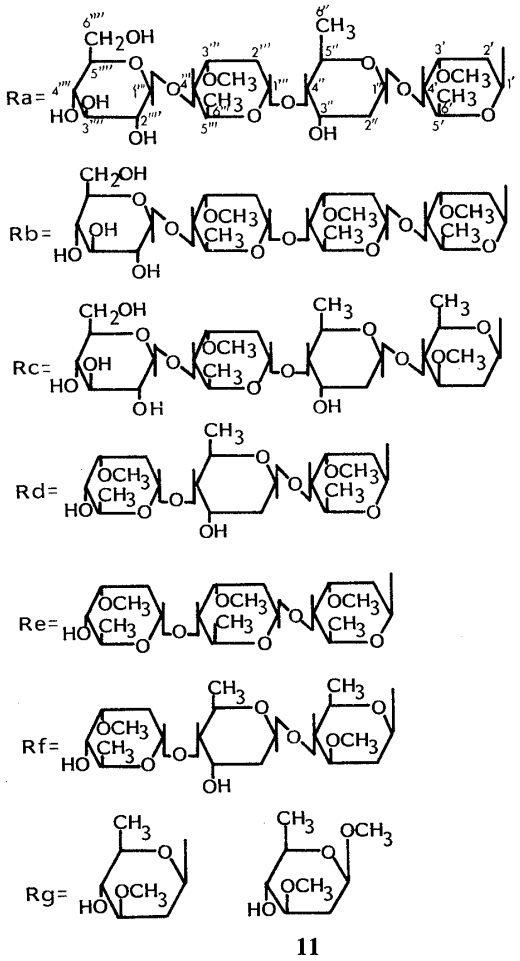
**Keywords**——glaucoside-H; glaucoside-I; glaucoside-J; glaucobiose; "Pai-ch'ien"; *Cynanchum glaucescens*; Asclepiadaceae; $^{13}C$ NMR

We have already reported in the previous papers[1,2] seven new glycosides, glaucoside-A, -B (**5**), -C (**4**), -D (**7**), -E, -F, and -G, obtained from the Chinese crude drug "Pai-ch'ien"[3a] ("Bai-qian"[3b]), dried root of *Cynanchum glaucescens* HAND-MAZZ (Asclepiadaceae). In this paper we wish to report the isolation and structural elucidation of three new glycosides named glaucoside-H (**1**), -I (**2**), and -J (**3**). The polar fractions of the crude glycosides of this drug were subjected to repeated silica gel and reversed phase gel column chromatography with various solvent systems to give **1**, **2**, and **3** (yields: 0.0227, 0.0050, and 0.0035% from the dried crude drug, respectively) as amorphous powders.

Glaucoside-H (**1**) has the molecular formula $C_{47}H_{72}O_{20}$ on the bases of its elemental analysis and field desorption mass spectrum (FD-MS) (*m/z*: 979 ($M^+ + Na$)), and gave glaucogenin-A[4] (**9**), digitoxose, cymarose, and an unidentified oligosaccharide on mild acidic hydrolysis; the former three compounds were identified by thin-layer chromatographic comparison with authentic samples. When **1** was hydrolyzed under strongly acidic conditions, only glucose was detectable in the hydrolysate. The oligosaccharide was commonly provided by mild hydrolysis of **1**, **2**, and **3**. The proton nuclear magnetic resonance ($^1H$ NMR) spectrum of **1** in deuterochloroform ($CDCl_3$)–tetradeuteromethanol ($CD_3OD$) (4:1) showed three secondary methyl and two methoxyl methyl peaks, and four anomeric proton signals at $\delta$ 4.38 (1H, d, $J=7.3$ Hz), 4.80 and 4.88 (each 1H, dd, $J=10$, 2 Hz), and 4.90 (1H, dd, $J=3$, 1 Hz). This indicated the presence of 2 mol of cymarose, 1 mol each of digitoxose and glucose in **1**: one of the three 2,6-dideoxysugars is $\alpha$-linked, while the others are $\beta$-linked. In the $^{13}C$ nuclear magnetic resonance ($^{13}C$ NMR) spectrum of **1** in pentadeuteropyridine ($C_5D_5N$) (Table I), glycosidation shifts were observed at C-2 (−2.6 ppm), C-3 (+8.5), and C-4 (−2.7) in the aglycone moiety, as in the cases of glaucoside-A, -B (**5**), -C (**4**), -D (**7**), -E, and -F

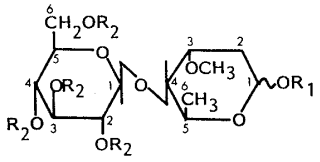


| | $R_1$ | $R_2$ |
|---|---|---|
| **1**: | Ra | H |
| **2**: | Rb | H |
| **3**: | Rc | OH |
| **4**: | Rd | H |
| **5**: | Re | H |
| **6**: | Rf | OH |
| **7**: | Rf | H |
| **8**: | Rg | OH |
| **9**: | H | H |
| **10**: | H | OH |

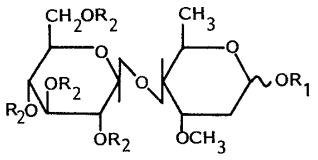


**11**

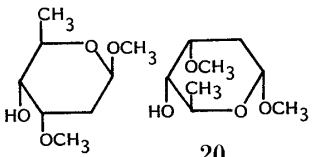
Chart 1



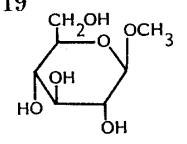
**12**: $R_1 = R_2 = H$
**13**: $R_1 = CH_3$, $\beta$; $R_2 = H$
**14**: $R_1 = CH_3$, $\alpha$; $R_2 = H$
**15**: $R_1 = Ac$, $\beta$; $R_2 = Ac$



**16**: $R_1 = R_2 = H$
**17**: $R_1 = CH_3$, $\beta$; $R_2 = H$
**18**: $R_1 = Ac$, $\beta$; $R_2 = Ac$



**19** **20**



**21**

Chart 2

previously reported, so that the sugar is linked to the C-3 hydroxyl group of the aglycone. Among the carbon signals due to the sugar moiety of **1**, two signal groups corresponding to $\beta$-linked cymaropyranose and digitoxopyranose, both of which were affected by glycosidation shifts[5,6] at the C-4 hydroxyl group,[1,2] were observed, so that the remaining cymaropyranose should be $\alpha$-linked. The five carbon signals distinguishable from the others by partially relaxed Fourier transform measurements[7] correspond to those of methyl $\beta$-D-glucopyranoside (**21**)[8] except for the anomeric carbon signal at $\delta$ 102.1 (d) (Table III); in order to clarify the nature of the significant up-field shift, the unidentified oligosaccharide was characterized and the $^{13}C$ NMR spectra of the methyl $\alpha$- and $\beta$-glycosides were studied in detail.

