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

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Seven new glycosides named wilfosides D1N (**7**), K1N (**8**), M1N (**9**), F1N (**10**), W1N (**11**), W3N (**12**), and G1G (**13**) were isolated from *Cynanchum wilfordi* HEMSLEY (Asclepiadaceae), and their structures were deduced on the basis of spectral and chemical evidence. A unique feature is that **7**—**11** and **13**, as well as wilfosides C1N (**2**), C2N (**3**), C1G (**5**), and C2G (**6**), each include both D- (**22**) and L-cymarose (**23**) in the sugar chain. L-Diginose (**24**) is also a constituent of their sugar chains. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) chemical shifts of methyl α- (**24a**) and β-L-diginopyranoside (**24b**) were assigned, and the conformations of **24a** and its acetate were studied.

Keywords——wilfosides D1N, K1N, M1N, F1N, W1N, W3N, G1G; D-cymarose; L-cymarose; ^{13}C-NMR; L-diginose; *Cynanchum wilfordi*; Asclepiadaceae

The dried root of *Cynanchum wilfordi* HEMSLEY (Asclepiadaceae) has been used as a substitute for the tonic crude drug "Ka-shu-uh" (何首烏), which is the dried root of *Poligonum multiflorum* THUMB. (Poligonaceae) in Korea. In 1975 we reported the isolation of C/D-*cis*-polyoxypregnane esters such as caudatin (**14**), kidjoranine (**16**), penupogenin (**21**), aglycone-D (**18**), and aglycone-E (**19**) from the hydrolysate of the crude glycosides of this plant.[2] Recently we reported the structure of wilforibiose (**26**), which has a unique 1,4-dioxane linkage and was isolated from the hydrolysate of the glycosides mixture.[3] In the previous paper,[4] we described the structure determination of six glycosides, wilfosides C3N (**1**), C1N (**2**), C2N (**3**), C3G (**4**), C1G (**5**), and C2G (**6**).

In this paper we wish to describe the isolation of seven additional glycosides, wilfosides D1N (**7**), K1N (**8**), M1N (**9**), F1N (**10**), W1N (**11**), W3N (**12**), and G1G (**13**). Furthermore, we assigned the carbon-13 nuclear magnetic resonance (^{13}C-NMR) chemical shifts of methyl α- (**24a**) and β-L-diginopyranoside (**24b**)[4-6] and studied the conformations of **24a** and its acetate on the basis of the proton nuclear magnetic resonance (^{1}H-NMR) spectra.

Among these new glycosides, **7**—**11** have the same sugar chain as **2** (Rb-type), as indicated by their ^{13}C-NMR spectra with partially relaxed Fourier-transform (PR-FT) measurements[7] (Table I). The acidic hydrolyses of **7**—**11** afforded cymarose and **24**, respectively, which were identified by thin layer chromatographic (TLC) comparison with authentic samples.

The aglycone moiety of **7** was determined to be an unknown derivative of C/D-*cis*-polyoxypregnane ester. The acidic hydrolysis of **7** afforded **15**, named cynanforidine. High-resolution electron impact mass spectrometry (HR-EI-MS) of **15** gave the molecular formula $C_{28}H_{36}O_7$. The 200 MHz ^{1}H-NMR spectrum of **15** suggested the presence of a substituted phenyl group: δ 7.44 (2H, t, J=7.8 Hz, 4′, 6′-CH), 7.55 (1H, tt, J=7.8, 1.3 Hz, 5′-

