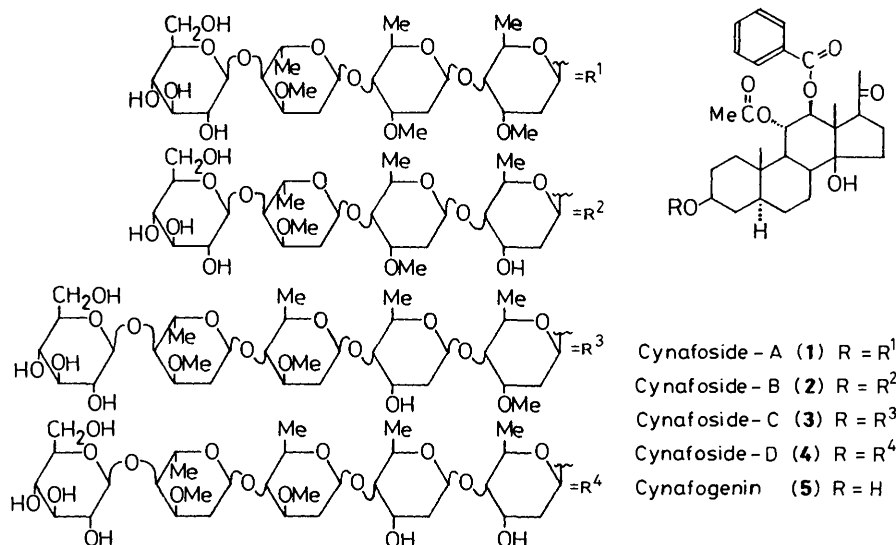
Studies on the Constituents of Asclepiadaceae Plants. Part 67.[1] Further Studies on Glycosides with a Novel Sugar Chain Containing a Pair of Optically Isomeric Sugars, D- and L-Cymarose, from *Cynanchum africanum*

Sachiko Tsukamoto, Koji Hayashi,* and Kô Kaneko
Faculty of Pharmaceutical Sciences, Hokkaido University, Kita-12-jo, Nishi-6-chome, Kita-ku, Sapporo 060, Japan
Hiroshi Mitsuhashi
Tsumura Laboratory, Yoshihara 3586, Ami-cho, Inashiki-gun, Ibaragi 300-11, Japan
Friedrich O. Snyckers and Theunis G. Fourie
Noristan Ltd., Noristan Building, 326 Marks Street, Waltloo, Pretoria, Republic of South Africa

Two new glycosides named cynafoside-C (**3**) and -D (**4**) were isolated from *Cynanchum africanum* R. Br. (Asclepiadaceae), and their structures were deduced on the basis of spectral and chemical evidence. The absolute configurations of cymarose, oleandrose, and digitoxose included in compounds (**3**) and (**4**) were each determined by h.p.l.c. analysis of their carbamoyl derivatives on a chiral column after acidic hydrolysis of the glycosides. A unique feature is that cynafoside-C (**3**), as well as cynafoside-A (**1**) and-B (**2**), contains a pair of optically isomeric sugars, D-and L-cymarose, in the sugar chain.

Cynanchum africanum R. Br. (Asclepiadaceaea) causes stock losses in South Africa owing to cynanchosis, an intoxication affecting the nervous and muscular systems.[2] In a previous paper[3] we reported the isolation and the structural elucidation of two glycosides, cynafoside-A (**1**) and -B (**2**), from the dried leaf and stem of this plant. In this paper we describe the structures of two additional glycosides named cynafoside-C (**3**) and -D (**4**). The absolute stereochemistry of the sugar moieties, cymarose, oleandrose, and digitoxose, was ascertained by using a chiral h.p.l.c. column, and was confirmed by comparison with that of authentic material.[4–6]



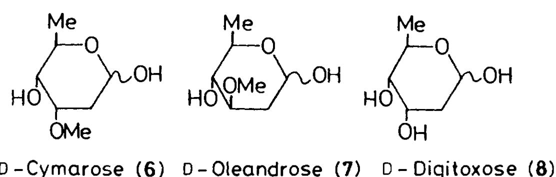
Results and Discussion

Compound (3) has the molecular formula $C_{63}H_{96}O_{24}$ on the basis of elemental analysis. The ^1H n.m.r. (500 MHz) and the ^{13}C n.m.r. spectra (Tables 1 and 2) suggested that the structure of cynafoside-C (3) was analogous to those of (1) and (2). Five anomeric carbon signals at δ_C 96.0, 97.2, 100.3, 101.2, and 102.1 revealed the presence of five sugars in compound (3). Acidic hydrolysis (0.025M H_2SO_4–75% MeOH; 60 °C; 15 min) of compound (3) afforded an aglycone (5) and a mixture of sugars. The mass spectrum of aglycone (5) gave a molecular ion peak at *m/z* 512. The ^1H n.m.r. spectrum (100 MHz) showed four tertiary methyl proton signals at δ_H 0.98, 1.16, 1.65, and 2.07, two vicinal methine proton signals bearing ester groups at δ_H 4.95 (1 H, d, *J* 9.8 Hz) and 5.44 (1 H, t, *J* 9.8 Hz), and five aromatic proton signals at δ_H 7.46—7.65 (3 H, m) and 8.06 (2 H, dd, *J* 8.3 and 2.0 Hz), which were characteristic of cynafogenin,[3] the aglycone common to both glycosides (1) and (2). By comparing m.p.s, specific rotations, and R_F-values on t.l.c. with those of an authentic sample, compound (5) was confirmed to be cynafogenin. The mixture of sugars was separated into four sugars (6), (7), (8), and (9) by column chromatography on silica gel. In the mass spectra of sugars (6), (7), and (8) molecular ion peaks were observed at *m/z* 162, 162, and 148, respectively, indicating monosaccharide units. In the ^1H n.m.r. spectrum ($CDCl_3$) of compound (6), four methoxy methyl groups appeared at δ_H 3.31, 3.37, 3.44, and 3.54 in the proportions *ca.* 15:10:9:7. The signal pattern was super-

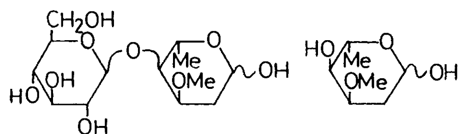
Table 1. ^{13}C N.m.r. chemical shifts (δ_C) of aglycone (**5**) and the aglycone moieties of glycosides (**3**), (**4**), and (**10**) in C_5D_5N

	(**5**)	(**3**)	(**4**)	(**10**)
C-1	39.7	37.9	38.1	38.1
C-2	32.8	30.3 (−2.5)	30.4 (−2.4)	30.4 (−2.4)
C-3	69.9	76.0 (+6.1)	76.0 (+6.1)	76.1 (+6.2)
C-4	39.7	35.4 (−4.3)	35.5 (−4.2)	35.5 (−4.2)
C-5	45.1	44.6	44.6	44.7
C-6	29.5^{a}	29.3^{a}	29.3^{a}	29.4^{a}
C-7	28.5^{a}	28.4^{a}	28.4^{a}	28.4^{a}
C-8	40.2	39.9	40.0	40.0
C-9	50.2	50.1	50.1	50.1
C-10	38.0	37.8	38.0	38.0
C-11	71.7	71.7	71.6	71.6
C-12	79.1	78.9	79.1^{b}	79.1
C-13	55.0	54.8	54.9	55.0
C-14	84.0	83.8	83.9	83.9
C-15	33.9	33.9	33.9	33.9
C-16	24.3	24.2	24.3	24.3
C-17	58.5	58.3	58.4	58.4
C-18	11.9	11.7	11.8	11.8
C-19	12.5	12.3	12.4	12.4
C-20	213.3	213.4	213.4	213.4
C-21	31.7	31.7	31.7	31.7
Me*C*O$_2$	170.4	170.2	170.4	170.2
*Me*CO$_2$	21.4	21.3	21.3	21.3
Ph*C*O$_2$	166.8	166.8	166.7	166.7
*ipso-Ph*CO$_2$	130.2	130.0	130.1	130.2
*o-Ph*CO$_2$	130.2	130.0	130.1	130.2
*m-Ph*CO$_2$	129.2	129.1	129.2	129.2
*p-Ph*CO$_2$	133.9	133.9	133.9	133.9

^{a,b} In each column assignments may be interchangeable between Tables 1 and 2. Values in parentheses are glycosidation shifts.