TABLE I. $^{13}C$ NMR Chemical Shifts for the Aglycone Moieties of **1**, **2**, and **3** and for **8**, **9**, and **10** (ppm in Pyridine-$d_5$)

| | **9** | **1** | **2** | **10** | **8** | **3** |
|---|---|---|---|---|---|---|
| C- 1 | 45.5 | 44.6 | 44.6 | 45.3 | 44.4 | 44.6 |
| C- 2 | 72.4 | 69.8 (−2.6)[a] | 69.8 | 73.2 | 69.8 (−3.4) | 69.9 (−3.3) |
| C- 3 | 76.7 | 85.2 (+8.5) | 85.2 | 76.6 | 85.2 (+8.6) | 84.9 (+8.3) |
| C- 4 | 40.1 | 37.4 (−2.7) | 37.4 | 40.1 | 37.1 (−3.0) | 37.1 (−3.0) |
| C- 5 | 140.9 | 139.4 | 139.4 | 141.6 | 140.5 | 140.6 |
| C- 6 | 120.2 | 120.5 | 120.4 | 126.9 | 127.5 | 127.6 |
| C- 7 | 30.1 | 30.0 | 30.0 | 23.6 | 23.5 | 23.6 |
| C- 8 | 53.2 | 52.9 | 52.9 | 51.4 | 51.2 | 51.3 |
| C- 9 | 40.4 | 40.1 | 40.1 | 50.3 | 50.1 | 50.3 |
| C-10 | 40.4 | 39.4 | 39.3 | 40.1 | 39.5 | 39.7 |
| C-11 | 23.9 | 23.8 | 23.7 | 67.8 | 67.7 | 67.9 |
| C-12 | 28.2 | 28.4 | 28.4 | 30.2 | 30.1 | 30.2 |
| C-13 | 118.5 | 118.2 | 118.2 | 118.6 | 118.5 | 118.6 |
| C-14 | 175.4 | 175.0 | 174.9 | 174.9 | 174.6 | 174.8 |
| C-15 | 67.8 | 67.5 | 67.6 | 67.9 | 67.7 | 67.9 |
| C-16 | 75.5 | 75.4 | 75.4 | 75.8 | 75.7 | 75.8 |
| C-17 | 56.2 | 56.0 | 56.0 | 56.4 | 56.2 | 56.3 |
| C-18 | 143.8 | 143.5 | 143.5 | 144.0 | 144.0 | 144.0 |
| C-19 | 19.2 | 18.9 | 18.9 | 19.0 | 18.7 | 18.8 |
| C-20 | 114.3 | 114.1 | 114.0 | 114.5 | 114.2 | 114.6 |
| C-21 | 24.8 | 24.7 | 24.7 | 24.8 | 24.7 | 24.8 |
| C- 1′ | | | | | 99.3 | |
| C- 2′ | | | | | 37.1 | |
| C- 3′ | | | | | 81.4 | |
| C- 4′ | | | | | 75.9 | |
| C- 5′ | | | | | 73.0 | |
| C- 6′ | | | | | 18.7 | |
| 3′-OMe | | | | | 57.0 | |

*a*) Values in parentheses are $\Delta\delta = \delta_1 - \delta_9$.

The polar fractions containing **1**, **2**, and **3** were hydrolyzed with 0.05 N $H_2SO_4$–75% methanol (MeOH), and the hydrolysates were subjected to repeated silica gel column chromatography to yield methyl glycosides **13** and **14** as colorless fine needles; both products gave a positive Keller–Kiliani reaction, indicating the presence of 2-deoxy sugars. Compounds **13** and **14** have the same molecular formula, $C_{14}H_{26}O_9$ (*m/z*: 339 ($M^+ + H$)), and showed one secondary methyl and two methoxyl methyl signals as well as two anomeric proton signals at $\delta$ 4.90 (1H, dd, $J$=9, 2 Hz) and 5.00 (1H, d, $J$=7.6 Hz) for **13** and at $\delta$ 4.67 (1H, dd, $J$=4, 2 Hz) and 4.99 (1H, d, $J$=7.6 Hz) for **14** in their $^1H$ NMR spectra, indicating that they are anomeric isomers of the 2,6-dideoxy sugar moieties. Each of them was further hydrolyzed with 0.05 N $H_2SO_4$ to give glaucobiose (**12**) as an amorphous hygroscopic white powder, $[\alpha]_D$ −72.6°, $C_{13}H_{24}O_9$ (*m/z*: 325 ($M^+ + H$)). Hydrolysis of **12** using snail enzyme ($\beta$-glucosidase) gave cymarose and glucose. The $^{13}C$-$^1H$ coupling constants on the anomeric centers[9] are 155.2 Hz for the glucose and 158.1 Hz for the cymarose in **13**, and 158.8 Hz for the glucose and 166.2 Hz for the cymarose in **14**, which indicate that **13** and **14** are methyl $\beta$-(**13**) and $\alpha$-glaucobioside (**14**), respectively. On acetylation, **12** afforded penta-*O*-acetyl glaucobiose (**15**), whose $^1H$ NMR (400 MHz) revealed all the proton signals without overlapping. The full assignments[10] are shown in Fig. 1. The prominent fragment ion peaks at *m/z*: 163 and 145 (base peak) in the FD-MS of **12** (Fig. 2), as well as the $^1H$ NMR data for **15** established the structure of **12** as 4-*O*-$\beta$-glucopyranosyl-cymaropyranose. The $^{13}C$ NMR

spectra of **13** and **14** were measured and their chemical shifts were assigned (Table II)[11] on the bases of those for methyl β-D-cymaropyranoside (**19**),[12] methyl α-L-cymaropyranoside (**20**),[2] and methyl β-D-glucopyranoside (**21**).[7] The glucosidation shift patterns in **13** and **14** were compared with that of the methyl β-glycoside (**17**) of strophanthobiose(4-*O*-β-D-glucopyranosyl-D-cymaropyranose) (**16**).[13] Significant differences were found in the glucosidation shift pattern (Table II) between **13** and **14**, and **17**. This was considered to be due to the

Table II. $^{13}C$ NMR Chemical Shifts for **13**, **14**, **17**, **19**, **20**, and **21** (ppm in Pyridine-$d_5$)

| | **19** | **21** | **17** | **13** | **20** | **14** |
|---|---|---|---|---|---|---|
| C-1 | 99.4 | | 99.3 | 99.2 | 97.6 | 97.5 |
| C-2 | 35.1 | | 36.1 | 35.2 | 31.9 | 31.9 |
| C-3 | 78.5 | | 77.8 (−0.7)[d] | 74.3[a] (−4.2 or −3.6) | 76.5 | 73.2 (−3.3) |
| C-4 | 74.0 | | 83.2 (+9.2) | 79.0 (+5.0) | 73.2 | 78.2[c] (+5.0 or +5.2) |
| C-5 | 71.0 | | 69.4 (−1.6) | 69.3 (−1.7) | 65.2 | 64.2 (−1.0) |
| C-6 | 18.9 | | 18.6 | 18.9 | 18.5 | 18.3 |
| -OMe | 56.0 | | 56.0 | 55.8 | 56.7 | 56.7 |
| | 57.8 | | 58.4 | 57.9 | 54.7 | 54.8 |
| C-1′ | | 105.4 | 106.5 (+1.1) | 101.8 (−3.6) | | 101.7 (−3.7) |
| C-2′ | | 74.8 | 75.4 | 74.9[a] | | 75.1 |
| C-3′ | | 78.1 | 78.4 | 78.4[b] | | 78.4[c] |
| C-4′ | | 71.4 | 71.9 | 71.6 | | 71.9 |
| C-5′ | | 78.1 | 78.4 | 78.2[b] | | 78.4[c] |
| C-6′ | | 62.5 | 63.1 | 62.7 | | 62.8 |
| -OMe | | 56.7 | | | | |

*a*), *b*), and *c*) Assignments may be interchanged.
*d*) Values in parentheses are $\Delta\delta = \delta_{17} - \delta_{21(19)}$.