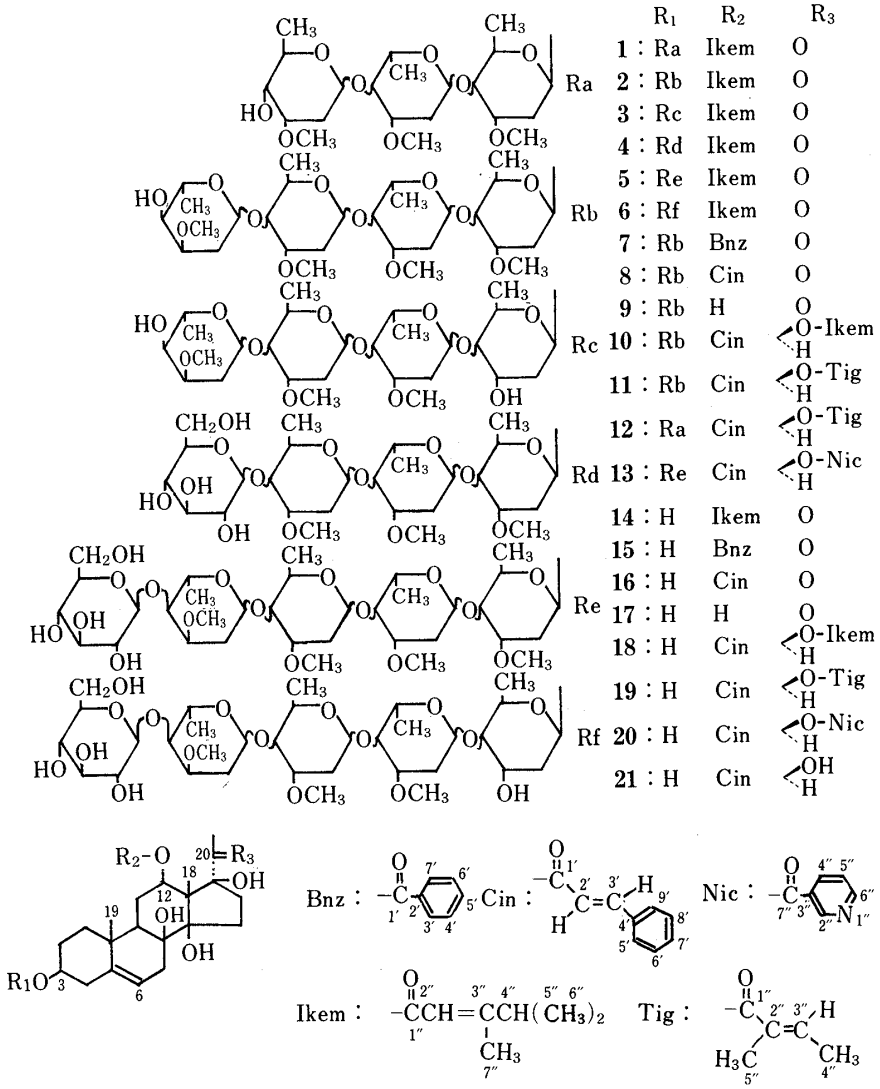

Chart 1

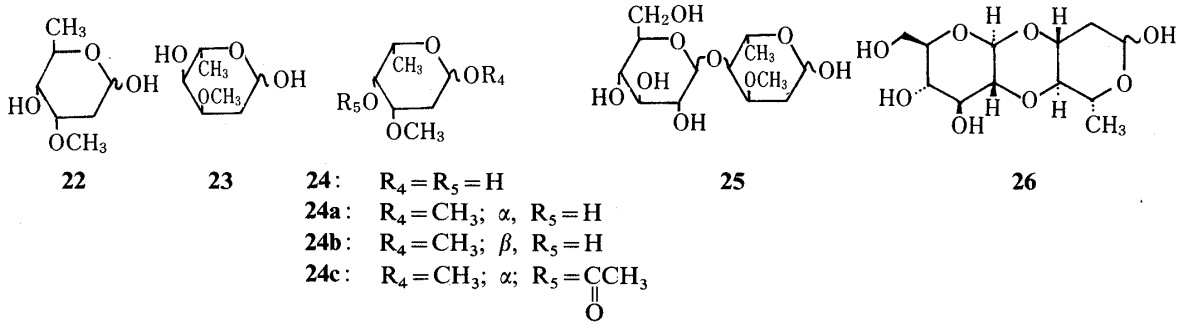

Chart 2

CH), and 7.95 (2H, dd, $J=7.8$, 1.3 Hz, 3′, 7′-CH), and a deacylmetaplexigenin (**17**) derivative: δ 1.15 (3H, s, 18-CH_3), 1.55 (3H, s, 19-CH_3), 2.07 (3H, s, 21-CH_3), 3.58 (1H, m, 3-CH_α), 4.86 (1H, t, $J=7.8$ Hz, 12-CH_α), and 5.39 (1H, br t, $J=3$ Hz, 6-CH). EI-MS showed peaks which indicated the presence of **17** and a benzoyl group at *m/z*: 484 (M^+), 441 ($M^+ - COCH_3$), 319 (441 − COC_6H_5–OH), 301 (319 − H_2O), 283 (301 − H_2O), 105 (COC_6H_5, base peak), 77 (C_6H_5), and 43 ($COCH_3$). By comparing the 50 MHz ^{13}C-NMR chemical shifts

TABLE I. ^{13}C-NMR Chemical Shifts[a] for Sugar Moieties of **7**—**11** and **2** (δ in ppm)

		7	**8**	**9**	**10**	**11**	**2**
D-cym	C-1	96.1	96.2	96.2	96.1	96.1	96.1
	C-2	35.3	35.4	35.4	35.3	35.2	35.2
	C-3	77.6[b]	77.6[b]	77.5[b]	77.6[b]	77.5[b]	77.4[b]
	C-4	82.3	82.3	82.3	82.3	82.3	82.3
	C-5	69.2	69.3	69.3	69.3	69.3	69.2
	C-6	18.8[d]	18.8[d]	18.8[d]	18.7[e]	18.6[e]	18.7[d]
	3-OCH_3	57.2[e]	57.3[e]	57.3[e]	57.2[g]	57.2[f]	57.2[f]
dig	C-1	100.9	100.9	100.9	100.8[j]	100.8[i]	100.8
	C-2	32.5	32.5	32.4	32.4	32.4	32.4
	C-3	73.9[f]	73.9[f]	73.9[f]	73.8[h]	73.7[g]	73.7[g]
	C-4	74.6[f]	74.7[f]	74.7[f]	74.5[h]	74.4[g]	74.6[g]
	C-5	67.5[f]	67.5[f]	67.5[f]	67.5[h]	67.5[g]	67.4[g]
	C-6	17.9	17.9	17.9	17.8	17.8	17.8
	3-OCH_3	55.3	55.3	55.4	55.3	55.3	55.3
D-cym	C-1	99.4[j]	99.4[j]	99.4[k]	99.3[k]	99.3[j]	99.3[l]
	C-2	36.3	36.4	36.4	36.3	36.3	36.3
	C-3	77.8	77.8	77.8	77.8	77.8	77.7
	C-4	82.3	82.3	82.3	82.3	82.3	82.3
	C-5	69.4	69.5	69.5	69.3	69.3	69.3
	C-6	18.6[d]	18.6[d]	18.6[d]	18.6[e]	18.6[e]	18.6[d]
	3-OCH_3	58.3[e]	58.3[e]	58.3[e]	58.2[g]	58.2[f]	58.2[f]
L-cym	C-1	99.0[l]	99.0[l]	99.0[l]	98.9[m]	98.9[l]	98.9[m]
	C-2	32.1	32.2	32.1	32.1	32.1	32.1
	C-3	76.4	76.4	76.4	76.3	76.3	76.3
	C-4	73.2	73.2	73.2	73.2	73.2	73.2
	C-5	66.5	66.5	66.5	66.3	66.3	66.3
	C-6	18.2[d]	18.2[d]	18.3[d]	18.0[e]	18.0[e]	18.1[d]
	3-OCH_3	56.6	56.6	56.6	56.5	56.6	56.5

a) Measured in C_5D_5N with TMS as an internal standard. *b*—*h*) Indicated assignments in each column may be interchangeable (Tables I and III). *i*—*m*) Methine carbon signals of the sugars were recovered at the following times in PR-FT measurements. *i*) 120 ms, *j*) 140 ms, *k*) 160 ms, *l*) 180 ms, *m*) 200 ms. L-cym, α-L-cymaropyranosyl; D-cym, β-D-cymaropyranosyl; dig, α-L-diginopyranosyl.

of **15** with those of **14**, **16**, and **17**, which were assigned by the OFR and INEPT methods (Table II), the structure of **15** was deduced to be 12-*O*-benzoyl-3β,8β,12β,14,17-pentahydroxy-14β,17α-pregn-5-en-20-one (12β-*O*-benzoyldeacylmetaplexigenin).

The 500 MHz ^{1}H-NMR spectrum of **7** showed four methoxyl methyl signals at δ 3.40, 3.41, 3.43, and 3.47 (each 3H, s) and two each of α- and β-linked anomeric proton signals at δ 4.78 (1H, dd, J=10, 2 Hz), 4.79 (1H, dd, J=3, 1 Hz), 4.84 (1H, dd, J=9.8, 2 Hz), and 4.98 (1H, dd, J=3.4, 1 Hz). In the 25 MHz ^{13}C-NMR spectrum of **7** (Table III) the glycosidation shifts[8] of the aglycone carbon signals were observed at C-2 (−2.2 ppm), C-3 (+6.1 ppm), and C-4 (−4.4 ppm), so the sugar moiety is linked to the C-3 hydroxyl group of **15**. Thus, the structure of **7** is established as cynanforidine 3-*O*-α-L-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-α-L-diginopyranosyl-(1→4)-β-D-cymaropyranoside.

The 500 MHz ^{1}H-NMR spectrum of **8** showed the signals due to a cinnamoyl group at δ 6.31 (1H, d, J=16.2 Hz, 3′-CH), 7.39 (3H, m, 6′, 7′, 8′-CH), 7.52 (2H, m, 5′, 9′-CH), and 7.62 (1H, d, J=16.2 Hz, 2′-CH). The spectrum of **9** showed no substituted group in the aglycone moiety. The spectrum of **10** indicated the presence of an ikemaoyl group, in addition to a cinnamoyl group, based on the signals at δ 1.01, 1.03 (each 3H, d, J=6.7 Hz, 5″, 6″-CH_3), 1.73 (3H, s, 7″-CH_3), 2.03 (1H, m, 4″-CH), and 5.68 (1H, br s, 2″-CH). In the

TABLE II. ^{13}C-NMR Chemical Shifts[a] for **14**—**20** (δ in ppm)

