[Chem. Pharm. Bull.]
35(1) 46-52 (1987)

Studies on the Constituents of Leguminous Plants. IX.¹⁾ The Structure of a New Triterpenoid Saponin from the Fruits of *Gymnocladus chinensis* BAILLON

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(Received May 29, 1986)

A new triterpenoid saponin, gymnocladus saponin G (**1**), having a glycosyl monoterpene carboxyl moiety and a 2-methylbutyloyl group, was isolated from the fruits of *Gymnocladus chinensis* BAILLON. On the basis of chemical and physicochemical evidence, its structure was characterized as 2 β ,23-dihydroxy-3-*O*-[β -D-xylopyranosyl-(1 $\rightarrow$ 2)- α -L-arabinopyranosyl-(1 $\rightarrow$ 6)- β -D-glucopyranosyl]-21-*O*-{(6*S*)-2-*trans*-2,6-dimethyl-6-[3-*O*-(β -D-glucopyranosyl)-4-*O*-(2-methylbutyryl)- α -L-arabinopyranosyloxy]-2,7-octadienoyl}acacic acid 28-*O*- β -D-xylopyranosyl-(1 $\rightarrow$ 3)- β -D-xylopyranosyl-(1 $\rightarrow$ 4)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 6)]- β -D-glucopyranoside.

Keywords—*Gymnocladus chinensis*; Leguminosae; gymnocladus saponin G; 2 β ,23-dihydroxyacacic acid; triterpenoid; saponin; monoterpene glycoside

In previous papers,¹⁻³⁾ we reported the structure elucidations of two monoterpene glycosides (**2** and **3**), and four triterpenoid saponins, gymnocladus saponins A (**4**), B (**5**), C (**6**) and D (**7**), isolated from the fruits of *Gymnocladus chinensis* BAILLON. Compounds **4**, **5** and **6** were 3-*O*-glycosides of 2 β ,23-dihydroxyacacic acid lactone (**8**), and **7** was a 3,28-bisglycoside of 2 β ,23-dihydroxyacacic acid (**9**), as shown in Chart 1. A new saponin, named gymnocladus saponin G (**1**) has now been isolated from the most polar fraction of the same source, and characterized as a 3,28-bisglycoside of **9**, bearing a glycosyl monoterpene carboxylate as an acyl side-chain, on the basis of carbon-13 nuclear magnetic resonance (¹³C-NMR) spectrometry and some chemical degradations.

Gymnocladus saponin G (**1**) was isolated from the crude saponin fraction by repeated chromatography on silica gel columns, gel filtration on Sephadex LH20, and finally high-performance liquid chromatography (HPLC), as a white powder, C₁₀₀H₁₆₀O₅₃·H₂O, [α]_D²⁶ -4.8°.

In the infrared (IR) spectrum (1680 cm⁻¹) and the ultraviolet (UV) spectrum ($\lambda_{\max}$ 217 nm), the saponin G (**1**) showed the presence of a conjugated acyl group, and in the ¹³C-NMR spectrum, **1** showed three singlet signals of carbonyl carbons at δ 176.7, 174.7 and 167.8, and four olefinic carbons at δ 143.7, 142.2, 128.6 and 115.2, in addition to δ 123.9 (C-12) and 143.3 (C-13). On acid hydrolysis of **1** with 10% H₂SO₄, 2 β ,23-dihydroxyacacic acid lactone (**8**)³⁾ and four kinds of sugars, glucose, xylose, arbinose and rhamnose, were obtained and identified by comparison with authentic samples.

On alkaline hydrolysis of **1** with 2% NaHCO₃ in ethanol, a partially deacylated compound (**10**) was obtained as a white powder, C₉₅H₁₅₂O₅₂·3H₂O, [α]_D²⁷ -23.2°. The IR spectrum (1680 cm⁻¹), the UV spectrum ($\lambda_{\max}$ 216 nm) and the ¹³C-NMR spectrum (signals at

δ 174.7 and 167.8 due to carbonyl carbons, and at δ 144.0, 142.3, 128.5 and 115.1 due to olefinic carbons) of **10** suggested the presence of a conjugated acyl group, which was not hydrolysed under the conditions used.