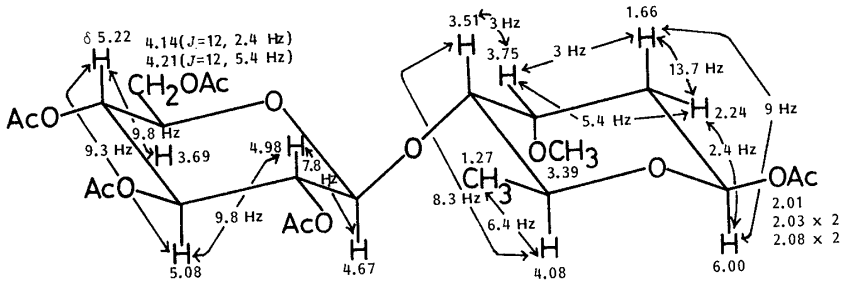



Fig. 1

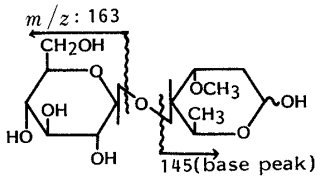



Fig. 2

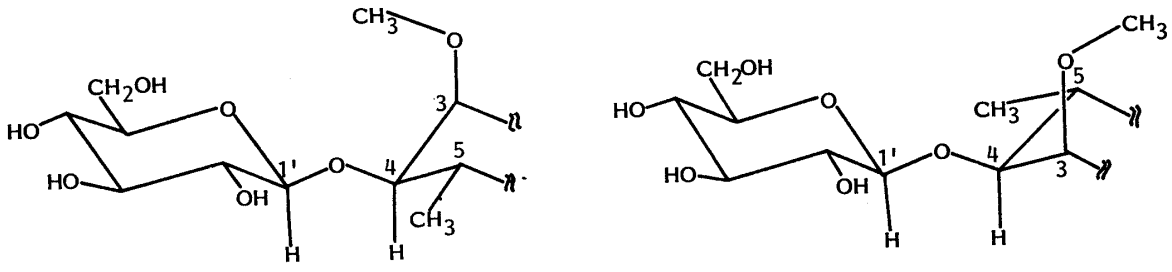



Fig. 3

position of β-alkyl substitution on the secondary alcohol in the aglycone in the most stable conformation averaged around the glycosidic linkage (Fig. 3), namely *syn* or *anti* to the glucopyranose-ring oxygen atom reported by Tanaka *et al.*[5] and Tori *et al.*[6] They reported that an alkyl substitution on the *syn*-β-carbon in a secondary alcohol moves the signal of the anomeric carbon of glucose (C-1′) up-field by *ca.* 4 ppm from that of **21** and the signal of the α-carbon of the aglycone (C-α) down-field by 5.5 ppm (±1.5 ppm), while on the *anti*-β-carbon, the C-1′ signal remained unchanged (±1.5 ppm) from that of **21** and that of C-α moves down-field by 10.4 ppm (±1.5 ppm). Evidently, the glucosidation shift pattern for **17** corresponds to *anti*-β-substitution while those of **13** and **14** correspond to the case of *syn*-β-substitution. Thus, the relative relationship between cymaropyranose and glucopyranose at the glycosidic linkage in **13** and **14** was clarified. As previously reported,[2] cymarose, digitoxose, and oleandrose, which constitute the glycosides of this drug, belong to L-, D-, and D-series, respectively; therefore the structure of **12** was established as 4-*O*-β-D-glucopyranosyl-L-cymaropyranose. When the carbon chemical shifts for the sugar moiety of **1** were compared with those for **13** and **14** (Table III), the remaining carbon chemical shifts for cymarose and glucose showed good agreement with those for **14**, indicating the presence of an α-linked glaucobiose moiety at the terminal of the sugar moiety in **1**. The carbon signal groups corresponding to **14** were commonly observed in the $^{13}C$ NMR spectra of **1**, **2**, and **3**, so that

TABLE III. $^{13}C$ NMR Chemical Shifts for the Sugar Moieties of **1**, **2**, and **3** and for **13** and **14** (ppm in Pyridine-$d_5$)

| | 1 | 2 | 3 | 14 | | 13 |
|---|---|---|---|---|---|---|
| C-1′ | 97.6 | 97.6 | 99.0[a] | | | |
| C-2′ | 36.8 | 36.9 | 37.7 | | | |
| C-3′ | 77.7 | 77.5 | 79.0 | | | |
| C-4′ | 82.7 | 82.6 | 82.5 | | | |
| C-5′ | 69.2 | 69.0 | 71.9 | | | |
| C-6′ | 18.1[a] | 18.1[a] | 18.2[b] | | | |
| 3′-OMe | 58.8 | 58.4 | 57.4[c] | | | |
| C-1″ | 98.1 | 98.6 | 98.4[a] | | | |
| C-2″ | 38.4 | 36.9 | 38.5 | | | |
| C-3″ | 68.6 | 77.6 | 69.1 | | | |
| C-4″ | 80.8 | 81.9 | 80.9 | | | |
| C-5″ | 67.5 | 69.1 | 67.9 | | | |
| C-6″ | 18.1[a] | 18.4[a] | 18.5[b] | | | |
| 3″-OMe | | 58.8 | | | | |
| C-1‴ | 100.1 | 100.1 | 98.3[a] | C-1 | 97.5 | 99.2 |
| C-2‴ | 32.0 | 32.1 | 32.4 | C-2 | 31.9 | 35.2 |
| C-3‴ | 73.4 | 73.1 | 73.6 | C-3 | 73.2 | 74.3[a] |
| C-4‴ | 77.9 | 78.1[b] | 78.3[d] | C-4 | 78.2[a] | 79.0 |
| C-5‴ | 65.9 | 64.9 | 66.0 | C-5 | 64.2 | 69.3 |
| C-6‴ | 18.4[a] | 18.4[a] | 18.5[b] | C-6 | 18.3 | 18.9 |
| 3‴-OMe | 57.0 | 56.7 | 57.1[c] | | | |
| C-1⁗ | 102.1 | 100.2 | 102.4 | C-1′ | 101.7 | 101.8 |
| C-2⁗ | 75.1 | 74.9 | 75.3 | C-2′ | 75.1 | 74.9[a] |
| C-3⁗ | 78.2[b] | 78.2[b] | 78.4[d] | C-3′ | 78.4[a] | 78.4[b] |
| C-4⁗ | 71.6 | 71.6 | 71.9 | C-4′ | 71.9 | 71.6 |
| C-5⁗ | 78.4[b] | 78.7[b] | 78.6[d] | C-5′ | 78.4[a] | 78.2[b] |
| C-6⁗ | 62.7 | 62.8 | 63.0 | C-6′ | 62.8 | 62.7 |
| | | | | -OMe | 54.8<br>56.7 | 54.8<br>56.7 |