	14	**15**	**16**	**17**	**18**	**19**	**20**
C-1	39.2	39.2	39.2	39.3	39.1	39.1	39.1
C-2	31.9	32.1	32.0	32.1	32.0	32.0	32.0
C-3	71.5	71.6	71.6	71.6	71.6	71.6	71.5
C-4	43.2	43.3	43.3	43.4	43.3	43.3	43.3
C-5	140.5	140.4	140.5	140.3	140.2	140.2	140.3
C-6	118.4	118.4	118.4	118.7	118.7	118.6	118.5
C-7	33.8[b]	33.9[b]	33.8[b]	34.2[b]	33.9[b]	33.8[b]	33.7[b]
C-8	74.3	74.5	74.4	74.3	74.4	74.4	74.4
C-9	44.5	44.5	44.6	45.0	44.1	44.1	44.1
C-10	37.3	37.4	37.4	37.3	37.3	37.3	37.3
C-11	25.0	25.1	25.1	29.5	25.7	25.7	25.7
C-12	72.5	74.1	73.7	69.0	74.6[c]	74.5[c]	74.6
C-13	57.9	58.4	58.1	60.4	57.0	57.0	57.1
C-14	89.4	89.6	89.5	89.3	88.9	88.8	88.9
C-15	34.7[b]	34.8[b]	34.8[b]	35.1[b]	35.0[b]	34.9[b]	34.9[b]
C-16	32.9[b]	33.3[b]	33.0[b]	32.8[b]	33.6[b]	33.8[b]	34.1[b]
C-17	92.3	92.5	92.4	92.5	87.7	87.7	87.5
C-18	10.7	10.8	10.6	9.4	11.5	11.4	11.4
C-19	18.3	18.4	18.4	18.5	18.2	18.2	18.2
C-20	209.2	210.0	209.7	209.6	74.0[c]	75.0[c]	76.4
C-21	27.5	27.8	27.7	27.8	15.4	15.4	15.4
	Ikem.	Bnz.	Cin.		Cin.	Cin.	Cin.
C-1′	165.9	165.3	165.8		166.8[d]	166.7	166.7
C-2′	114.1	131.3	119.2		120.7	120.6	120.2
C-3′	165.2	128.9	144.8		143.7	143.7	144.0
C-4′	38.1	129.9	135.0		135.3	135.2	134.9
C-5′	20.8[c]	133.2	128.5		128.5	128.5	128.4
C-6′	20.9[c]	129.9	129.3		129.1	129.2	129.2
C-7′	16.4	128.9	130.5		130.4	130.4	130.5
C-8′			129.3		129.1	129.2	129.2
C-9′			128.5		128.5	128.5	128.4
					Ikem.	Tig.	Nic.
C-1″					166.1[d]	166.7	
C-2″					114.3	129.5	153.7
C-3″					165.9	137.6	127.0
C-4″					38.2	14.1	137.3
C-5″					20.8[e]	12.2	123.6
C-6″					20.9[e]		151.4
C-7″					16.2		164.6

a) Measured in C_5D_5N with TMS as an internal standard. *b*—*e*) Indicated assignments in each column may be interchangeable.

spectrum of **11**, the presence of a tigloyl group was suggested by the signals at δ 1.70 (3H, dd, J=7.3, 1.5 Hz, 4″-CH_3), 1.74 (3H, t, J=1.5 Hz, 5″-CH_3), and 6.76 (1H, dq, J=7.3 Hz, 3″-CH), in addition to a cinnamoyl group. These ^{1}H-NMR spectra suggested that the aglycone moieties of **8**, **9**, **10**, and **11** are **16**, **17**, **18**, and **19**, respectively. These results were supported by the ^{13}C-NMR spectra (Table III), and **18** and **19** were named cynanforine and wilforidine.[2] In the spectra of the aglycones of **8**, **9**, **10**, **11**, **12**, and **13**, the glycosidation shifts[8] were observed at C-2, C-3, and C-4 in each case (Tables II, III, and IV), and hence the sugar moieties are linked to the hydroxyl group at C-3 of **16**, **17**, **18**, **19**, **19**, and gagaminine (**20**).[9] Consequently, the structures of **8**, **9**, **10**, and **11** are confirmed to be kidjoranine 3-*O*-α-L-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-α-L-diginopyranosyl-(1→4)-β-D-cymaro-

TABLE III. ^{13}C-NMR Chemical Shifts[a] for Aglycone Moieties of 7—13 (δ in ppm)

	7	8	9	10	11	12	13
C-1	39.2	39.3	39.4	39.2	39.2	39.4	39.2
C-2	29.9 (−2.2)	29.9	30.0	29.8	29.8	29.9	29.8
C-3	77.7[b] (+6.1)	77.7[b]	77.8[b]	77.7[b]	77.7[b]	77.7[b]	77.6
C-4	38.9 (−4.4)	39.0	39.0	38.8	38.7	38.9	38.8
C-5	139.3	139.4	139.5	139.1	139.1	139.4	139.3
C-6	119.1	119.4	119.4	119.4	119.3	119.3	119.2
C-7	33.8[c]	33.9[c]	34.2	33.8	33.8	33.9[c]	33.6[b]
C-8	74.5	74.3	74.3	74.2	74.2	74.4	74.3
C-9	44.4	44.6	45.0	44.0	44.0	44.2	44.1
C-10	37.4	37.4	37.4	37.2	37.2	37.3	37.3
C-11	25.0	25.1	29.4	25.6	25.6	25.7	25.6
C-12	74.0	73.6	69.0	74.5[d]	74.5[d]	74.5[d]	74.5
C-13	58.3	58.1	60.4	56.9	56.9	57.1	57.1
C-14	89.5	89.5	89.3	88.8	88.7	88.8	88.9
C-15	34.8[c]	34.8[c]	35.1[c]	34.9[c]	34.9[c]	35.0[c]	34.9[b]
C-16	33.1[c]	33.1[c]	32.8[c]	33.6[c]	33.9[c]	34.0[c]	34.0[b]
C-17	92.4	92.4	92.5	87.6	87.7	87.8	87.4
C-18	10.8	10.7	9.3	11.6	11.4	11.4	11.4
C-19	18.4[d]	18.5[d]	18.4[d]	18.4[e]	18.4[e]	18.1[e]	18.2[c]
C-20	210.9	209.7	209.5	74.0[d]	74.9[d]	75.0[d]	76.4
C-21	27.8	27.7	27.8	15.4	15.4	15.4	15.4
	Bnz.	Cin.		Cin.	Cin.	Cin.	Cin.
C-1′	165.2	165.8		166.8[f]	166.6[f]	166.8	166.6
C-2′	131.2	119.2		120.5	120.5	120.7	120.2
C-3′	128.8	144.9		143.7	143.6	143.7	144.0
C-4′	129.9	135.8		135.2	135.2	135.7	134.8
C-5′	133.2	128.6		128.5	128.5	128.5	128.4
C-6′	129.9	129.3		129.1	129.2	129.2	129.2
C-7′	128.8	130.6		130.4	130.4	130.4	130.5
C-8′		129.3		129.1	129.2	129.2	129.2
C-9′		128.6		128.5	128.5	128.5	128.5
				Ikem.	Tig.	Tig.	Nic.
C-1″				166.1[f]	166.7[f]	166.8	
C-2″				114.3	129.4	129.6	153.7
C-3″				165.8	137.6	137.5	126.9
C-4″				38.2	14.1	14.1	137.3
C-5″				20.8	12.2	12.2	123.7
C-6″				20.8			151.4
C-7″				16.2			164.6

a) Measured in C_5D_5N with TMS as an internal standard. *b*—*h*) Indicated assignments in each column may be interchangeable (Tables I, III, and IV). ( ): Glycosidation shifts.

pyranoside, deacylmetaplexigenin 3-*O*-α-L-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-α-L-diginopyranosyl-(1→4)-β-D-cymaropyranoside, cynanforine 3-*O*-α-L-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-α-L-diginopyranosyl-(1→4)-β-D-cymaropyranoside, and wilforidine 3-*O*-α-L-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-α-L-diginopyranosyl-(1→4)-β-D-cymaropyranoside, respectively.

The ^{13}C-NMR spectrum of **12** (Tables III and IV) indicated that the same sugar moiety as that of **1** was linked to the hydroxyl group at C-3 of **19**. Therefore, the structure of **12** is established to be wilforidine 3-*O*-β-D-cymaropyranosyl-(1→4)-α-L-diginopyranosyl-(1→4)-β-D-cymaropyranoside, corresponding to **11** without the terminal α-L-cymaropyranose.