D-Cymarose (**6**) D-Oleandrose (**7**) D-Digitoxose (**8**)



Glaucobiose (**9**) L-Cymarose (**11**)

imposable on that of cymarose. The ^{1}H n.m.r. spectrum of compound (**7**) in $CDCl_3$ was characteristic of oleandrose. The signals of α-and β-oleandropyranoses were observed in the ratio *ca.* 2:1. The ^{1}H n.m.r. spectrum ($CDCl_3$) of compound (**8**) revealed the signals due to β-digitoxopyranose. In $CDCl_3$ digitoxose exists mostly as the β-digitoxopyranose form. The absolute configurations of compounds (**6**), (**7**), and (**8**) were each determined on the basis of h.p.l.c. analysis on a chiral column after conversion into methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)glycosides for (**6**)[4] and (**7**)[5] and the 1-*O*-(3,5-dinitrophenylcarbamoyl)-3,4-*O*-isopropylidene derivative for (**8**).[6] The results of this h.p.l.c. analysis apparently demonstrated that these sugars all belonged to the D-series by direct comparison with authentic samples of their D- and L-enantiomers (Figure 1). The chromatogram of the samples derived from compounds (**6**) and (**7**) showed four peaks. They correspond to carbamates of the four methyl glycosides

Table 2. ^{13}C N.m.r. chemical shifts (δ_C) of the sugar moieties of glycosides (**1**), (**2**), (**3**), (**4**), and (**10**) in C_5D_5N

	(**1**)	(**2**)	(**3**)	(**4**)	(**10**)
	D-Cym	Digit	D-Cym	Digit	D-Cym
C-1	95.9	95.9	96.0	96.0	96.1
C-2	37.1^{a}	39.0	37.1	39.0	37.3
C-3	77.9^{b}	68.5	78.0	68.7^{c}	78.1
C-4	83.2^{c}	83.3	83.2^{b}	83.4^{d}	83.4^{b}
C-5	69.1^{d}	67.4	68.9	67.5^{e}	69.1
C-6	18.5^{e}	18.6^{a}	18.5^{c}	18.7^{f}	18.6^{c}
3-OMe	58.7^{f}		58.8^{d}		58.9^{d}
	D-Cym	D-Cym	Digit	Digit	Digit
C-1	100.2	99.6	100.3	99.8	100.5
C-2	36.9^{a}	36.8	38.6	38.7^{c}	39.0
C-3	77.6^{b}	77.6	68.3	68.7	68.5
C-4	82.1^{c}	82.1	83.1^{b}	83.2^{d}	83.3^{b}
C-5	68.9^{d}	69.2	67.4	67.4^{e}	67.5
C-6	18.4^{e}	18.6^{a}	18.5^{c}	18.6^{f}	18.6^{c}
3-OMe	58.4^{f}	58.5			
			D-Ole	D-Ole	D-Ole
C-1			101.2	101.4	101.4
C-2			36.8	36.8	36.9
C-3			78.9	79.0^{b}	79.1
C-4			81.5^{b}	81.6^{d}	81.5^{b}
C-5			72.0	72.1	72.2
C-6			18.5^{c}	18.4^{f}	18.6^{c}
3-OMe			56.3^{d}	56.4^{g}	56.4^{d}
	L-Cym	L-Cym	L-Cym	L-Cym	L-Cym
C-1	98.8	98.9	97.2	97.3	97.3*
C-2	32.1	32.2	32.1	32.2	32.2*
C-3	73.2	73.3	73.5	73.6	76.7*
C-4	78.9	78.9	78.9	79.0^{b}	73.4*
C-5	65.1	65.1	64.7	64.7	66.0*
C-6	18.4^{e}	18.5^{a}	18.3^{c}	18.4^{f}	18.5^{d}
3-OMe	56.7	56.7	56.8^{d}	56.9^{g}	56.9
	Glc	Glc	Glc	Glc	
C-1	102.2*	102.2*	102.1*	102.3*	
C-2	75.1*	75.2*	75.2*	75.3*	
C-3	78.3*^{,g}	78.3*^{,b}	71.1*^{,e}	78.4*^{,b}	
C-4	71.7*	71.7*	71.7*	73.8*	
C-5	78.4*^{,g}	78.5*^{,b}	78.2*^{,e}	78.6*^{,h}	
C-6	62.9	62.9	62.8	62.9	

$^{a-h}$ In each column assignments may be interchangeable between Tables 1 and 2. * The chemical shifts have the longest dipole–dipole relaxation times (PRFT measurements).

Abbreviations are as follows: D-Cym, β-D-cymaropyranose; L-Cym, α-L-cymaropyranose; D-Ole, β-D-oleandropyranose; Digit, β-D-digitoxopyranose; Glc, β-D-glucopyranose.

and their retention times are noted in Tables 3 and 4. Retention times of peaks 1 and 3 for cymarose and peaks 2 and 4 for oleandrose were clearly different between D- and L-enantiomers. The chromatogram of the sample derived from compound (**8**) showed one peak [1-*O*-(3,5-dinitrophenylcarbamoyl)-3,4-*O*-isopropylidene-α-digitoxopyranose], whose retention time agreed with that of the D-enantiomer (Table 5). The analysis was performed with (**6**) (1.9 mg), (**7**) (1.4 mg), and (**8**) (1.1 mg) obtained from (**3**) (17.2 mg). It is noteworthy that the absolute configuration of compounds (**6**), (**7**), and (**8**) was unequivocally established with a small amount of glycoside. A protonated molecular ion peak at *m/z* 325 suggested that the residual sugar (**9**) was a disaccharide having a specific rotation of −65°. Comparison of the ^{13}C n.m.r. spectrum (C_5D_5N) with that of an authentic sample confirmed sugar (**9**) to be glaucobiose[7] (4-*O*-β-D-glucopyranosyl-L-cymaropyranose).

Table 3. Retention times (min) of four peaks of the high-performance liquid chromatograms of carbamates derived from cymarose

Peak	D-Cymarose	(7) from (3)	L-Cymarose
1	8.8	8.8	9.8
2	11.2	11.2	11.2
3	13.0	13.0	14.4
4	20.0	20.0	20.0

Peak 1, Methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)-α-cymaropyranoside. Peak 2, Methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)-β-cymarofuranoside. Peak 3, Methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)-β-cymaropyranoside. Peak 4, Methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)-α-cymarofuranoside.