*a*—*d*) Assignments in each column may be interchanged.

the three glycosides possessed α-linked glaucobiose at the terminal of their sugar moieties. Hydrolysis of **1** using snail enzyme gave glaucoside-C (**4**)[2] and glucose; the former was identical with an authentic sample on the bases of specific rotation, elemental analysis, and spectral evidence (infrared (IR), FD-MS, $^1$H NMR, and $^{13}$C NMR). Consequently, the structure of **1** was deduced to be glaucogenin-A 3-*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-L-cymaropyranoside.

Glaucoside-I (**2**), $C_{48}H_{74}O_{20}$, liberated **9**, cymarose, and **12** on acidic hydrolysis. The $^1$H NMR spectrum of **2** showed three secondary methyl and methoxyl methyl peaks, and four anomeric proton signals at δ 4.38 (1H, d, $J$=7.3 Hz) and 4.76 (3H, overlapped). The $^{13}$C NMR spectrum of **2** (Tables I and III) is analogous to that of **1**: signals due to the α-linked glaucobiose moieties are nearly superimposable, while the other carbon signals due to sugars are assignable to two sets of β-linked cymaropyranose glycosylated at the C-4 hydroxyl group. Enzymatic hydrolysis of **2** gave glaucoside-B[2] (**5**) as a deglucosyl derivative; this product was identical with an authentic sample in IR, $^1$H NMR, and FD-MS comparisons, establishing the structure of the sugar moiety unambiguously. Thus, the structure of **2** was established as glaucogenin-A 3-*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl-β-L-(1→4)-cymaropyranosyl-β-L- (1→4)-cymaropyranoside.

Glaucoside-J (**3**), $C_{47}H_{72}O_{21}$, afforded glaucogenin-B (**10**),[4] oleandrose, digitoxose, and **12** on acidic hydrolysis. The $^1$H NMR spectrum of **3** displayed three secondary methyl and methoxyl methyl peaks, and four anomeric proton signals at δ 4.38 (1H, d, $J$=7.8 Hz), 4.55 and 5.01 (each 1H, dd, $J$=10, 2 Hz), and 4.91 (1H, dd, $J$=4, 2 Hz). In the $^{13}$C NMR spectrum of **3**, signals due to the aglycone moiety (Table I) were assigned on the basis of those of **10**, in which glycosidation shifts were observed at C-2 (−3.3 ppm), C-3 (+8.3), and C-4 (−3.0), as with the glycosides of **9** so far obtained; therefore **3** is a glycoside which is glycosylated at the C-3 hydroxyl group. On the other hand, the sugar carbon signals (Table III) were assignable to β-linked digitoxopyranose and oleandropyranose, both of which are glycosylated at the C-4 hydroxyl group, along with α-linked glaucobiose. The FD-MS of **3** gave no useful information on the structure of the sugar moiety. However, the FD-MS of the deglucosyl derivative (**6**) of **3**, which was obtained by enzymatic hydrolysis of **3**, showed prominent fragment ion peaks at $m/z$: 666 ($M^+$ − 144), 536 (666 − 130), and 392 (536 − 144). This indicated that digitoxose is located between oleandrose and cymarose in the sugar sequence of **3**. Although a sufficient amount of **6** for measuring the $^{13}$C NMR spectrum was not available, the $^1$H NMR spectrum of **6** suggested strongly that the structure of the sugar moiety is the same as that of glaucoside-D (**7**)[2] on the basis of the near identity between the signals of the sugar moieties of **6** and **7**. The previous paper[1] reported the low hydrolyzability of the β-D-oleandropyranosyl linkage at the C-3 hydroxyl group of glaucogenin-A (**9**) compared with the β-L-cymaropyranosyl linkage at that position. If the sugar attached to the aglycone were oleandrose in **3**, we would expect **3** to yield glaucogenin-B 3-*O*-β-D-oleandropyranoside (**8**) on the basis of the close structural similarity between **9** and **10**. In fact, **3** was hydrolyzed to furnish **8** under mild acidic conditions; this product was identified by comparison of its EI-MS and $^1$H NMR spectra with those of an authentic sample which had been isolated and characterized from the hydrolysates obtained by mild acidic hydrolysis of the crude glycosides. Taken together, these results led to the structure of **3** as glaucogenin-B 3-*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl-(1→4)-β-D-digitoxopyranosyl-(1→4)-β-D-oleandropyranoside.

Thus the structures of **1**, **2**, and **3** were elucidated. Compounds **1** and **2** were found to correspond to 4‴-*O*-β-D-glucopyranosyl derivatives of glaucoside-C (**4**) and glaucoside-B (**5**) previously reported,[2] respectively, while the sugar moiety of **3** corresponds to that of glaucoside-D (**7**) previously reported.[2] These three new glycosides **1**, **2**, and **3** possess sugar sequences which obey a general rule pointed out by Shoji *et al.*[14] for cardiac and pregnane-

type glycosides of asclepiadaceae plants; 2,6-dideoxysugar, 6-deoxysugar, and glucose are linked with the aglycone in that order. Further investigation on the glycosides of this drug is under way.

## Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter at room temperature. IR spectra were recorded on a JASCO A-102 spectrometer. $^1$H NMR spectra were run on an FX-500 (400 MHz) or an FX-200 (200 MHz) spectrometer in $CDCl_3$ or in a mixture of $CDCl_3$–$CD_3OD$, and $^{13}$C NMR spectra on a FX-200 (50 MHz) or a FX-100 (25 MHz) machine in $C_5D_5N$ solution with tetramethylsilane as an standard. FD-MS was determined with a JEOL JMS-01SG-2 mass spectrometer. Thin layer chromatography (TLC) was performed on Merck precoated plates (Kieselgel 60 $F_{254}$, or PR-18 $F_{254}$ (reversed phase)). Column chromatography was carried out on Wakogel C-200 (200 mesh) or Wakogel ODS-30K (reversed phase).