TABLE IV. ^{13}C-NMR Chemical Shifts[a] for Sugar Moieties of **12**, **13**, **1**, and **5** (δ in ppm)

		12	**1**	**13**	**5**
D-cym	C-1	96.2	96.1	96.1	96.1
	C-2	35.4	35.3	35.4	35.3[b]
	C-3	77.6[b]	77.5	77.6	77.5[c]
	C-4	82.3	82.3	82.3	82.3[d]
	C-5	69.3	69.2	69.3	69.2[e]
	C-6	18.8[e]	18.7[b]	18.7[c]	18.7[f]
	3-OCH_3	57.3[f]	57.2[c]	57.2[d]	57.2[g]
dig	C-1	100.9[k]	100.8[k]	100.9	100.9
	C-2	32.5	32.5	32.2	32.4
	C-3	74.0[g]	73.9[d]	73.9[e]	73.9[h]
	C-4	74.7[g]	74.6[d]	74.5[e]	74.6[h]
	C-5	67.7[g]	67.5[d]	67.5[e]	67.5[h]
	C-6	17.9	17.8	17.8	17.8
	3-OCH_3	55.4	55.3	55.3	55.3
D-cym	C-1	99.5[l]	99.4[l]	99.4	99.4
	C-2	35.4	35.3	36.2	36.2[b]
	C-3	78.9	78.8	77.6	77.7[c]
	C-4	74.2	74.1	82.3	82.4[d]
	C-5	71.2	71.0	69.3	69.3[e]
	C-6	18.8[e]	18.1[b]	18.5[c]	18.5[f]
	3-OCH_3	57.9[f]	57.9[c]	58.3[d]	58.3[g]
L-cym	C-1			98.9	98.9
	C-2			32.2	32.2
	C-3			73.3	73.3
	C-4			78.9	78.8
	C-5			65.3	65.2
	C-6			18.0[c]	18.2[f]
	3-OCH_3			56.7	56.7
glc	C-1			102.3[i]	102.2[i]
	C-2			75.2	75.2
	C-3			78.4[f]	78.5
	C-4			71.8	71.7
	C-5			78.5[f]	78.5
	C-6			63.0	62.9

a) Measured in C_5D_5N with TMS as an internal standard. *b*—*h*) Indicated assignments in each column may be interchangeable (Tables III and IV). *i*—*l*) Methine carbon signals of the sugars were recovered at the following times by PR-FT measurements. *i*) 120 ms, *j*) 140 ms, *k*) 160 ms, *l*) 180 ms. L-cym, α-L-cymaropyranosyl; D-cym, β-D-cymaropyranosyl; dig, α-L-diginopyranosyl; glc, β-D-glucopyranosyl.

The 500 MHz ^{1}H-NMR spectrum of **13** indicated that the aglycone moiety is **20**, based on the signals of a nicotinoyl group, at δ 7.19 (1H, dd, J=7.8, 4.9 Hz, 5″-CH), 8.10 (1H, ddd, J=7.8, 4.5, 2.5 Hz, 4″-CH), 8.72 (1H, dd, J=4.9, 2.5 Hz, 6″-CH), and 9.18 (1H, d, J=4.5 Hz, 2″-CH). The acidic hydrolysis of **13** gave cymarose, **24**, and glaucobiose (**25**),[10] which were identified by TLC comparison with authentic samples. The ^{13}C-NMR spectrum of **13** (Table IV) showed that the sugar moiety is the same as that of **5** (Re-type). Thus, **13** was identified as gagaminine 3-*O*-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-α-L-diginopyranosyl-(1→4)-β-D-cymaropyranoside.

The glycosides with the sugar moieties of Rb, Rc, Re, and Rf-types (Chart 1) are believed to be the first examples which contain a pair of optically isomeric sugars in each molecule.

In the 500 MHz ^{1}H-NMR spectrum of **24a** the signal of 2-CH_{eq} at δ 1.90 is split into double double double doublets (dddd, J=13.1, 5.5, 1.3, 1 Hz), and irradiation of a signal at

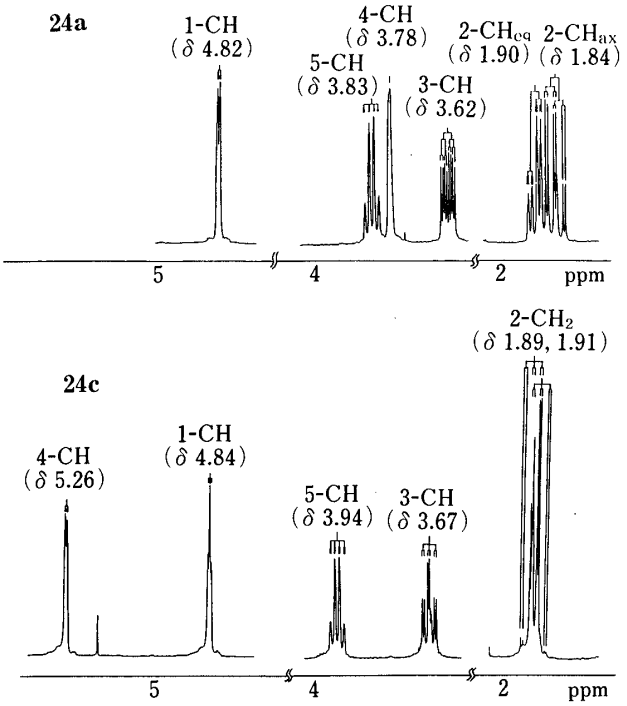

Fig. 1. Partial ^{1}H-NMR Spectra of **24a** and **24c** (500 MHz, $CDCl_3$)

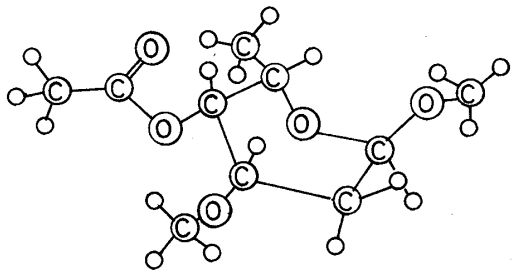

Fig. 2. Model of **24c**

TABLE V. ^{1}H-NMR Coupling Constants for **24c** (Hz)

$J_{1,2}$	2.3	$J_{2',3}$	7.9
$J_{1,2'}$	2.3	$J_{3,4}$	3.1
$J_{2,2'}$	7.9	$J_{4,5}$	0.5
$J_{2,3}$	7.9	$J_{5,6}$	6.4

Two protons at C-2 were not assigned.

TABLE VI. ^{13}C-NMR Chemical Shifts[a] for **24a** and **24b** (δ in ppm)

	24a	**24b**
C-1	99.2	101.8
C-2	30.4	32.5
C-3	75.9	79.0
C-4	67.6	67.0
C-5	66.8	71.4
C-6	17.5	17.5
3-OCH_3	54.5	55.3
	55.0	55.9

a) Measured in C_5D_5N with TMS as an internal standard.

δ 3.78 (4-CH) caused the dddd signal of 2-CH_{eq} to collapse to ddd. This long-range coupling is attributed to the W-conformation of the four sigma bonds between 2-CH_{eq} and 4-CH in the $^1C_4$-conformation of **24a**. Acetylation of **24a** gave a monoacetate (**24c**), whose 500 MHz ^{1}H-NMR spectrum showed a shift of the 4-CH signal from δ 3.78 to 5.26. However, owing to the acetylation, the conformation of **24a** in deuterochloroform ($CDCl_3$) was changed into a twisted boat form (**24c**) as illustrated in Fig. 2, as inferred from the dihedral angle dependent on proton coupling constants[11] (Fig. 1 and Table V). It was suspected that the twisted boat form of **24c** decreased the repulsion between 3-OCH_3 and 4-$OCOCH_3$.