Table 4. Retention times (min) of four peaks on the high-performance liquid chromatograms of carbamates derived from oleandrose

Peak	D-Oleandrose	(7) from (3)	(7) from (4)	L-Oleandrose
1	10.7	10.7	10.7	11.2
2	14.0	14.0	14.0	15.3
3	17.1	17.1	17.1	17.9
4	25.4	25.4	25.4	29.6

Peak 1, Methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)-α-oleandrofuranoside. Peak 2, Methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)-β-oleandrofuranoside. Peak 3, Methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)-α-oleandropyranoside. Peak 4, Methyl 4-*O*-(3,5-dinitrophenylcarbamoyl)-β-oleandropyranoside.

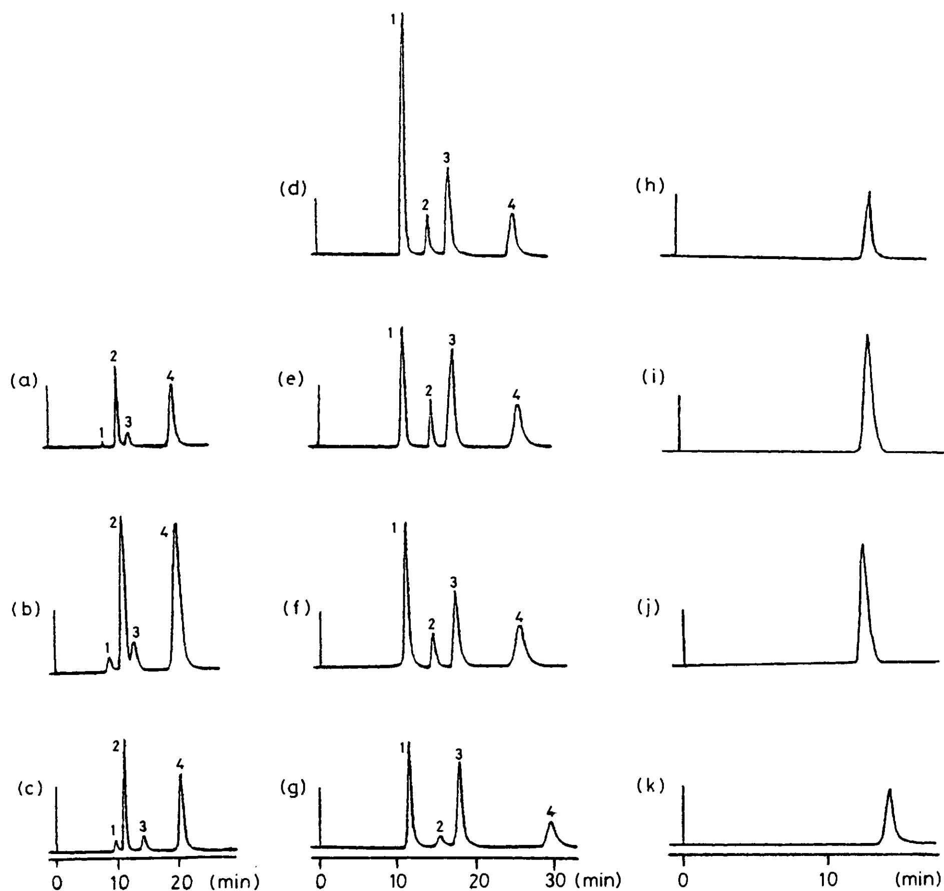


Figure 1. High-performance liquid chromatogram of carbamates derived from (a) authentic D-cymarose, (b) (**6**) in (**3**), (c) authentic L-cymarose, (d) authentic D-oleandrose, (e) (**7**) in (**3**), (f) (**7**) in (**4**), (g) authentic L-oleandrose, (h) authentic D-digitoxose, (i) (**8**) in (**3**), (j) (**8**) in (**4**), and (k) authentic L-digitoxose. Conditions: column, SUMIPAX OA-1000 (5μ; 4 mm i.d. × 15 cm); mobile phase, hexane–1,2-dichloroethane–ethanol (30:6:1) for cymarose, hexane–1,2-dichloroethane–ethanol (40:5:2) for oleandrose, and hexane–1,2-dichloroethane–ethanol (150:3:8) for digitoxose; flow rate, 1 ml min^{-1}; detector, u.v. (254 nm)

The terminal β-D-glucopyranosyl signals of compound (**3**) were easily distinguished from other sugar signals by partially relaxed Fourier-transform (PRFT) measurements[8] in the ^{13}C n.m.r. spectrum (Table 2). The enzymatic hydrolysis of cynafoside-C (**3**) with snail β-glucosidase gave deglucosyl-(**3**), compound (**10**). The terminal sugar of compound (**10**) was confirmed to be L-cymarose (**11**) by the presence of glaucobiose (**9**) in the acidic hydrolysate of compound (**3**). In the 500 MHz ^{1}H n.m.r. spectrum of compound (**10**), one α-linkage and three β-linkages of four 2-deoxy sugars were revealed by the coupling constants of anomeric protons at δ_H 4.51 (1 H, dd, *J* 9.5 and 1.8 Hz), 4.83 (2 H, dd, *J* 10 and 2 Hz), and 4.86 (1 H, dd, *J* 3 and 1 Hz), and all of the sugar signals were completely assigned to protons of α- and β-cymaropyranose, β-D-oleandropyranose, and β-D-digitoxopyranose by means of the proton decoupling measurements. The acetylation of compound (**10**) gave diacetate (**12**). Owing to the acetylation, the 3-H signal of β-D-digitoxopyranose was shifted from δ_H 4.20 (1 H, ddd, *J* 3, 3, and 2.9 Hz) to δ_H 5.34 and the 4-H signal of α-cymaropyranose was similarly shifted from δ_H 3.26 (1 H, dd, *J* 9.3 and 2.9 Hz) to δ_H 4.41, indicating that the C-3 hydroxy group of the digitoxose moiety (**8**) was free in compound (**10**) and that the terminal

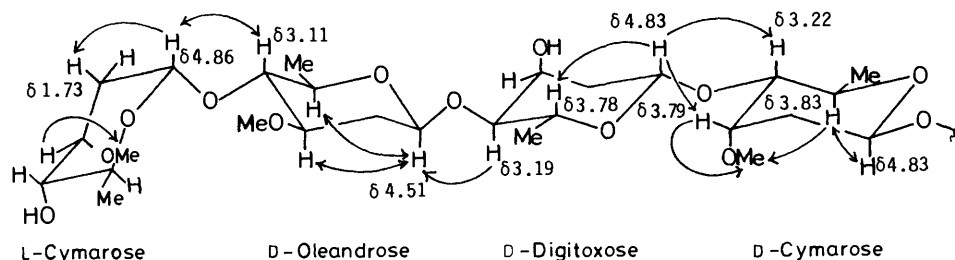


Figure 2. Results of n.O.e. experiments with compound (**10**)