**Isolation of the Glycosides, 1, 2, and 3**——A part of the crude glycosides (30 g) previously reported[3] was applied to a column of silica gel (600 g of Wakogel C-200), and the material was eluted with solvent of increasing polarity from benzene–acetone (5 : 1) to acetone. Elution with benzene–acetone (5 : 1) removed most of the less polar glycosides previously reported.[1,3] Elution with benzene–acetone (3 : 1) gave a fraction (17 g) which contained **1**, **2**, and **3**. The fraction was rechromatographed with 6% MeOH in chloroform ($CHCl_3$) on a column of silica gel (200 g of Wakogel C-200) to give a fraction (1.21 g) which contained mainly **1** and **2**. Further elution with 10% MeOH in $CHCl_3$ afforded a fraction (1.92 g) which contained **3**. The fraction containing **1** and **2** (1.21 g) was rechromatographed on a column of Wakogel ODS-30K (20 g) with MeOH–$H_2O$ (4 : 1) to furnish a fraction (720 mg) which was further rechromatographed on a column of silica gel (80 g of Wakogel C-200) with $CHCl_3$–MeOH–$H_2O$ (8 : 2 : 1, lower phase) to give **1** (270 mg) and **2** (60 mg) as amorphous white powders. The fraction containing **3** (1.92 g) was rechromatographed on a column of silica gel (80 g of Wakogel C-200) with 15% MeOH in aqueous saturated ethyl acetate (EtOAc), then with $CHCl_3$–MeOH–$H_2O$ (8 : 2 : 1, lower phase) to afford a fraction (92 mg) which contained mainly **3**. This fraction was further rechromatographed on a column of Wakogel ODS-30K (10 g) with MeOH–$H_2O$ (2 : 1) to yield 42 mg of **3** as an amorphous white powder. The *Rf* values of **1**, **2**, and **3** on TLC with $CHCl_3$–MeOH–$H_2O$ (9 : 3 : 1, lower phase) were 0.51, 0.50, and 0.37, respectively.

**Glaucoside-H (1)**——An amorphous powder, mp 156—159 °C, $[\alpha]_D$ −26.8° ($c$=1.14, $CHCl_3$). *Anal.* Calcd for $C_{47}H_{72}O_{20}\cdot 2H_2O$: C, 56.85; H, 7.71. Found: C, 56.54; H, 7.53. IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3600—3200, 1730, 1710, 1655, 1310, 1210, 1160, 1080, 950. FD-MS *m/z*: 979 ($M^+$+Na), 957 ($M^+$+H), 956 ($M^+$), 776 ($M^+$−glucose), 650 ($M^+$−glaucobiose+$H_2O$, base peak). $^1$H NMR (400 MHz, $CDCl_3$–$CD_3OD$=4 : 1) $\delta$: 0.95 (3H, s, 19-$CH_3$), 1.01 (1H, t, $J$=12 Hz, 1-CHα), 1.24, 1.25 (3H, and 6H, respectively, each d, $J$=6.4 Hz, 6′-, 6″-, and 6‴-$CH_3$), 1.54 (3H, s, 21-$CH_3$), 3.45, 3.46 (each 3H, 3′- and 3‴-$OCH_3$), 3.69 (1H, ddd, $J$=12, 10, 5 Hz, 2-CH), 4.18 (1H, dd, $J$=7.3 Hz, 1⁗-CH), 4.80, 4.88 (each 1H, dd, $J$=10, 2 Hz, 1′- and 1″-CH), 4.90 (1H, dd, $J$=3, 1 Hz, 1‴-CH), 5.33 (1H, ddd, $J$=10, 8, 7 Hz, 16-CH), 5.44 (1H, d, $J$=5 Hz, 6-CH), 6.28 (1H, d, $J$=2 Hz, 18-CH). $^{13}$C NMR (25 MHz): see Tables I and III.

**Glaucoside-I (2)**——An amorphous powder, mp 150—152 °C, $[\alpha]_D$ −19.6° ($c$=0.46, $CHCl_3$). *Anal.* Calcd for $C_{48}H_{74}O_{20}\cdot 2H_2O$: C, 57.24; H, 7.75. Found: C, 57.34; H, 7.92. IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3600—3200, 1730, 1710, 1655, 1310, 1160, 1080, 990. FD-MS *m/z*: 1009 ($M^+$+K, base peak), 994 ($M^+$+Na+H), 993 ($M^+$+Na), 971 ($M^+$+H), 970 ($M^+$), 664, 520, 376. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.96 (3H, s, 19-$CH_3$), 1.01 (1H, t, $J$=12 Hz, 1-CHα), 1.21, 1.24, 1.25 (each 3H, d, $J$=6 Hz, 6′-, 6″-, and 6‴-$CH_3$), 3.38, 3.45, 3.46 (each 3H, s, 3′-, 3″-, and 3‴-$OCH_3$), 3.86 (1H, dd, $J$=10, 9 Hz, 15-CHβ), 4.15 (1H, dd, $J$=9, 7 Hz, 15-CHα), 4.56 (1H, d, $J$=7.3 Hz, 1⁗-CH), 4.78 (3H, m, 1′-, 1″-, and 1‴-CH), 5.30 (1H, ddd, $J$=10, 8, 7 Hz, 16-CH), 5.41 (1H, d, $J$=4.5 Hz, 6-CH), 6.27 (1H, d, $J$=2 Hz, 18-CH). $^{13}$C NMR (25 MHz): see Tables I and III.

**Glaucoside-J (3)**——An amorphous powder, mp 134—139 °C, $[\alpha]_D$ −25.3° ($c$=1.01, $CHCl_3$). *Anal.* Calcd for $C_{47}H_{72}O_{21}\cdot H_2O$: C, 56.96; H, 7.53. Found: C, 56.96; H, 7.51. IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3600—3200, 1730, 1710, 1655, 1360, 1310, 1160, 1100, 1050, 940. FD-MS *m/z*: 1011 ($M^+$+K), 995 ($M^+$+Na), 536. $^1$H NMR (400 MHz, $CDCl_3$–$CD_3OD$=4 : 1) $\delta$: 0.98 (1H, t, $J$=12 Hz, 1-CHα), 1.00 (3H, s, 19-$CH_3$), 1.26 (6H, d, $J$=6.8 Hz, 6′- and 6‴-$CH_3$), 1.32 (3H, d, $J$=6.3 Hz, 6″-$CH_3$), 1.54 (1H, s, 21-$CH_3$), 3.36, 3.44 (each 3H, s, 3′- and 3‴-$OCH_3$), 4.38 (1H, d, $J$=7.8 Hz, 1⁗-CH), 4.55 (1H, dd, $J$=10, 2 Hz, 1′-CH), 4.91 (1H, dd, $J$=4, 2 Hz, 1‴-CH), 5.01 (1H, dd, $J$=10, 2 Hz, 1″-CH), 5.34 (1H, ddd, $J$=10, 8, 7 Hz, 16-CH), 5.42 (1H, br s, 6-CH), 6.28 (1H, d, $J$=2 Hz, 18-CH). $^{13}$C NMR (25 MHz): see Tables I and III.