All the carbon chemical shifts of **24a** and **24b** in pentadeuteropyridine (C_5D_5N) were assigned by means of selective decoupling (SEL) experiments (Table VI). Irradiation of signals at δ 3.76 (3-CH), 3.90 (5-CH), and 3.99 (4-CH) in the spectrum of **24a** caused the doublet signals at δ 75.9, 66.8, and 67.6 to collapse to singlets, and irradiation at δ 3.37 (3-CH), 3.90 (5-CH), and 3.89 (4-CH) in the case of **24b** caused the doublet signals at δ 79.0, 71.9,

and 67.0 to collapse to singlets, respectively. The orientation of the methoxyl group at C-1 has a considerable effect on the carbon chemical shifts, especially that of C-5 ($\delta_{24a} - \delta_{24b} = -5.1$).

Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Optical rotations were measured in $CHCl_3$ with a JASCO DIP-4 digital polarimeter at room temperature. Ultraviolet (UV) spectra were obtained in ethanol with a Shimadzu UV-220 spectrometer, and absorption maxima are given in nm. Infrared (IR) spectra were recorded in $CHCl_3$ on a JASCO A-102 spectrometer. ^{1}H-NMR spectra were run on JEOL FX-500 (500 MHz) and FX-200 (200 MHz) spectrometers in $CDCl_3$ or C_5D_5N, and ^{13}C-NMR spectra on JEOL FX-200 (50 MHz) and FX-100 (25 MHz) machines in C_5D_5N with tetramethylsilane as an internal standard. EI-MS was carried out with a JEOL LMS-D-300 mass spectrometer. TLC was performed on Merck precoated plates (Kiesel gel 60 F_{254}) with the following solvent systems: Rf_1 MeOH–$CHCl_3$ (5:95 (v/v)), Rf_2 MeOH–$CHCl_3$ (1:9), Rf_3 MeOH–$CHCl_3$ (15:85), Rf_4 H_2O–MeOH–$CHCl_3$ (1:3:12, lower layer), and Rf_5 acetone–hexane (1:1). Column chromatography was carried out on Wakogel C-200 (200 mesh) or Lobar column Lichroprep RP-8 (reversed phase).

Isolation of Glycosides——The crude glycosides (137.7 g) reported in the previous paper[4] were subjected to column chromatography on silica gel using solvents of increasing polarity from $CHCl_3$ to MeOH–$CHCl_3$ (2:8 (v/v)) to separate fraction A (47.27 g, a crude fraction containing **1**—**3** and **7**—**12**), fraction B (39.19 g, a crude fraction containing **4**—**6** and **13**), and fraction C (28.50 g). Fraction A (37.50 g) was rechromatographed on silica gel using solvents of increasing polarity from MeOH–$CHCl_3$ (2:98) to MeOH–$CHCl_3$ (4:96) to separate fraction A2 (7.10 g, a crude fraction containing **1**, **2**, and **10**—**12**), fraction A3 (21.59 g, a crude fraction containing **3**, **7**, and **8**), and fraction A4 (2.65 g, a crude fraction containing **9**). Rechromatography of fraction A2 on silica gel with acetone–hexane (1:2) and MeOH–$CHCl_3$ (2:98), and on a reversed phase gel column with H_2O–MeOH (20:80) gave **10** (168.4 mg, yield: 0.0059% from the dried root), **11** (185.1, 0.0068%), and **12** (13.2 mg, 0.0005%). Rechromatography of fraction A3 on silica gel with acetone–hexane (2:3 and 1:2) and on the reversed phase gel column with H_2O–MeOH (20:80 and 25:75) afforded **8** (442.5 mg, 0.016%), and further rechromatography on silica gel with MeOH–$CHCl_3$ (2:98) gave **7** (188.0 mg, 0.0068%). Rechromatography of fraction A4 on silica gel with acetone–hexane (1:1) and MeOH–$CHCl_3$ (4:96, 2:98, and 3:97), and on the reversed phase gel column with H_2O–MeOH (15:85) afforded **9** (23.9 mg, 0.0009%). Rechromatography of fraction B4 on silica gel with MeOH–$CHCl_3$ (8:92) and hexane–acetone (1:3), and on the reversed phase gel column with H_2O–MeOH (15:85) gave **13** (110.8 mg, 0.014%). *Rf* values: **7** (Rf_1 0.36, Rf_5 0.35), **8** (Rf_1 0.40, Rf_5 0.35), **9** (Rf_1 0.22, Rf_5 0.31), **10** (Rf_1 0.40, Rf_5 0.47), **11** (Rf_1 0.38, Rf_5 0.43), **12** (Rf_1 0.40, Rf_5 0.46), and **13** (Rf_3 0.45).

Wilfoside D1N (7)——An amorphous powder, mp 143—145 °C, $[\alpha]_D^{17}$ −46.9° (c=1.08, $CHCl_3$). *Anal.* Calcd for $C_{56}H_{84}O_{19} \cdot H_2O$: C, 62.32; H, 8.03. Found: C, 62.30; H, 8.07. UV $\lambda_{max}^{ethanol}$ nm (log ε): 284 (3.92), 277 (4.13), 233 (3.58), 212 (3.57). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), 1710 (C=O), 1640 (C=C–C=O), 1600, 1490, 1465 (C_6H_5), 1160 (C–O–C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.13 (3H, s, 18-CH_3), 1.22, 1.23, 1.24, 1.26 (each 3H, d, J=6.4 Hz), 1.55 (3H, s, 19-CH_3), 2.07 (3H, s, 21-CH_3), 2.86 (1H, m, 3-CH_α), 3.24, 3.30 (each 1H, dd, J=9.8, 2.8 Hz, 4-CH of cymaropyranose), 3.40, 3.41, 3.43, 3.47 (each 3H, s, 3-OCH_3 of sugar moiety), 3.70, 3.77 (each ddd, J=3, 3, 2.8 Hz, 3-CH of cymaropyranose), 3.83 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.85 (1H, br s, 4-CH of α-L-diginopyranose), 3.86 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.96 (1H, dq, J=6.7, 0.5 Hz, 5-CH of α-L-diginopyranose), 4.05 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 4.78 (1H, dd, J=10, 2 Hz, anomeric H), 4.79 (1H, dd, J=3, 1 Hz, anomeric H), 4.84 (1H, dd, J=9.8, 2 Hz, anomeric H), 4.85 (1H, t, J=7.9 Hz, 12-CH_α), 4.98 (1H, dd, J=3.4, 1 Hz, anomeric H), 5.39 (1H, br s, 6-CH), 7.43 (2H, t, J=7.4 Hz, 4′, 6′-CH), 7.56 (1H, tt, J=7.4, 1.2 Hz, 5′-CH), 7.94 (2H, dd, J=7.4, 1.2 Hz, 3′, 7′-CH). ^{13}C-NMR (25 MHz, C_5D_5N): see Tables I and III.