sugar was α-L-cymaropyranose. The sugar sequence of compound (**10**) was suggested by the nuclear Overhauser effect (n.O.e.) difference spectra (Figure 2). Irradiation at δ_H 4.86 (1 H, dd, J 3 and 1 Hz, 1-H of α-L-cymaropyranose) caused enhancement at δ_H 3.11 (1 H, t, J 8.8 Hz, 4-H of β-D-oleandropyranose) as well as at δ_H 1.73 (1 H, ddd, J 15.0, 4.8, and 3.7 Hz, 2-H_{ax} of α-L-cymaropyranose). Irradiation at δ_H 3.11 also caused enhancement at δ_H 4.86, which showed that the cymarose (**11**) was α-linked to the C-4 hydroxy group of (**7**). Irradiation at δ_H 3.19 (1 H, dd, J 9.3 and 2.9 Hz, 4-H of β-D-digitoxopyranose) caused n.O.e. at δ_H 4.51 (1 H, dd, J 9.5 and 1.8 Hz, 1-H of β-D-oleandropyranose), and thus the oleandrose moiety (**7**) was β-linked to the C-4 hydroxy group of digitoxose (**8**). Irradiation at δ_H 4.83 (2 H, dd, J 10 and 2 Hz, 1-H of β-D-cymaropyranose and β-D-digitoxopyranose) caused n.O.e. enhancements at δ_H 3.22 (1 H, dd, J 9.3 and 2.9 Hz, 4-H) of β-D-cymaropyranose) and δ_H 3.79 (1 H, ddd, J 3, 3, and 2.9 Hz, 3-H of β-D-cymaropyranose) as well as at δ_H 3.78 and 3.83 (each 1 H, dq, J 9.3 and 6.2 Hz, 5-H of β-D-digitoxopyranose and β-D-cymaropyranose, respectively), which indicated that the digitoxose moiety (**8**) was β-linked to the C-4 hydroxy group of cymarose (**6**). In the ^{13}C n.m.r. spectrum of compound (**3**), the glycosidation shifts[9] of the aglycone carbon signals observed at C-2 (−2.5 p.p.m.), C-3 (+6.1), and C-4 (−4.3) (Table 1) suggested that the sugar moiety was linked to the C-3 hydroxy group of aglycone (**5**). Consequently, the structure of compound (**3**) was established as cynafogenin 3-*O*-β-D-glucopyranosyl-(1 ⟶ 4)-α-L-cymaropyranosyl-(1 ⟶ 4)-β-D-oleandropyranosyl-(1 ⟶ 4)-β-D-digitoxopyranosyl-(1 ⟶ 4)-β-D-cymaropyranoside.

Compound (**4**) has the molecular formula $C_{62}H_{94}O_{24}$ on the basis of elemental analysis, and field-desorption mass spectrometry (f.d.-m.s.) gave an ion peak at m/z 1 245 [$(M + Na)^+$]. Acidic hydrolysis of compound (**4**) afforded an aglycone (**5**) and three sugars (**7**), (**8**), and (**9**), which were identified by comparisons of their physicochemical properties and ^1H or ^{13}C n.m.r. spectra. The absolute stereochemistry of compounds (**7**) (1.5 mg) and (**8**) (2.8 mg) from cynafoside-D (**4**) was also determined to be the D-series by the same methods as for compound (**3**) (Figure 1 and Tables 4 and 5). In the ^{13}C n.m.r. spectrum of compound (**4**) (Tables 1 and 2), however, five anomeric carbon signals at δ_C 96.0, 97.2, 100.3, 101.2, and 102.1 indicated that this glycoside contained five sugars. The proton decoupling measurements (500 MHz) of compound (**4**) revealed all of the proton signals of α-L-cymaropyranose, two β-D-digitoxopyranoses, and β-D-oleandropyranose except for those of the methyl groups. The terminal sugar of compound (**4**) was confirmed to be β-D-glucopyranose by PRFT experiments.[8] The n.O.e. difference spectrum of (**4**) (Figure 3) showed that L-cymarose (**11**) was α-linked to the C-4 hydroxy group of (**7**); irradiation of δ_H 4.87 (1 H, dd, J 3 and 1 Hz, 1-H of α-L-cymaropyranose) caused enhancement at δ_H 3.12 (1 H, t, J 9.3 Hz, 4-H of β-D-oleandropyranose), and hence the residual two molecules of digitoxose (**8**) were located between the aglycone (**5**) and the oleandrose moiety (**7**). Acetylation of cynafoside-D (**4**) gave hexa-acetate (**13**) and caused acetylation shifts of the 3-H signals of two β-D-digitoxopyranoses from δ_H 4.22 (2 H, ddd, J 3, 3, and 2.9 Hz) to δ_H 5.31 and δ_H 5.37, in addition to those of the 2-H, 3-H, 4-H, and 6-H_2 signals of β-D-glucopyranose. These shifts suggested that the oleandrose moiety (**7**) was linked to the C-4 hydroxy group of digitoxose (**8**), which was in turn linked to another digitoxose (**8**) moiety. The glycosidation shifts[9] of the aglycone carbon signals were observed at C-2, C-3, and C-4 (Table 1), which showed that the sugar moiety was linked to the C-3 hydroxy group of aglycone (**5**). Therefore, the structure of compound (**4**) was deduced to be cynafogenin 3-*O*-β-D-glucopyranosyl-(1 ⟶ 4)-α-L-cymaropyranosyl-(1 ⟶ 4)-β-D-oleandropyranosyl-(1 ⟶ 4)-β-D-digitoxopyranosyl-(1 ⟶ 4)-β-D-digitoxopyranoside.

Table 5. Retention times (min) of 1-*O*-(3,5-dinitrophenylcarbamoyl)-3,4-*O*-isopropylidene-α-digitoxopyranose on the high-performance liquid chromatograms

D-Digitoxose	(**8**) from (**3**)	(**8**) from (**4**)	L-Digitoxose
13.5	13.5	13.5	14.3

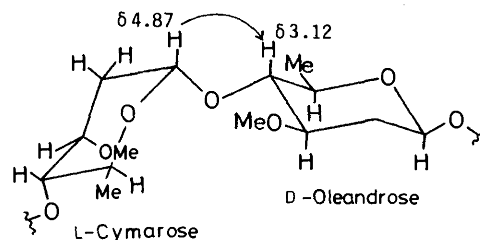


Figure 3. Results of n.O.e. experiments with compound (**4**)

Conclusions.—We have already reported the technique to determine the absolute configurations of cymarose,[4] oleandrose,[5] and digitoxose[6] by h.p.l.c. with a chiral column. This is the first report to apply the technique to the structural elucidation of glycosides containing cymarose, oleandrose, and digitoxose. It is noticeable that the technique can be performed with a small amount of glycoside [(**3**) (17.2 mg) and (**4**) (20.1 mg)].

Cynafoside-A (**1**), -B (**2**), and -C (**3**) are the second set of examples of glycosides in which a pair of optically isomeric sugars, D- and L-cymaroses, exists in the sugar chain, following the example of the wilfosides,[10] isolated from *Cynanchum wilfordi* HEMSLEY.