**Hydrolysis of 1 with 1 N $H_2SO_4$–50% MeOH**——A solution of 2 mg of **1** in 2 ml of MeOH was treated with 2 ml of 2 N $H_2SO_4$, and the mixture was refluxed for 3 h, then diluted with 2 ml of water and concentrated to 1/2 the initial volume. The solution was again kept at around 90 °C for a further 3 h, then neutralized with 10% NaOH. The precipitates deposited by addition of MeOH was filtered off, and the filtrate was concentrated to give a dark-brown tar, which was analyzed by TLC with $CHCl_3$–MeOH–$H_2O$ (4 : 3 : 1, lower phase); glucose was detected by

comparison with an authentic sample (*Rf*, 0.47).

**Enzymatic Hydrolysis of 1, 2, and 3 with Snail Enzyme (β-Glucosidase)**——A suspension of **1** (94 mg) in 5 ml of 0.3 M NaOAc buffer adjusted to pH 5.5 was treated with a suspension of snail digestive glands (100 mg) in 5 ml of the buffer, and the mixture was allowed to stand at 37 °C for 126 h. TLC analysis with hexane–acetone (1 : 1) revealed the formation of **4** (*Rf*, 0.43). The solution was concentrated and the residue was subjected to silica gel column chromatography with hexane–acetone (2 : 1) to give **4** (46 mg), then with 10% MeOH in $CHCl_3$ to afford **1** (27 mg), both as amorphous white powders. Further elution with MeOH–$CHCl_3$ (1 : 1) gave a fraction in which glucose was detected (solvent: $CHCl_3$–MeOH–$H_2O$ (4 : 3 : 1, lower phase); *Rf*, 0.47).

Compound **4**: mp 116—122 °C, $[\alpha]_D$ −13.1° ($c$=1.74, $CHCl_3$). *Anal.* Calcd for $C_{41}H_{62}O_{15}$: C, 61.95; H, 7.86. Found: C, 62.11; H, 8.09. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3550, 3450, 1730, 1710, 1655, 1310, 1160, 1110, 1015, 880. FD-MS $m/z$: 795 ($M^+$+H), 794 ($M^+$, base peak), 650 ($M^+$−144), 520 (650−130), 376 (520−144). $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$: 0.94 (3H, s, 19-$CH_3$), 1.01 (1H, t, $J$=12 Hz, 1-CHα), 1.22 (3H, d, $J$=5.4 Hz, 6′-, 6″-, or 6‴-$CH_3$), 1.26 (6H, d, $J$=5.9 Hz, 6′-, 6″-, or 6‴-$CH_3$), 1.53 (3H, s, 21-$CH_3$), 3.42, 3.46 (each 3H, s, 3′- and 3‴-$OCH_3$), 3.84 (1H, dd, $J$=10, 9 Hz, 15-CHβ), 4.15 (1H, dd, $J$=9, 7 Hz, 15-CHα), 4.79, 4.85 (each 1H, dd, $J$=10, 2 Hz, 1′- or 1″-CH), 4.91 (1H, br d, $J$=4 Hz, 1‴-CH), 5.29 (1H, ddd, $J$=10, 8, 7 Hz, 16-CH), 5.40 (1H, d, $J$=4.5 Hz, 6-CH), 6.27 (1H, d, $J$=2 Hz, 18-CH). $^{13}C$ NMR (25 MHz): 18.1 (q), 18.3 (q), 18.4 (q), 18.9 (q), 23.8 (t), 24.8 (q), 28.4 (t), 29.9 (t), 32.2 (t), 36.9 (t), 37.4 (t), 38.3 (t), 39.4 (s), 40.1 (d), 44.6 (t), 52.9 (d), 56.0 (d), 56.9 (q), 58.8 (q), 67.0 (d), 67.6 (d), 67.6 (t), 68.6 (d), 69.2 (d), 69.8 (t), 72.5 (d), 74.5 (d), 76.4 (d), 77.7 (d), 80.6 (d), 82.7 (d), 85.3 (d), 97.6 (d), 98.2 (d), 110.2 (d), 114.1 (s), 118.2 (s), 120.5 (d), 139.5 (s), 143.5 (d), 174.9 (s). The specific rotation, elemental analysis, IR, FD-MS, $^1H$ NMR, and $^{13}C$ NMR data were identical with those of glaucoside-C previously reported.[3]

Similarly, a suspension of **2** (12 mg) in 2 ml of the buffer was mixed with a suspension of snail digestive glands (40 mg) in 2 ml of the buffer, and the mixture was allowed to stand at 37 °C for 126 h. TLC analysis with hexane–acetone (1 : 1) revealed the formation of **5** (*Rf*, 0.52). The solution was concentrated and subjected to silica gel column chromatography with hexane–acetone (3 : 1) to give **5** (3.5 mg) as an amorphous white powder. Further elution with $CHCl_3$–MeOH (1 : 1) yielded a fraction in which glucose was detected similarly.

Compound **5**: IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3550, 3450, 1730, 1710, 1655, 1450, 1310, 1160, 1090, 1050, 860. FD-MS $m/z$: 809 ($M^+$+H), 808 ($M^+$, base peak), 664 (808−144), 520 (664−144), 376 (520−144). $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$: 0.94 (3H, s, 19-$CH_3$), 1.01 (1H, t, $J$=12 Hz, 1-CHα), 1.21, 1.24, and 1.27 (each 3H, d, $J$=6 Hz, 6′, 6″-, and 6‴-$CH_3$), 1.53 (3H, s, 21-$CH_3$), 3.39, 3.46, and 3.49 (each 3H, s, 3′, 3″-, and 3‴-$OCH_3$), 3.85 (1H, dd, $J$=10, 9 Hz, 15-CHβ), 4.15 (1H, dd, $J$=9, 7 Hz, 15-CHα), 5.32 (1H, ddd, $J$=10, 8, 7 Hz, 16-CH), 5.42 (1H, d, $J$=5 Hz, 6-CH), 6.27 (1H, d, $J$=2 Hz, 18-CH). The spectral data were identical with those of glaucoside-B previously reported.[3]

Compound **3** (12 mg) was subjected to the same procedure as in the case of **2**, and the formation of **6** was revealed by TLC analysis (solvent: hexane–acetone = 1 : 1; *Rf*, 0.38). The same work-up as described above gave a residue, which was subjected to silica gel column chromatography with hexane–acetone (2 : 1) to give **6** (6.2 mg) as an amorphous white powder. Further elution with $CHCl_3$–MeOH (1 : 1) furnished a fraction in which glucose was detected similarly.