Acidic Hydrolysis of 7——A solution of **7** (95.4 mg) in MeOH (30 ml) was allowed to react with 0.2 N H_2SO_4 (10 ml) at 60 °C for 20 min, then H_2O (30 ml) was added and the whole mixture was concentrated to 40 ml. The solution was kept at 60 °C for a further 30 min, and extracted with ether (40 ml). The ether layer was washed with satd. $NaHCO_3$ (10 ml × 2) and satd. NaCl (10 ml × 2), and the solvent was evaporated off to give **15** (23.1 mg). Rf_2 0.34, Rf_5 0.41. mp 142—145 °C, $[\alpha]_D^{18}$ −3.8° (c=1.26, $CHCl_3$). *Anal.* Calcd for $C_{28}H_{36}O_7 \cdot 1/2H_2O$: C, 68.13; H, 7.56. Found: C, 68.31; H, 7.86. UV $\lambda_{max}^{ethanol}$ nm (log ε): 281 (3.10), 273 (3.11), 230 (3.59), 207 (3.50). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3455 (OH), 1710 (C=O), 1635 (C=C–C=O), 1600, 1585, 1490, 1450 (C_6H_5), 1180 (C–O–C). EI-MS *m/z*: 484 (M^+), 441 ($M^+ - COCH_3$), 319 ($M^+ - COCH_3 - COC_6H_5 - OH$), 301 (319 − H_2O), 283 (319 − $2H_2O$), 105 (COC_6H_5, base peak), 77 (105 − CO), 43 ($COCH_3$). HR-EI-MS: Calcd for $C_{28}H_{36}O_7$: 484.2460. Found: 484.2432. ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.15, 1.55, 2.07 (each 3H, s, 18, 19, 21-CH_3), 3.58 (1H, m, 3-CH_α), 4.86 (1H, t, J=7.8 Hz, 12-CH_α), 5.39 (1H, br t, J=3 Hz, 6-CH), 7.44 (2H, t, J=7.8 Hz, 4′, 6′-CH), 7.55 (1H, tt, J=7.8, 1.3 Hz, 5′-CH), 7.95 (2H, dd, J=7.8, 1.3 Hz, 3′, 7′-CH). ^{13}C-NMR (50 MHz, C_5D_5N): see Table II. The aqueous layer was neutralized with satd. $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to give a mixture of cymarose and **24**, which were identified by TLC comparison with authentic samples. *Rf* values: cymarose (Rf_4 0.59, Rf_5 0.42) and **24** (Rf_4 0.56, Rf_5 0.35).

Wilfoside K1N (8)——An amorphous powder, mp 183—187 °C, $[\alpha]_D^{18}$ −23.2° (c=1.06, $CHCl_3$). *Anal.* Calcd for $C_{58}H_{86}O_{19}\cdot 1/3H_2O$: C, 63.72; H, 7.93. Found: C, 63.76; H, 8.08. UV $\lambda_{max}^{ethanol}$ nm (log ε): 277 (3.86), 221 (3.87), 217 (3.83), 205 (4.01). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430 (OH), 1700 (C=O), 1635 (C=C–C=O), 1580, 1495, 1465 (C_6H_5), 1160 (C–O–C). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.14 (3H, s, 18-CH_3), 1.22, 1.23, 1.24, 1.26 (each 3H, d, J=6.4 Hz, 6-CH_3 of sugar moiety), 1.47, 2.20 (each 3H, s, 19, 21-CH_3), 2.86 (1H, m, 3-CH_α), 3.24, 3.30 (each 1H, dd, J=9.5, 2.8 Hz, 4-CH of cymaropyranose), 3.39, 3.41, 3.43, 3.47 (each 3H, s, 3-OCH_3 of sugar moiety), 3.70, 3.77 (each 1H, ddd, J=3, 3, 2.8 Hz, 3-CH of cymaropyranose), 3.83 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.85 (1H, br s, 4-CH of α-L-diginopyranose), 3.86 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.96 (1H, dq, J=6.7, 0.5 Hz, 5-CH of α-L-diginopyranose), 4.05 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 4.70 (1H, m, 12-CH_α), 4.77 (1H, dd, J=10, 2 Hz, anomeric H), 4.79 (1H, dd, J=3, 1 Hz, anomeric H), 4.84 (1H, dd, J=9.8, 2 Hz, anomeric H), 4.98 (1H, dd, J=3.4, 1 Hz, anomeric H), 5.38 (1H, br s, 6-CH), 6.31 (1H, d, J=16.2 Hz, 3′-CH), 7.39 (3H, m, 6′, 7′, 8′-CH), 7.52 (2H, m, 5′, 9′-CH), 7.62 (1H, d, J=16.2 Hz, 2′-CH). ^{13}C-NMR (50 MHz, C_5D_5N): see Tables I and III.

Acidic Hydrolysis of 8——A solution of **8** (1 mg) in MeOH (3 ml) was allowed to react with 0.2 N H_2SO_4 (1 ml) at 60 °C for 15 min, then H_2O (3 ml) was added and the whole mixture was concentrated to 4 ml. The solution was kept at 60 °C for a further 30 min, and neutralized with satd. $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to dryness. The products were identified as **16**, cymarose, and **24** by TLC comparison with authentic samples. *Rf* values: **16** (Rf_2 0.34, Rf_5 0.44), cymarose (Rf_4 0.59, Rf_5 0.42), and **24** (Rf_4 0.56, Rf_5 0.35).

Wilfoside M1N (9)——An amorphous powder, mp 141—143 °C, $[\alpha]_D^{15}$ −40.3° (c=1.73, $CHCl_3$). *Anal.* Calcd for $C_{49}H_{80}O_{18}$: C, 61.48; H, 8.43. Found: C, 61.68; H, 8.40. UV $\lambda_{max}^{ethanol}$ nm (log ε): 280 (3.71), 2.07 (4.36). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), 1710 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.16 (3H, s, 18-CH_3), 1.22, 1.23, 1.24, 1.25 (each 3H, d, J=6.4 Hz, 6-CH_3 of sugar moiety), 1.27, 2.35 (each 3H, s, 19, 21-CH_3), 3.25, 3.30 (each 1H, dd, J=9.8, 2.9 Hz, 4-CH of cymaropyranose), 3.39, 3.41, 3.42, 3.47 (each 3H, s, 3-OCH_3 of sugar moiety), 3.70, 3.77 (each 1H, ddd, J=3, 3, 2.9 Hz, 3-CH of cymaropyranose), 3.83 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.85 (1H, br s, 4-CH of α-L-diginopyranose), 3.86 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.96 (1H, dq, J=6.7, 0.5 Hz, 5-CH of α-L-diginopyranose), 4.04 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 4.77 (1H, dd, J=10, 2 Hz, anomeric H), 4.78 (1H, dd, J=3, 1 Hz, anomeric H), 4.83 (1H, dd, J=9.6, 2 Hz, anomeric H), 4.99 (1H, dd, J=3, 1 Hz, anomeric H), 5.37 (1H, br s, 6-CH). ^{13}C-NMR (50 MHz, C_5D_5N): see Tables I and III.

Acidic Hydrolysis of 9——A solution of **9** (1 mg) in MeOH (3 ml) was allowed to react with 0.2 N H_2SO_4 (1 ml) at 60 °C for 15 min, then H_2O (3 ml) was added and the whole mixture was concentrated to 4 ml. The solution was kept at 60 °C for a further 30 min, and neutralized with satd. $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to dryness. The products were identified as **17**, cymarose, and **24** by TLC comparison with authentic samples. *Rf* values: **17** (Rf_2 0.22, Rf_5 0.29), cymarose (Rf_4 0.59, Rf_5 0.42), and **24** (Rf_4 0.56, Rf_5 0.35).