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured in $CHCl_3$ (except

where stated otherwise) with a JASCO DIP-4 digital polarimeter at room temperature. U.v. spectra were obtained in ethanol with a Shimadzu UV-220 spectrometer. I.r. spectra were recorded in $CHCl_3$ on a JASCO A-102 spectrometer. ^1H N.m.r. spectra were recorded on JEOL GX-500 (500 MHz) and FX-100 (100 MHz) spectrometers in $CDCl_3$, and ^{13}C n.m.r. spectra on JEOL GX-270 (67.80 MHz) and FX-90Q (22.5 MHz) machines in C_5D_5N with tetramethylsilane as internal standard. Electron-impact mass spectrometry (e.i.-m.s.) was carried out with a JEOL LMS-D-300 mass spectrometer, and f.d.-m.s. with a JEOL JMS-01SG-2 mass spectrometer. H.p.l.c. was conducted with a Waters 204 compact model, using columns of M&S PACK C18 (10 mm i.d. × 30 cm) or SUMIPAX OA-1000 (5μ; 4 mm i.d. × 15 cm) (Sumitomo Chemical Co., Ltd.). T.l.c. was performed on Merck precoated plates (Kieselgel 60 F_{254}) with the following solvent systems: (A) MeOH–$CHCl_3$ (5:95), (B) MeOH–$CHCl_3$ (15:85), (C) water–MeOH–$CHCl_3$ [(1:3:12), lower layer], and (D) acetone–hexane (1:1). Column chromatography was carried out on Wakogel C-200 (200 mesh) or Lobar column Lichroprep RP-8 (reversed phase). The abbreviations used are as follows: cym, cymaropyranose; ole, oleandropyranose; digit, digitoxopyranose; glc, glucopyranose.

Isolation of Glycosides.—The crude glycoside (79.89 g) reported in a previous paper[3] was subjected to column chromatography on silica gel with solvents of increasing polarity from $CHCl_3$ to MeOH–$CHCl_3$ (1:1), to separate fraction A (19.72 g), fraction B (12.17 g), and fraction C (20.04 g). Fraction B was rechromatographed on silica gel with MeOH–$CHCl_3$ (7:93) to separate fraction B1 [2.47 g, a crude fraction containing compounds (**1**) and (**3**)] and fraction B2 [3.08 g; a crude fraction containing compounds (**2**) and (**4**)]. Rechromatography of fraction B1 on silica gel with hexane–acetone (2:5) and MeOH–$CHCl_3$ (5:95), and further chromatography on reversed-phase gel with water–MeOH (15:85 and 20:80), afforded a crude fraction containing compound (**3**), which was purified by h.p.l.c. on a M&S PACK C18 column to give cynafoside-C (**3**) (92.3 mg, 0.0017% from the dried plant), R_F(B) 0.56. Rechromatography of fraction B2 on silica gel with hexane–acetone (1:3 and 1:2) and MeOH–$CHCl_3$ (6:94 and 7:93) and, further chromatography on reversed-phase gel with water–MeOH (15:85), afforded a crude fraction containing compound (**4**), which was purified by h.p.l.c. (M&S PACK C18 column) to give cynafoside-D (**4**) (93.1 mg, 0.0017%), R_F(B) 0.51.

Cynafoside-C (**3**). This was obtained as an *amorphous powder*, m.p. 88—90 °C (Found: C, 60.4; H, 7.95. $C_{63}H_{96}O_{24}{\cdot}H_2O$ requires C, 60.3; H, 7.9%); $[\alpha]_D^{14}$ +7.6° (*c* 1.06) $\lambda_{max.}$ 230 (log ε 3.82), 278 (2.48), and 285 nm (2.46); $\nu_{max.}$ 3 420, 1 730, 1 710, 1 700, 1 600, 1 580, 1 490, and 1 160 cm^{-1}; δ_H (500 MHz) 0.95 (3 H, s, 19-H_3), 1.15 (3 H, s, 18-H_3), 1.21, 1.23, 1.24, 1.27 (each 3 H, d, *J* 6.3 Hz, 6-H_3 of sugars), 1.65 (3 H, s, $MeCO_2$), 2.07 (3 H, s, 21-H_3), 2.23 (1 H, ddd, *J* 15.0, 3.3, and 1 Hz, 2-H_{eq} of α-L-cym), 2.35 (1 H, ddd, *J* 12.5, 4.4, and 1.5 Hz, 2-H_{eq} of β-D-ole), 3.12 (1 H, t, *J* 8.8 Hz, 4-H of β-D-ole), 3.20 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of β-D-digit), 3.22 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of β-D-cym), 3.26 (1 H, ddd, *J* 11.0, 8.8, and 4.4 Hz, 3-H of β-D-ole), 3.26 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of α-L-cym), 3.32 (1 H, dq, *J* 8.8 and 6.3 Hz, 5-H of β-D-ole), 3.36 (3 H, s, 3-OMe of β-D-ole), 3.37 (3 H, s, 3-OMe of α-L-cym), 3.43 (3 H, s, 3-OMe of β-D-cym), 3.57 (1 H, tt, *J* 11.0 and 4.9 Hz, 3-H), 3.79 (1 H, dq, *J* 9.3 and 6.3 Hz, 5-H of β-D-digit), 3.80 (1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of β-D-cym), 3.83 (1 H, dq, *J* 9.3 and 6.3 Hz, 5-H of β-D-cym), 4.20 (1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of β-D-digit), 4.37 (1 H, d, *J* 7.8 Hz, 1-H of β-D-glc), 4.52 (1 H, dd, *J* 9.8 and 1.5 Hz, 1-H of β-D-ole), 4.83 (2 H, dd, *J* 10 and 2 Hz, 1-H of β-D-cym and β-D-digit), 4.86 (1 H, dd, *J* 3 and 1 Hz, 1-H of α-L-cym), 4.99 (1 H, d, *J* 10.3 Hz, 12-H), 5.41 (1 H, t, *J* 10.3 Hz, 11-H), 7.49 (2 H, t, *J* 7.8 Hz, *m*-ArH), 7.62 (1 H, tt, *J* 7.8 and 1.5 Hz, *p*-ArH), and 8.05 (2 H, dd, *J* 7.8 and 1.5 Hz, *o*-ArH); δ_C (67.80 MHz) see Tables 1 and 2.

Acidic Hydrolysis of Cynafoside-C (**3**).—A solution of compound (**3**) (17.2 mg) in MeOH (15 ml) was allowed to react with 0.1 M H_2SO_4 (5 ml) at 60 °C for 15 min, then water (15 ml) was added and the mixture was concentrated to 20 ml. The solution was kept at 60 °C for a further 30 min, and extracted with ether (20 ml). The ether layer was washed successively with saturated aqueous $NaHCO_3$ (7 ml × 3) and saturated aqueous NaCl (7 ml × 3), and the solvent was evaporated off to give the aglycone (**5**) (6.5 mg) as an amorphous powder, R_F(A) 0.53 and R_F(D) 0.58; m.p. 86—89 °C; $[\alpha]_D^{16}$ +74.2° (*c* 0.65); e.i.-m.s. *m/z* 512 (M^+), 105 ($C_6H_5CO^+$, base peak), and 43 (CH_3CO^+); δ_H (100 MHz) 0.98 (3 H, s, 19-H_3), 1.16 (3 H, s, 18-H_3), 1.65 (3 H, s, OCO-Me), 2.07 (3 H, s, 21-H_3), 4.95 (1 H, d, *J* 9.8 Hz, 12-H), 5.44 (1 H, t, *J* 9.8 Hz, 11-H), 7.46—7.65 (3 H, m, *m*- and *p*-ArH), and 8.06 (2 H, dd, *J* 8.3 and 2.0 Hz, *o*-ArH).