On hydrolysis of **1** with 10% KOH in ethanol, two prosapogenins, (**6**) and (**11**), and a monoterpene glycoside (**12**) were obtained. The prosapogenin (**6**) was found to be identical with gymnocladus saponin C,³⁾ based on thin layer chromatography (TLC), IR and ¹³C-NMR. In the ¹³C-NMR of **11**, a signal assigned to carbonyl carbon at δ 179.6 was found instead of the signal due to the lactone group in **4**, **5** and **6**, and the chemical shifts of the sugar carbons and the A, B ring residue of the triterpene moiety closely resembled those of **6**.³⁾ Therefore, **6** is a cyclization product of **11**. The sugar moiety at C-3 of the saponin G (**1**) was also characterized as a β -D-xylopyranosyl-(1 $\rightarrow$ 2)- α -L-arabinopyranosyl-(1 $\rightarrow$ 6)- β -D-glucopyranosyl group. The monoterpene glycoside (**12**) showed four olefinic carbons at δ 144.0, 141.5, 129.6 and 115.0, and two anomeric carbons at δ 106.0 and 99.9 in the ¹³C-NMR, and was identical with the deacyl monoterpene glycoside²⁾ obtained from **3** by alkaline hydrolysis with 1% KOH.

On methylation by Hakomori's method,⁴⁾ **1** and **10** gave the same permethylate (**13**), showing an absorption maximum at 212 nm in the UV spectrum, and signals due to a terminal olefin at δ 5.13 (dd, J =18.0, 2.5 Hz), 5.20 (dd, J =11.5, 2.5 Hz) and 5.82 (dd, J =18.0, 11.5 Hz), and ten anomeric protons of sugars at δ 4.19 (d, J =7.5 Hz), 4.24 (d, J =7.5 Hz), 4.43 (d, J =6.5 Hz), 4.45 (d, J =7.0 Hz), 4.54 (d, J =3.5 Hz), 4.61 (d, J =7.0 Hz), 4.69 (d, J =7.5 Hz), 4.83 (brs), 5.10 (brs) and 5.58 (d, J =7.0 Hz) in the ¹H-NMR spectrum.

On reduction with lithium aluminum hydride (LiAlH₄), **13** gave a mixture of a monoterpene glycoside (**14**), a triterpene glycoside (**15**) and an oligosaccharide alcohol (**16**). On the basis of spectral comparisons, the monoterpene glycoside (**14**) was shown to be

identical with the permethylate of (6*S*)-2-*trans*-6-[β -D-glucopyranosyl-(1 $\rightarrow$ 3)- α -L-arabinopyranosyloxy]-2,6-dimethyl-2,7-octadienol, which was derived from the acid (3).²⁾

The triterpene glycoside (15) was methanolized with 2*N* hydrogen chloride (HCl) in methanol to afford methyl 2,3,4-tri-*O*-methyl-D-xylopyranoside, methyl 3,4-di-*O*-methyl-L-arabinopyranoside, methyl 2,3,4-tri-*O*-methyl-D-glucopyranoside and a triterpene alcohol (17). The triterpene alcohol (17) was identical with an authentic sample of olean-12-ene-2 β ,16 β ,23-tri-*O*-methyl-3 β ,21 β ,28-triol (17) derived from the saponin D (7),¹⁾ on the basis of

TABLE I. ^{13}C -NMR Chemical Shifts (δ) of the Triterpene Moiety and Sugars at C-3 in Pyridine- d_5 ^{a)}