Wilfoside F1N (10)——An amorphous powder, mp 140—144 °C, $[\alpha]_D^{17}$ +32.6° (c=1.03, $CHCl_3$). *Anal.* Calcd for $C_{65}H_{98}O_{20}\cdot 2/3\ H_2O$: C, 64.43; H, 8.27. Found: C, 64.32; H, 8.20. UV $\lambda_{max}^{ethanol}$ nm (log ε): 289 (4.04), 222 (4.11), 215 (4.14), 212 (4.10). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1710 (C=O), 1640 (C=C–C=O), 1580, 1495, 1450 (C_6H_5), 1160 (C–O–C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.01, 1.03 (each 3H, d, J=6.7 Hz, 5″, 6″-CH), 1.15 (3H, s, 18-CH_3), 1.22 (3H, d, J=6.4 Hz, 6-CH_3 of sugar moiety), 1.23 (3H, s, 21-CH_3), 1.24, 1.26 (each 3H, d, J=6.4 Hz, 6-CH_3 of sugar moiety), 1.54, 1.73 (each 3H, s, 19, 7″-CH_3), 3.24, 3.30 (each 1H, dd, J=9.8, 3.1 Hz, 4-CH of cymaropyranose), 3.39, 3.41, 3.42, 3.46 (each 3H, s, 3-OCH_3 of sugar moiety), 3.70, 3.76 (each 1H, ddd, J=3.1, 3, 3 Hz, 3-CH of cymaropyranose), 3.82 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.85 (1H, br s, 4-CH of α-L-diginopyranose), 3.86 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.96 (1H, dq, J=6.8, 0.5 Hz, 5-CH of α-L-diginopyranose), 4.05 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 4.66 (1H, q, J=6.1 Hz, 20-CH), 4.77 (1H, dd, J=10, 2 Hz, anomeric H), 4.79 (1H, dd, J=3, 1 Hz, anomeric H), 4.83 (1H, dd, J=10, 2 Hz, anomeric H), 4.98 (1H, dd, J=3.4, 1 Hz, anomeric H), 5.38 (1H, br s, 6-CH), 5.68 (1H, br s, 2″-CH), 6.24 (1H, d, J=15.9 Hz, 3′-CH), 7.35 (3H, m, 6′, 7′, 8′-CH), 7.46 (2H, m, 5′, 9′-CH), 7.57 (1H, d, J=15.9 Hz, 2′-CH). ^{13}C-NMR (500 MHz, C_5D_5N): see Tables I and III.

Acidic Hydrolysis of 10——A solution of **10** (1 mg) in MeOH (3 ml) was allowed to react with 0.2 N H_2SO_4 (1 ml) at 60 °C for 15 min, then H_2O (3 ml) was added and the whole mixture was concentrated to 4 ml. The solution was kept at 60 °C for a further 30 min, and neutralized with satd. $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to dryness. The products were identified as **18**, cymarose, and **24** by TLC comparison with authentic samples. *Rf* values: **18** (Rf_2 0.40, Rf_5 0.53), cymarose (Rf_4 0.59, Rf_5 0.42), and **24** (Rf_4 0.56, Rf_5 0.35).

Wilfoside W1N (11)——An amorphous powder, mp 143.5—146 °C, $[\alpha]_D^{17}$ +33.0° (c=0.94, $CHCl_3$). *Anal.* Calcd for $C_{63}H_{94}O_{20}\cdot 1/2\ H_2O$: C, 64.10; H, 8.11. Found: C, 64.14; H, 8.23. UV $\lambda_{max}^{ethanol}$ nm (log ε): 276 (4.02), 222 (4.06), 216 (4.01), 210 (4.07). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (OH), 1710 (C=O), 1640 (C=C–C=O), 1600, 1580, 1500, 1450 (C_6H_5), 1160 (C–O–C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.15 (3H, s, 18-CH_3), 1.22 (3H, d, J=6.4 Hz, 6-CH_3 of sugar moiety), 1.23 (3H, d, J=6.1 Hz, 21-CH_3), 1.26 (3H, d, J=6.4 Hz, 6-CH_3 of sugar moiety), 1.54 (3H, s, 19-CH_3), 1.70 (3H, dd, J=7.3, 1.5 Hz, 4″-CH_3), 1.74 (3H, t, J=1.5 Hz, 5″-CH_3), 3.24, 3.31 (each 1H, dd, J=9.8, 3.0 Hz, 4-CH of cymaropyranose), 3.39, 3.41, 3.42, 3.46 (each 3H, s, 3-OCH_3 of sugar moiety), 3.70, 3.76 (each 1H, ddd, J=3.0, 3, 3 Hz, 3-CH of cymaropyranose), 3.82 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.85 (1H, br s, 4-CH of α-L-diginopyranose), 3.86 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.96 (1H, dq, J=6.7, 0.5 Hz, 5-CH of α-L-

diginopyranose), 4.05 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 4.71 (1H, q, J=6.1 Hz, 20-CH), 4.77 (1H, dd, J=10, 2 Hz, anomeric H), 4.79 (1H, dd, J=3, 1 Hz, anomeric H), 4.83 (1H, dd, J=10, 2 Hz, anomeric H), 4.98 (1H, dd, J=3.4, 1 Hz, anomeric H), 5.37 (1H, br s, 6-CH), 6.23 (1H, d, J=16.0 Hz, 3′-CH), 6.76 (1H, dq, J=7.3, 1.5 Hz, 3″-CH), 7.37 (3H, m, 6′, 7′, 8′-CH), 7.47 (2H, m, 5′, 9′-CH), 7.53 (1H, d, J=16.0 Hz, 2′-CH). ^{13}C-NMR (25 MHz, C_5D_5N): Tables I and III.

Acidic Hydrolysis of 11——A solution of **11** (1 mg) in MeOH (3 ml) was allowed to react with 0.2 N H_2SO_4 (1 ml) at 60 °C for 15 min, then H_2O (3 ml) was added and the whole mixture was concentrated to 4 ml. The solution was kept at 60 °C for a further 30 min, and neutralized with satd. $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to dryness. The products were identified as **19**, cymarose, and **24** by TLC comparison with authentic samples, *Rf* values: **19** (Rf_2 0.39, Rf_5 0.49), cymarose (Rf_4 0.59, Rf_5 0.42), and **24** (Rf_4 0.56, Rf_5 0.35).

Wilfoside W3N (12)——An amorphous powder, mp 120—123 °C, $[\alpha]_D^{15}$ +43.3° (c=1.03, $CHCl_3$). *Anal.* Calcd for $C_{56}H_{82}O_{17}$: C, 65.47; H, 8.05. Found: C, 65.57; H, 7.95. UV $\lambda_{max}^{ethanol}$ nm (log ε): 278 (3.96), 223 (4.07), 218 (4.12), 206 (4.05). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), 1700 (C=O), 1640 (C=C–C=O), 1600, 1580, 1500, 1450 (C_6H_5), 1160 (C–O–C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.15 (3H, s, 18-CH_3), 1.23, 1.24, 1.30 (each 3H, d, J=6.4 Hz, 6-CH_3 of sugar moiety), 1.55 (3H, s, 19-CH_3), 1.71 (3H, dd, J=7.3, 1.5 Hz, 4″-CH_3), 1.73 (3H, t, J=1.5 Hz, 5″-CH_3), 3.24, 3.31 (each 1H, dd, J=9.5, 3.0 Hz, 4-CH of cymaropyranose), 3.415 (3H, s, 3-OCH_3 of sugar moiety), 3.424 (6H, s, 3-OCH_3 ×2 of sugar moiety), 3.56 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.65, 3.70 (each 1H, ddd, J=3.0, 3, 3 Hz, 3-CH of cymaropyranose), 3.83 (1H, dq, J=8.9, 6.4 Hz, 5-CH of cymaropyranose), 3.86 (1H, br s, 4-CH of α-L-diginopyranose), 3.97 (1H, dq, J=6.7, 0.5 Hz, 5-CH of α-L-diginopyranose), 4.69 (1H, dd, J=10, 2 Hz, anomeric H), 4.71 (1H, q, J=6.4 Hz, 20-CH), 4.77 (1H, dd, J=11.3, 4.0 Hz, 12-CH_α), 4.84 (1H, dd, J=9.6, 2 Hz, anomeric H), 4.98 (1H, dd, J=3.4, 1 Hz, anomeric H), 5.38 (1H, br s, 6-CH), 6.23 (1H, d, J=16.2 Hz, 3′-CH), 6.76 (1H, dq, J=7.3, 1.5 Hz, 3″-CH), 7.37 (3H, m, 6′, 7′, 8′-CH), 7.47 (2H, m, 5′, 9′-CH), 7.53 (1H, d, J=16.2 Hz, 2′-CH). ^{13}C-NMR (50 MHz, C_5D_5N): see Tables III and IV.