The aqueous layer was neutralized with saturated aqueous $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to give a syrup, which was chromatographed on silica gel with solvents of increasing polarity from $CHCl_3$ to MeOH–$CHCl_3$ (2:8) to afford separation into the monosaccharides (**6**) [1.9 mg, R_F(C) 0.59 and R_F(D) 0.42], (**7**) [1.4 mg, R_F(C) 0.54 and R_F(D) 0.41], (**8**) [1.1 mg, R_F(C) 0.42 and R_F(D) 0.04], and (**9**) [2.2 mg, R_F(C) 0.16]. For (**6**), f.d.-m.s. *m/z* 162 (M^+); δ_H (100 MHz) 3.31, 3.37, 3.44, and 3.54 (each 3 H, s, 3-OMe of α- and β-D-cymaropyranoses and α-and β-D-cymarofuranoses. The intensities of the signals were in the proportions 15:10:9:7). For (**7**), f.d.-m.s. *m/z* 162 (M^+); δ_H (100 MHz) for α-D-oleandropyranose 1.29 (3 H, d, *J* 5.9 Hz, 6-H_3), 1.50 (1 H, ddd, *J* 13.2, 11.2, and 3 Hz, 2-H_{ax}), 2.34 (1 H, ddd, *J* 13.2, 4.9, and 1 Hz, 2-H_{eq}), 3.15 (1 H, t, *J* 9.3 Hz, 4-H), 3.41 (3 H, s, 3-OMe), 3.60 (1 H, ddd, *J* 11.2, 9.3, and 4.9 Hz, 3-H), 3.94 (1 H, dq, *J* 9.8 and 5.9 Hz, 5-H), and 5.35 (1 H, dd, *J* 3 and 1 Hz, 1-H); δ_H for β-D-oleandropyranose 1.35 (3 H, d, *J* 5.4 Hz, 6-H_3) and 4.82 (1 H, dd, *J* 9.3 and 2 Hz, 1-H). The signal intensities of α- and β-D-oleandropyranoses were in the ratio 2:1. For (**8**), $[\alpha]_D^{16}$ +44° (*c* 0.10 in water); f.d.-m.s. *m/z* 148 (M^+); δ_H (100 MHz) for β-D-digitoxopyranose 1.30 (3 H, d, *J* 6.4 Hz, 6-H_3), 1.67 (1 H, ddd, *J* 13.7, 9.8, and 2.9 Hz, 2-H_{ax}), 2.17 (1 H, dt, *J* 13.7 and 2.4 Hz, 2-H_{eq}), 3.25 (1 H, dd, *J* 9.8 and 3.4 Hz, 4-H), 3.78 (1 H, dq, *J* 9.3 and 6.4 Hz, 5-H), 4.08 (1 H, ddd, *J* 3.4, 2.9, and 2.4 Hz, 3-H), and 5.10 (1 H, dd, *J* 9.8 and 2.4 Hz, 1-H). For (**9**), $[\alpha]_D^{16}$ −65° (*c* 0.17 in water [lit.,[7] −72.6° (*c* 0.81 in water)]; f.d.-m.s. *m/z* 325 [$(M + H)^+$]; δ_C (22.5 MHz) for β-glaucobiose (main) 19.2, 37.4, 58.1, 62.9, 69.2, 71.9, 75.0, 75.2, 78.4 (2 C), 79.6, 92.5, and 101.9; δ_C for α-glaucobiose (minor) 18.5, 34.0, 64.7, 78.9, 91.6, and 102.4.

Absolute Configurations of Monosaccharides (**6**),[4] (**7**),[5] *and* (**8**).[6]—A solution of compound (**6**) (1.8 mg) in MeOH (0.5 ml) was allowed to react with 1% H_2SO_4–MeOH (0.5 ml) at room temperature for 20 min, then water (1.0 ml) was added and the reaction mixture was neutralized with saturated aqueous $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to give a mixture of methyl cymarosides. The product was dissolved in dry toluene (0.25 ml) and allowed to react with 3,5-dinitrophenyl isocyanate (*ca.* 3 mg) in the presence of dry pyridine (0.25 ml) at 60 °C for 30 min, then the solvent was evaporated off to afford a mixture of carbamates. The mixture was dissolved in MeOH (1 ml) and analysed by a chiral h.p.l.c. column (SUMIPAX OA-1000) with hexane–1,2-dichloroethane–ethanol (30:6:1), and the chromatogram was as depicted in Figure 1.

In the case of compound (**7**) (1.3 mg), a mixture of carbamates was prepared by the same procedure described above and

analysed by the chiral h.p.l.c. column with hexane–dichloromethane–ethanol (40:5:2). The chromatogram was as shown in Figure 1.

A mixture of compound (**8**) (1.1 mg), 2,2-dimethoxypropane (3.0 mg), and a trace of toluene-*p*-sulphonic acid in *N,N*-dimethylformamide (0.2 ml) was stirred at room temperature for 30 min, and then poured into aqueous potassium carbonate. The product was extracted with $CHCl_3$ and the extract washed with water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave the isopropylidene derivative, which was carbamoylated by the same procedure described above. The carbamate was analysed by the chiral h.p.l.c. column with hexane–1,2-dichloroethane–ethanol (150:3:8) and the chromatogram was as shown in Figure 1.

Deglucosyl-(**3**), *Compound* (**10**).—A suspension (5 ml) of compound (**3**) (41.3 mg) in 0.3M NaOAc buffer solution adjusted to pH 5.5 was treated with a suspension (7 ml) of snail (*Fruticola gainesil*) β-glucosidase (176.3 mg) at 37 °C for 65 h. The products were extracted with $CHCl_3$ (40 ml) and the solvent was evaporated off to give a syrup, which was chromatographed to afford deglucosyl-(**3**), compound (**10**) (14.8 mg), as an amorphous powder, R_F(A) 0.54 and R_F(D) 0.57; m.p. 124—127 °C; $[\alpha]_D^{14}$ +13.5° (*c* 1.04); f.d.-m.s. *m/z* 1 113 [$(M + K)^+$], 1 097 [$(M + Na)^+$], and 1 074 (M^+); $\lambda_{max.}$ 230 (log ε 4.12), 278 (3.08), and 285 nm (2.98); $\nu_{max.}$ 3 400, 1 730, 1 710, 1 700, 1 600, 1 580, 1 490, and 1 160 cm^{-1}; δ_H (500 MHz) 0.95 (3 H, s, 19-H_3), 1.15 (3 H, s, 18-H_3), 1.21, 1.23, 1.25, 1.27 (each 3 H, d, *J* 6.2 Hz, 6-H_3 of sugar), 1.51 (1 H, ddd, *J* 12.5, 11.0, and 9.8 Hz, 2-H_{ax} of β-D-ole), 1.54 (1 H, ddd, *J* 14.3, 9.5, and 2.9 Hz, 2-H_{eq} of β-D-cym), 1.64 (3 H, s, $MeCO_2$), 1.73 (1 H, ddd, *J* 15.0, 4.8, and 3.7 Hz, 2-H_{ax} of α-L-cym), 1.76 (1 H, ddd, *J* 13.7, 9.3, and 2.9 Hz, 2-H_{ax} of β-D-digit), 2.07 (3 H, s, 21-H_3), 2.13 (1 H, dt, *J* 13.7 and 2.4 Hz, 2-H_{eq} of β-D-digit), 2.24 (1 H, ddd, *J* 14.3, 3.7, and 2.2 Hz, 2-H_{eq} of β-D-cym), 2.24 (1 H, ddd, *J* 15.0, 3.3, and 1.5 Hz, 2-H_{eq} of α-L-cym), 2.34 (1 H, ddd, *J* 12.5, 4.4, and 2.2 Hz, 2-H_{eq} of β-D-ole), 3.11 (1 H, t, *J* 8.8 Hz, 4-H of β-D-ole), 3.19 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of β-D-digit), 3.22 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of β-D-cym), 3.25 (1 H, ddd, *J* 11.0, 8.8, and 4.4 Hz, 3-H of β-D-ole), 3.26 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of α-L-cym), 3.31 (1 H, dq, *J* 8.8 and 6.2 Hz, 5-H of β-D-ole), 3.37, 3.38, 3.43 (each 3 H, s, 3-OMe of α-L-cym, β-D-ole, and β-D-cym, respectively), 3.57 (1 H, tt, *J* 11.0 and 4.9 Hz, 3-H), 3.59 (1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of α-L-cym), 3.78 (1 H, dq, *J* 9.3 and 6.2 Hz, 5-H of β-D-digit), 3.79 (1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of β-D-cym), 3.83 (1 H, dq, *J* 9.3 and 6.2 Hz, 5-H of β-D-cym), 4.07 (1 H, dq, *J* 9.3 and 6.2 Hz, 5-H of α-L-cym), 4.20 (1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of β-D-digit), 4.51 (1 H, dd, *J* 9.5 and 1.8 Hz, 1-H of β-D-ole), 4.83 (2 H, dd, *J* 10 and 2 Hz, 1-H of β-D-cym and β-D-digit), 4.86 (1 H, dd, *J* 3 and 1 Hz, 1-H of α-L-cym), 4.99 (1 H, d, *J* 9.9 Hz, 12-H), 5.41 (1 H, t, *J* 9.9 Hz, 11-H), 7.49 (2 H, t, *J* 7.7 Hz, *m*-ArH), 7.62 (1 H, tt, *J* 7.7 and 1.5 Hz, *p*-ArH), and 8.05 (2 H, dd, *J* 7.7 and 1.5 Hz, *o*-ArH); δ_C (67.94 MHz) see Tables 1 and 2.