Compound **6**: An amorphous white powder, mp 126—132 °C, $[\alpha]_D$ −1.9° ($c$=0.62, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3600, 3550, 3450, 1730, 1710, 1310, 1160, 1110, 1080, 1050, 910, 860. FD-MS $m/z$: 811 ($M^+$+H), 810 ($M^+$, base peak), 666 ($M^+$−144), 536 (666−130), 392 (536−144). $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$: 0.96 (1H, t, $J$=12 Hz, 1-CHα), 1.00 (3H, s, 19-$CH_3$), 1.26 (6H, d, $J$=5.4 Hz, 6′- and 6‴-$CH_3$), 1.32 (3H, d, $J$=5.9 Hz, 6″-$CH_3$), 1.54 (3H, s, 21-$CH_3$), 3.42 (6H, s, 3′- and 3‴-$OCH_3$), 3.62 (1H, m, 3″- or 3‴-CH), 3.84 (1H, dd, $J$=10, 9 Hz, 15-CHβ), 4.06 (1H, m, 3″- or 3‴-CH), 4.17 (1H, dd, $J$=9, 7 Hz, 15-CHα), 4.49 (1H, dd, $J$=10, 2 Hz, 1′-CH), 4.90 (1H, br d, $J$=3 Hz, 1‴-CH), 5.00 (1H, dd, $J$=10, 2 Hz, 1″-CH), 5.37 (1H, ddd, $J$=10, 8, 7 Hz, 6-CH), 5.40 (1H, br s, 6-CH), 6.28 (1H, d, $J$=2 Hz, 18-CH).

**Isolation and Characterization of 8**——A part (40 g) of the hexane–benzene (1 : 1)-soluble and benzene-soluble portion of the crude glycosides was subjected to mild acidic hydrolysis, and the hydrolysates were applied to a column of silica gel (200 g of Wakogel C-300) to give the fraction (13.14 g) previously reported,[13] which contained **8** and **9**. This fraction was rechromatographed with hexane–EtOAc (1 : 2) to give a fraction which contained mainly **8**. During concentration of this fraction, precipitates of **8** were deposited. Filtration yielded a pure sample of **8** (49 mg) as an amorphous white powder.

Compound **8**: An amorphous powder, mp 228—233 °C, $[\alpha]_D$ +51.7° ($c$=1.01, $CHCl_3$). *Anal.* Calcd for $C_{28}H_{40}O_{10}$: C, 62.67; H, 7.51. Found: C, 62.68; H, 7.35. IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3600, 3450, 1730, 1710, 1655, 1310, 1170, 1070, 980, 880. EI-MS $m/z$: 536 ($M^+$), 392 ($M^+$−144), 374, 328, 144, 137, 113, 95, 87 (base peak), 69, 43. $^1H$ NMR (200 MHz, $CDCl_3$) $\delta$: 0.98 (1H, t, $J$=12 Hz, 1-CHα), 1.00 (3H, s, 19-$CH_3$), 1.35 (3H, d, $J$=5.9 Hz, 6′-$CH_3$), 3.41 (3H, s, 3′-$OCH_3$), 3.84 (1H, dd, $J$=10, 9 Hz, 15-CHβ), 4.17 (1H, dd, $J$=9, 7 Hz, 15-CHα), 5.36 (1H, ddd, $J$=10, 8, 7 Hz, 16-CH), 5.41 (1H, br s, 6-CH), 6.27 (1H, d, $J$=2 Hz, 18-CH). $^{13}C$ NMR (50 MHz): see Table I. A solution of **8** (2 mg) in 2 ml of MeOH was treated with 2 ml of 0.1 N $H_2SO_4$, and kept at around 80 °C for 30 min, then the mixture was diluted with 2 ml of water and concentrated to 1/2 the initial volume. The solution was kept at around 80 °C for a further 30 min, then neutralized with aqueous saturated $Ba(OH)_2$, and the precipitates were filtered off. The filtrate was concentrated to give a yellow syrup, which was analyzed by TLC with three solvent systems: solvent A, $CHCl_3$–

MeOH (9 : 1); solvent B, methylene chloride–ethanol (9 : 1); and benzene–acetone (5 : 3). When **8** was hydrolyzed, **10** and oleandrose were identified with solvent A; *Rf*, 0.24 and 0.43: solvent B; *Rf*, 0.27 and 0.40: solvent C; *Rf*, 0.20 and 0.43, respectively. The carbon chemical shifts for **8** (Table I) were assigned on the bases of those for **10** and methyl β-D-oleandropyranoside (**11**).[5a,6] The sugar carbon signals of **8** were in good agreement with those for **11**. The position at which the sugar was linked was established as the C-3 hydroxyl group of the aglycone on the basis that glycosidation shifts were affected centered at C-3 of **8** as in the cases of glycosides of **9** so far obtained.

**Hydrolysis of 3 with 0.05 N $H_2SO_4$–75% MeOH**——A solution of **3** (10 mg) in 3 ml of MeOH was treated with 1 ml of 0.2 N $H_2SO_4$, and the mixture was kept at around 50 °C for 20 min. TLC analysis with $CHCl_3$–acetone (3 : 2) revealed the formation of **8** (*Rf*, 0.31) and **10** (*Rf*, 0.16) as well as methyl glycosides. The solution was neutralized with saturated aqueous $Ba(OH)_2$ and the precipitates were filtered off. The filtrate was concentrated and the residue was subjected to silica gel column chromatography with $CHCl_3$–acetone (3 : 1) to give **8** (1 mg) as a colorless solid, EI-MS *m/z*: 536 ($M^+$), 392, 374 (392 − $H_2O$), 328, 236, 221, 145, 137, 113, 109, 95, 87, 69, 59, 44, 43. High-resolution EI-MS *m/z*: Calcd for $C_{28}H_{40}O_{10}$: 536.2621. Found: 536.2627. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 0.98 (1H, t, *J* = 12 Hz, 1-CHα), 1.00 (3H, d, *J* = 6.4 Hz, 6′-$CH_3$), 1.54 (3H, s, 21-$CH_3$), 3.41 (3H, s, 3′-$OCH_3$), 3.85 (1H, dd, *J* = 10, 9 Hz, 15-CHβ), 4.17 (1H, dd, *J* = 9, 7 Hz, 15-CHα), 4.54 (1H, dd, *J* = 10, 2 Hz, 1′-CH), 5.37 (1H, ddd, *J* = 10, 8, 7 Hz, 16-CH), 5.42 (1H, br s, 6-CH), 6.28 (1H, d, *J* = 2 Hz, 18-CH). The EI-MS and $^1H$ NMR data were identical with those of an authentic sample.

**Isolation of 12, 13, and 14**——The glycosides fraction (18 g) with polarity corresponding to those of **1**, **2**, and **3** was dissolved in 300 ml of MeOH and the solution was warmed to 70 °C, then treated with 100 ml of 0.2 N $H_2SO_4$ prewarmed to 70 °C. The mixture was kept at around 70 °C. After 30 min, the solution was neutralized with saturated aqueous $Ba(OH)_2$, and filtered. The filtrate was concentrated and chromatographed on a column of silica gel (200 g of Wakogel C-200) with benzene–acetone–MeOH (20 : 10 : 1) to give a fraction (2.5 g) which contained **13** and **14**. Rechromatography of the fraction with $CHCl_3$–MeOH–$H_2O$ (8 : 2 : 1, lower phase) afforded a fraction (900 mg) which consisted of **13** and **14**. A part of the fraction (300 mg) was further rechromatographed with the same solvent to give **13** (180 mg) and **14** (70 mg) as white powders. Crystallization from hexane–EtOAc yielded **13** (137 mg) and **14** (54 mg) as colorless fine needles. The remaining portion of the fraction (600 mg) was suspended in 10 ml of 0.05 N $H_2SO_4$ prewarmed to 70 °C. The solution was kept at around 70 °C for 50 min, then neutralized with saturated aqueous $Ba(OH)_2$. After removal of the precipitates by filtration, the filtrate was concentrated, and the residue was purified by silica gel column chromatography with $CHCl_3$–MeOH–$H_2O$ (8 : 2 : 1, lower phase) to give **12** (380 mg) as a hygroscopic white powder.