Acidic Hydrolysis of 12——A solution of **12** (1 mg) in MeOH (3 ml) was allowed to react with 0.2 N H_2SO_4 (1 ml) at 60 °C for 15 min, then H_2O (3 ml) was added and the whole mixture was concentrated to 4 ml. The solution was kept at 60 °C for a further 30 min, and neutralized with satd. $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to dryness. The products were identified as **19**, cymarose, and **24** by TLC comparison with authentic samples. *Rf* values: **19** (Rf_2 0.39, Rf_5 0.49), cymarose (Rf_4 0.59, Rf_5 0.42), and **24** (Rf_4 0.56, Rf_5 0.35).

Wilfoside G1G (13)——An amorphous powder, mp 164—167 °C, $[\alpha]_D^{17}$ +28.2° (c=0.98, $CHCl_3$). *Anal.* Calcd for $C_{70}H_{101}NO_{25}\cdot 1/2\ H_2O$: C, 61.57; H, 7.52; N, 1.03. Found: C, 61.37; H, 7.73; N, 0.77. UV $\lambda_{max}^{ethanol}$ nm (log ε): 220 (4.49), 279 (4.43). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1720, 1690 (C=O), 1640 (C=C–C=O), 1590 (C_6H_5), 1160 (C–O–C). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.12 (3H, s, 18-CH_3), 1.21, 1.23 (each 3H, d, J=6.4 Hz, 6-CH_3 of sugar moiety), 1.62 (3H, s, 19-CH_3), 3.38, 3.41, 3.42, 3.45 (each 3H, s, 3-OCH_3 of sugar moiety), 4.39 (1H, d, J=7.3 Hz, anomeric H of β-D-glucopyranose), 4.76 (1H, dd, J=10, 2 Hz, anomeric H), 4.98 (1H, dd, J=3, 1 Hz, anomeric H), 5.37 (1H, br s, 6-CH), 6.08 (1H, d, J=16.1 Hz, 3′-CH), 7.19 (1H, dd, J=7.8, 4.9 Hz, 5″-CH), 7.39 (1H, d, J=16.1 Hz, 2′-CH), 8.10 (1H, ddd, J=7.8, 4.5, 2.5 Hz, 4″-CH), 8.72 (1H, dd, J=4.9, 2.5 Hz, 6″-CH), 9.18 (1H, d, J=4.5 Hz, 2″-CH). ^{13}C-NMR (50 MHz, C_5D_5N): see Tables III and IV.

Acidic Hydrolysis of 13——A solution of **13** (1 mg) in MeOH (3 ml) was allowed to react with 0.2 N H_2SO_4 (1 ml) at 60 °C for 15 min, then H_2O (3 ml) was added and the whole mixture was concentrared to 4 ml. The solution was kept at 60 °C for a further 30 min, and neutralized with satd. $Ba(OH)_2$. The precipitates were filtered off and the filtrate was evaporated to dryness. The products were identified as **20**, cymarose, **24**, and **25** by TLC comparison with authentic samples. *Rf* values: **20** (Rf_2 0.24, Rf_5 0.28), cymarose (Rf_4 0.59, Rf_5 0.42), **24** (Rf_4 0.56, Rf_5 0.35), and **25** (Rf_4 0.16, Rf_5 0.01).

Methyl α-L-Diginopyranoside (24a)——^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.31 (3H, d, J=6.7 Hz, 6-CH_3), 1.84 (1H, ddd, J=13.1, 11.6, 3.4 Hz, 2-CH_{ax}), 1.90 (1H, dddd, J=13.1, 5.5, 1.3, 1 Hz, 2-CH_{eq}), 3.33, 3.39 (each 3H, s, 1, 3-OCH_3), 3.62 (1H, ddd, J=11.6, 5.5, 3.1 Hz, 3-CH), 3.78 (1H, ddd, J=3.1, 1, 0.6 Hz, 4-CH), 3.83 (1H, dq, J=6.7, 1 Hz, 5-CH), 4.82 (1H, dd, J=3.4, 1.3 Hz, 1-CH). ^{1}H-NMR (200 MHz, C_5D_5N) δ: 1.50 (3H, d, J=6.4 Hz, 6-CH_3), 1.97 (1H, ddt, J=12.2, 4.9, 1.0 Hz, 2-CH_{eq}), 2.30 (1H, dt, J=12.2, 3.4 Hz, 2-CH_{ax}), 3.33, 3.34 (each 3H, s, 1, 3-OCH_3), 3.77 (1H, ddd, J=12.2, 4.9, 2.9 Hz, 3-CH), 3.91 (1H, ddd, J=2.9, 1.0, 1 Hz, 4-CH), 4.89 (1H, dd, J=3.4, 1.0 Hz, 1-CH). ^{13}C-NMR (50 MHz, C_5D_5N): see Table VI.

Acetyl-24a (24c)——Compound **24a** (7.4 mg) was dissolved in pyridine (1 ml), and acetic anhydride (0.8 ml) was added. The reaction mixture was kept at room temperature overnight, then H_2O (20 ml) was added, and the whole was extracted with $CHCl_3$ (10 ml). The $CHCl_3$ layer was washed with 2 N HCl (10 ml ×2), satd. $NaHCO_3$ (10 ml ×2), and satd. NaCl (10 ml ×2), and dried over anhydrous sodium sulfate. Then, the solvent was evaporated off to give **24c** (7.7 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.16 (3H, d, J=6.4 Hz, 6-CH_3), 1.89, 1.91 (each 1H, dt, J=7.9, 2.3 Hz, 2-CH_2), 2.16 (3H, s, 4-$OCOCH_3$), 3.341, 3.345 (each 3H, s, 1, 3-OCH_3), 3.67 (1H, dt, J=7.9, 3.1 Hz, 3-CH), 3.94 (1H, dq, J=6.4, 0.5 Hz, 5-CH), 4.84 (1H, t, J=2.3 Hz, 1-CH), 5.26 (1H, dd, J=3.1, 0.5 Hz, 4-CH).

Methyl β-L-Diginopyranoside (24b)——^{1}H-NMR (500 MHz, C_5D_5N) δ: 1.53 (3H, d, J=6.4 Hz, 6-CH_3), 2.08 (1H, ddd, J=11.7, 4.9, 2.4 Hz, 2-CH_{eq}), 2.23 (1H, dt, J=11.7, 9.8 Hz, 2-CH_{ax}), 3.37 (3H, s, –OCH_3), 3.37 (1H, ddd, J=11.7, 4.9, 2.9 Hz, 3-CH), 3.52 (1H, dq, J=6.4, 1.0 Hz, 5-CH), 3.53 (3H, s, –OCH_3), 3.88 (1H, dd, J=2.9, 1.0 Hz,

4-CH), 4.44 (1H, dd, $J=9.3$, 2.4 Hz, 1-CH). ^{13}C-NMR (50 MHz, C_5D_5N): see Table VI.

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