Di-O-*acetyl*-(**10**), *Compound* (**12**).—A mixture of compounds (**10**) (2.4 mg), pyridine (0.5 ml), and acetic anhydride (0.4 ml) was stirred at room temperature. After 16 h, the mixture was worked up by the standard procedure to give the diacetate (**12**) (2.0 mg), δ_H (500 MHz) 0.95 (3 H, s, 19-H_3), 1.15 (3 H, s, 18-H_3), 1.21, 1.22, 1.23, 1.26 (each 3 H, d, *J* 6.2 Hz, 6-H_3 of sugars), 1.64 (3 H, s, $MeCO_2$), 2.06 (3 H, s, 21-H_3), 2.09, 2.11 (each 3 H, s, OAc), 3.10 (1 H, t, *J* 8.8 Hz, 4-H of β-D-ole), 3.19 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of β-D-digit), 3.21 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of β-D-cym), 3.35, 3.36, 3.43 (each 3 H, s, 3-OMe of sugar), 3.55 (1 H, tt, *J*, 11.0 and 4.9 Hz, 3-H), 3.73 (1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of α-L-cym), 3.80 (1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of β-D-cym), 4.41 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of α-L-cym), 4.45 (1 H, dd, *J* 9.5 and 1.8 Hz, 1-H of β-D-ole), 4.83 (2 H, dd, *J* 10 and 2 Hz, 1-H of β-D-cym and β-D-digit), 4.86 (1 H, dd, *J* 3 and 1 Hz, 1-H of α-L-cym), 4.99 (1 H, d, *J* 10.3 Hz, 12-H), 5.34 (1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of β-D-digit), 5.41 (1 H, t, *J* 10.3 Hz, 11-H), 7.49 (2 H, t, *J* 7.3 Hz, *m*-ArH, 7.61 (1 H, t, *J* 7.3 Hz, *p*-ArH), and 8.05 (2 H, d, *J* 7.3 Hz, *o*-ArH).

Cynafoside-D (**4**).—An amorphous powder, m.p. 153—155 °C (Found: C, 58.7; H, 7.6. $C_{62}H_{94}O_{24} \cdot \frac{5}{2}H_2O$ requires C, 58.7; H, 7.9%); $[\alpha]_D^{16}$ +12.8° (*c* 1.00) f.d.-m.s. *m/z* 1 245 [$(M + Na)^+$]; $\lambda_{max.}$ 230 (log ε 3.68), 275 (2.39), and 282 nm (2.39); $\nu_{max.}$ 3 400, 1 730, 1 710, 1 600, 1 580, 1 490, and 1 160 cm^{-1}; δ_H (500 MHz) 0.95 (3 H, s, 19-H_3), 1.15 (3 H, s, 18-H_3), 1.22, 1.23, 1.25, 1.27 (each 3 H, d, *J* 5.9 Hz, 6-H_3 of sugars), 1.51 (1 H, ddd, *J* 12.5, 11.0, and 9.8 Hz, 2-H_{ax} of β-D-ole), 1.64 (3 H, s, $MeCO_2$), 1.68, 1.71 (each 1 H, ddd, *J* 13.7, 9.3, and 2.9 Hz, 2-H_{ax} of β-D-digit), 1.79 (1 H, ddd, *J* 15.0, 4.8, and 3.7 Hz, 2-H_{ax} of α-L-cym), 2.06 (3 H, s, 21-H_3), 2.04, 2.12 (each 1 H, dt, *J* 13.7 and 2.4 Hz, 2-H_{eq} of β-D-digit), 2.22 (1 H, ddd, *J* 15.0, 3.3, and 1.5 Hz, 2-H_{eq} of α-L-cym), 2.35 (1 H, ddd, *J* 12.5, 4.4, and 2.2 Hz, 2-H_{eq} of β-D-ole), 3.12 (1 H, t, *J* 9.3 Hz, 4-H of β-D-ole), 3.19, 3.22 (each 1 H, d, *J* 9.3 and 2.9 Hz, 4-H of β-D-digit), 3.26 (1 H, ddd, *J* 11.0, 8.8, and 4.4 Hz, 3-H of β-D-ole), 3.31 (1 H, dq, *J* 8.8 and 5.9 Hz, 5-H of β-D-ole), 3.36, 3.37 (each 3 H, s, 3-OMe of α-L-cym and β-D-ole), 3.54 (1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of α-L-cym), 3.73 (1 H, ddd, *J* 3.7, 3.3, and 2.9 Hz, 3-H of α-L-cym), 3.77, 3.83 (each 1 H, dq, *J* 9.3 and 5.9 Hz, 5-H of β-D-digit), 3.80, 3.88 (each 1 H, dd, *J* 11.5 and 4.6 Hz and *J* 11.5 and 3.3 Hz, respectively, together 6-H_2 of β-D-glc), 4.22 (2 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of β-D-digit), 4.25 (1 H, dq, *J* 9.3 and 5.9 Hz, 5-H of α-L-cym), 4.38 (1 H, d, *J* 7.3 Hz, 1-H of β-D-glc), 4.52 (1 H, dd, *J* 9.8 and 2 Hz, 1-H of β-D-ole), 4.87 (1 H, dd, *J* 3 and 1 Hz, 1-H of α-L-cym), 4.89, 4.91 (each 1 H, dd, *J* 10 and 2 Hz, 1-H of β-D-digit), 4.99 (1 H, d, *J* 9.8 Hz, 12-H), 5.41 (1 H, t, *J* 9.8 Hz, 11-H), 7.49 (2 H, t, *J* 7.3 Hz, *m*-ArH), 7.62 (1 H, t, *J* 7.3 Hz, *p*-ArH), and 8.05 (2 H, d, *J* 7.3 Hz, *o*-ArH); δ_C (67.5 MHz) see Tables 1 and 2.