Compound **13**: Colorless fine needles, mp 95—98 °C, $[\alpha]_D$ −32.1° (*c* = 1.00, MeOH). *Anal.* Calcd for $C_{14}H_{26}O_9 \cdot 1/2H_2O$: C, 48.41; H, 7.75. Found: C, 48.15; H, 7.93. FD-MS *m/z*: 339 ($M^+ + H$), 338 ($M^+$), 145 (base peak). $^1H$ NMR (200 MHz, $C_5D_5N$) δ: 1.49 (3H, d, *J* = 6.3 Hz, 6-$CH_3$), 1.68 (1H, ddd, *J* = 13.5, 9, 2 Hz, 2-CHβ), 2.30 (1H, ddd, *J* = 13.5, 4, 2 Hz, 2-CHα), 3.46, 3.56 (each 3H, s, 1- and 3-$OCH_3$), 4.90 (1H, dd, *J* = 9, 2 Hz, 1-CH), 5.00 (1H, d, *J* = 7.6 Hz, 1′-CH). $^{13}C$ NMR (25 MHz): see Table II.

Compound **14**: Colorless fine needles, mp 143—145 °C, $[\alpha]_D$ −156° (*c* = 1.00, MeOH). *Anal.* Calcd for $C_{14}H_{26}O_9 \cdot 1/4H_2O$: C, 49.04; H, 7.79. Found: C, 49.03; H, 7.92. FD-MS *m/z*: 339 ($M^+ + H$), 236 (base peak), 163, 145. $^1H$ NMR (200 MHz, $C_5D_5N$) δ: 1.41 (3H, d, *J* = 6.6 Hz, 6-$CH_3$), 1.69 (1H, ddd, *J* = 14, 4, 3.5 Hz, 2-CHβ), 2.30 (1H, ddd, *J* = 14, 4, 2 Hz, 2-CHα), 3.30, 3.47 (each 3H, s, 1- and 3-$OCH_3$), 4.67 (1H, dd, *J* = 4, 2 Hz, 1-CH), 4.99 (1H, d, *J* = 7.6 Hz, 1′-CH). $^{13}C$ NMR (25 MHz): see Table II.

Compound **12**: An amorphous powder, $[\alpha]_D$ −72.6° (*c* = 0.81, $H_2O$). *Anal.* Calcd for $C_{13}H_{24}O_9O \cdot 3/2H_2$: C, 44.44; H, 7.75. Found: C, 44.18; H, 7.93. FD-MS *m/z*: 325 ($M^+ + H$), 307 ($M^+ + H - H_2O$), 163, 145 (base peak).

**Acetylation of 12**——A solution of 170 mg of **12** in 2 ml of pyridine was treated with 1 ml of acetic anhydride, and the mixture was allowed to stand at room temperature for 12 h. Usual work-up gave a crystalline solid (190 mg), which was recrystallized from ethanol to yield **15** (160 mg) as colorless fine needles, mp 163—165.5 °C, $[\alpha]_D$ −33.2° (*c* = 1.71, $CHCl_3$). *Anal.* Calcd for $C_{23}H_{34}O_{14}$: C, 51.68; H, 6.41. Found: C, 51.93; H, 6.37. FD-MS *m/z*: 535 ($M^+ + H$), 534 ($M^+$), 474 ($M^+ - AcOH$), 331 (base peak). $^1H$ NMR (400 MHz, $CDCl_3$) δ: 1.27 (3H, d, *J* = 6.4 Hz, 6-$CH_3$), 1.66 (1H, ddd, *J* = 13.7, 9, 3 Hz, 2-CHβ), 2.01, 2.03 × 2, 2.08 × 2 (each 3H, s, −O(C=O)$CH_3$), 2.24 (1H, ddd, *J* = 13.7, 5.4, 2.4 Hz, 2-CHα), 3.39 (3H, s, 3-$OCH_3$), 3.51 (1H, dd, *J* = 8.3, 3 Hz, 4-CH), 3.69 (1H, ddd, *J* = 9.8, 5.4, 2.4 Hz, 5′-CH), 3.75 (1H, ddd, *J* = 5.4, 3.3 Hz, 3-CH), 4.08 (1H, dq, *J* = 8.3, 6.4 Hz, 5-CH), 4.14 (1H, dd, *J* = 12, 2.4 Hz, 6′-CHa), 4.21 (1H, dd, *J* = 12, 5.4 Hz, 6′-CHb), 4.67 (1H, d, *J* = 7.8 Hz, 1′-CH), 4.98 (1H, dd, *J* = 9.8, 7.8 Hz, 2′-CH), 5.08 (1H, dd, *J* = 9.8, 9.3 Hz, 3′-CH), 5.22 (1H, dd, *J* = 9.8, 9.3 Hz, 4′-CH), 6.00 (1H, dd, *J* = 9, 2.4 Hz, 1-CH). These $^1H$ NMR data are nearly identical with those for penta-*O*-acetyl strophanthobiose (**18**).

**Hydrolysis of 1, 2, and 3 with 0.05 N $H_2SO_4$–50% MeOH**——Each of the three glycosides (2 mg) was subjected to acidic hydrolysis in the same manner as described in the case of **8**, and the products were analyzed by TLC with solvents A, B, and C. When **1** was hydrolyzed, **9**, cymarose, and digitoxose were identified by TLC comparisons with authentic samples (*Rf* values are 0.51, 0.47, and 0.21 with solvent A; 0.53, 0.42, and 0.21 with solvent B; and 0.43, 0.43, and 0.17 with solvent C, respectively). In the same manner, cymarose and **9** were identified in the hydrolysate of **2**. Oleandrose (*Rf* 0.43, 0.33, and 0.31 with solvents A, B, and C, respectively), digitoxose, and **10** (*Rf* 0.24, 0.27, and 0.20 with solvents A, B, and C, respectively) were identified similarly. Compound **12** was identified in the hydrolysates

of **1**, **2**, and **3** by comparison with an authentic sample with three solvent systems: *Rf* 0.20 with $CHCl_3$–MeOH–$H_2O$ (8:2:1, lower phase); *Rf* 0.31 with $CHCl_3$–MeOH (4:1); *Rf* 0.21 with benzene–acetone–MeOH (3:3:1).

**Enzymatic Hydrolysis of 12**——Compound **12** (4 mg) was subjected to the same procedure as in the cases of **1**, **2**, and **3**, and cymarose and glucose were detected in the suspension similarly.

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