Acidic Hydrolysis of Cyanofoside-D (**4**).—Compound (**4**) (20.1 mg) was allowed to react by the same procedure as for (**3**), and the products were separated to provide aglycone (**5**) (6.3 mg), and carbohydrates (**7**) (1.5 mg), (**8**) (2.8 mg), and (**9**) (3.0 mg). For (**5**), R_F(A) 0.53 and R_F(D) 0.58; m.p. 90—92 °C; $[\alpha]_D^{17}$ +78.1° (*c* 0.63); e.i.-m.s. *m/z* 512 (M^+), 105 ($C_6H_5CO^+$, base peak), and 43 (CH_3CO^+); δ_H (100 MHz) 0.98 (3 H, s, 19-H_3), 1.16 (3 H, s, 18-H_3), 1.65 (3 H, s, $MeCO_2$), 2.07 (3 H, s, 21-H_3), 4.99 (1 H, d, *J* 9.8 Hz, 12-H), 5.43 (1 H, t, *J* 9.8 Hz, 11-H), 7.48—7.65 (3 H, m, *m*- and *p*-ArH), and 8.06 (2 H, dd, *J* 8.3 and 2.0 Hz, *o*-ArH). For (**7**), R_F(C) 0.54 and R_F(D) 0.41; f.d.-m.s. *m/z* 162 (M^+); δ_H (100 MHz) for α-D-oleandropyranose 1.29 (3 H, d, *J* 5.9 Hz, 6-H_3), 2.38 (1 H, ddd, *J* 13.2, 4.9, and 1 Hz, 2-H_{eq}), 3.16 (1 H, t, *J* 9.3 Hz, 4-H), 3.41 (3 H, s, 3-OMe), 3.58 (1 H, ddd, *J* 11.2, 9.3, and 4.9 Hz, 3-H), 3.94 (1 H, dq, *J* 9.3 and 5.9 Hz, 5-H), and 5.37 (1 H, dd, *J* 3 and 1 Hz, 1-H); δ_H for β-D-oleandropyranose 1.35 (3 H, d, *J* 5.4 Hz, 6-H_3) and 4.83 (1 H, dd, *J* 10 and 2 Hz, 1-H) (α:β 2:1). For (**8**), R_F(C) 0.42 and R_F(D) 0.04; $[\alpha]_D^{17}$ +42° (*c* 0.28 in water); f.d.-m.s. *m/z* 148 (M^+); δ_H (100 MHz) for β-D-digitoxopyranose 1.30 (3 H, d, *J* 6.2 Hz, 6-H_3), 1.66 (1 H, ddd, *J* 13.2, 9.6, and 2.9 Hz, 2-H_{ax}), 2.17 (1 H, dt, *J* 13.2 and 2.2 Hz, 2-H_{eq}), 3.25 (1 H, dd, *J* 9.6 and 3.4 Hz, 4-H), 3.78 (1 H, dq, *J* 9.6 and 6.2 Hz, 5-H), 4.07 (1 H, ddd, *J* 3.4, 2.9, and 2.2 Hz, 3-H), and 5.10 (1 H, dd, *J* 9.6 and 2.2 Hz, 1-H). For (**9**), R_F(C) 0.16; $[\alpha]_D^{17}$ −68° (*c* 0.30 in water); f.d.-m.s. *m/z* 325 [$(M + H)^+$]; δ_C (22.5 MHz) for β-glaucobiose (main) 19.2, 37.4, 58.1, 62.9, 69.1, 71.8, 75.0, 75.2, 78.5 (2 C), 79.6, 92.5, and 101.9. For the h.p.l.c. experiment on a chiral column (SUMIPAX OA-1000), carbohydrates (**7**) (1.5 mg) and (**8**) (1.8 mg) were each converted into the carbamates by the procedure described above. The chromatogram was as shown in Figure 1.

Hexa-O-*acetyl*-(**4**), *Compound* (**13**).—Acetylation of compound (**4**) (2.0 mg) was carried out by the same procedure as for compound (**10**), to afford the hexa-acetate (**13**) (1.8 mg), δ_H (500 MHz) 0.95 (3 H, s, 19-H_3), 1.15 (3 H, s, 18-H_3), 1.21, 1.22, 1.23 (each 3 H, d, *J* 5.9 Hz, 6-H_3 of sugars), 1.64 (3 H, s, $MeCO_2$), 2.005, 2.012, 2.02, 2.08, 2.09 (each 3 H, s, OAc), 2.07 (6 H, s, 21-H_3 and OAc), 3.07 (1 H, t, *J* 9.3 Hz, 4-H of β-D-ole), 3.18 (1 H, ddd, *J* 11.0, 8.8, and 4.4 Hz, 3-H of β-D-ole), 3.24, 3.27 (each 1 H, dd, *J* 9.3 and 2.9 Hz, 4-H of β-D-digit), 3.33, 3.34 (each 3 H, s, 3-OMe of α-L-cym and β-D-ole), 3.50 (1 H, dd, *J* 7.8 and 3.4 Hz, 4-H of α-L-cym), 3.57 (1 H, ddd, *J* 3.4, 3, and 3 Hz, 3-H of α-L-cym), 3.81, 3.82 (each 1 H, dq, *J* 9.3 and 5.9 Hz, 5-H of β-D-digit), 4.13, 4.22 (each 1 H, dd, *J* 12.2 and 2.9 Hz and *J* 12.2 and 4.9 Hz, respectively, 6-H_2 of β-D-glc), 4.24 (1 H, dq, *J* 9.3 and 5.9 Hz, 5-H of α-L-cym), 4.41 (1 H, dd, *J* 10 and 2 Hz, 1-H of β-D-ole), 4.67 (1 H, d, *J* 7.0 Hz, 1-H of β-D-glc and 1 H, dd, *J* 9.8 and 2 Hz, 1-H of β-D-digit), 4.78 (1 H, dd, *J* 9.8 and 2 Hz, 1-H of β-D-digit), 4.83 (1 H, dd, *J* 3 and 1.5 Hz, 1-H of α-L-cym), 4.96 (1 H, dd, *J* 9.8 and 7.0 Hz, 2-H of β-D-glc), 4.99 (1 H, d, *J* 9.8 Hz, 12-H), 5.07, 5.22 (each 1 H, t, *J* 9.8 Hz, 3- and 4-H of β-D-glc), 5.31, 5.37 (each 1 H, ddd, *J* 3, 3, and 2.9 Hz, 3-H of β-D-digit), 5.41 (1 H, t, *J* 9.8 Hz, 11-H), 7.49 (2 H, t, *J* 7.8 Hz, *m*-ArH), 7.62 (1 H, t, *J* 7.8 Hz, *p*-ArH), and 8.05 (2 H, d, *J* 7.8 Hz, *o*-ArH).

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