Carbon	11	10 $\Delta\delta$ 10–11	1 $\Delta\delta$ 1–10	Carbon	11	10 $\Delta\delta$ 10–11	1 $\Delta\delta$ 1–10
1	44.0	44.0 (± 0)	44.1 ($+0.1$)	26	17.6 ^{c)}	17.5 ^{c)} (-0.1)	17.5 ^{c)} (± 0)
2	70.4	70.4 (± 0)	70.4 (± 0)	27	27.3	27.2 (-0.1)	27.1 (-0.1)
3	83.3	83.5 ($+0.2$)	83.5 (± 0)	28	179.6	174.7	174.7 (± 0)
4	42.7	42.7 (± 0)	42.7 (± 0)	29	30.0	29.2 (-0.8)	29.1 (-0.1)
5	47.6 ^{b)}	47.5 ^{b)} (-0.1)	47.5 ^{b)} (± 0)	30	18.4	19.2 ($+0.8$)	19.2 (± 0)
6	18.0	18.2 ($+0.2$)	18.3 ($+0.1$)	glc			
7	33.2	33.2 (± 0)	33.2 (± 0)	1	105.6	105.6 (± 0)	105.6 (± 0)
8	40.0	40.2 ($+0.2$)	40.2 (± 0)	2	75.4	75.4 (± 0)	75.4 (± 0)
9	47.7 ^{b)}	47.8 ^{b)} ($+0.1$)	47.7 ^{b)} (-0.1)	3	78.1	78.1 (± 0)	78.1 (± 0)
10	36.9	37.0 ($+0.1$)	37.0 (± 0)	4	71.6	71.6 (± 0)	71.5 (-0.1)
11	24.1	24.1 (± 0)	24.1 (± 0)	5	75.9	76.0 ($+0.1$)	75.9 (-0.1)
12	122.8	123.9 ($+1.1$)	123.9 (± 0)	6	68.4	68.4 (± 0)	68.3 (-0.1)
13	144.5	143.3 (-1.2)	143.3 (± 0)	ara			
14	42.2	42.2 (± 0)	42.2 (± 0)	1	101.6	101.5 (-0.1)	101.5 (± 0)
15	35.8	35.9 ($+0.1$)	35.9 (± 0)	2	79.3	79.4 ($+0.1$)	79.3 (-0.1)
16	73.6	73.4 (-0.2)	73.4 (± 0)	3	72.2	72.2 (± 0)	72.2 (± 0)
17	51.8	51.8 (± 0)	51.7 (-0.1)	4	67.3	67.4 ($+0.1$)	67.3 (-0.1)
18	41.0	40.9 (-0.1)	40.8 (-0.1)	5	63.6	63.6 (± 0)	63.6 (± 0)
19	48.5	47.9 (-0.6)	48.0 ($+0.1$)	xyl			
20	36.7	35.4 (-1.3)	35.3 (-0.1)	1	105.7	105.8 ($+0.1$)	105.7 (-0.1)
21	74.7	77.0 ($+2.6$)	77.0 (± 0)	2	75.0	75.0 (± 0)	74.9 (-0.1)
22	41.8	36.4 (-5.4)	36.5 ($+0.1$)	3	77.9	77.9 (± 0)	77.9 (± 0)
23	65.4	65.5 ($+0.1$)	65.6 ($+0.1$)	4	70.8	70.7 (-0.1)	70.7 (± 0)
24	15.0	15.0 (± 0)	15.0 (± 0)	5	67.0	67.0 (± 0)	67.0 (± 0)
25	17.3 ^{c)}	17.3 ^{c)} (± 0)	17.3 ^{c)} (± 0)				

a) Measured with TMS as an internal standard, at 75.0 MHz, on a Varian XL 300. b, c) Assignments may be interchanged in each column.

TLC behavior, and IR and ^1H -NMR spectral comparisons. These observations indicate the position of the glycosyl monoterpene carboxylate group in the saponin G (**1**) to be C-21.

The ^1H -NMR spectrum of the methylated oligosaccharide (**16**) showed four anomeric protons at δ 4.59 (d, $J=8.0$ Hz), 4.70 (d, $J=8.3$ Hz), 4.88 (d, $J=2.1$ Hz) and 5.06 (d, $J=3.2$ Hz). On partial methanolysis of **16** with 1 N HCl in methanol, two oligosaccharides, **18** and **19** were obtained. In the ^1H -NMR spectrum, **18** showed two signals of anomeric protons at δ 4.87 (d, $J=1.7$ Hz) and 5.08 (d, $J=1.6$ Hz), and **19** showed three signals of anomeric protons at δ 4.67 (d, $J=7.5$ Hz), 4.87 (d, $J=1.5$ Hz) and 5.05 (d, $J=1.5$ Hz). Comparisons of TLC, optical rotation, and IR and ^1H -NMR spectra showed that **16**, **18** and **19** were identical with authentic samples obtained from gleditsia saponin C, which was isolated from the fruits of *Gleditsia japonica*.⁵⁾ The oligosaccharide moiety at C-28 in the saponin G (**1**) was thus characterized as β -D-xylopyranosyl-(1 $\rightarrow$ 3)- β -D-xylopyranosyl-(1 $\rightarrow$ 4)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 6)]- β -D-glucopyranosyl. It has been noted from the biogenetic point of view that the saponin G (**1**) and gleditsia saponin C have the same sugar moieties, including configurations and sequences, at C-3 and C-28.

As shown in Tables I and II, in the ^{13}C -NMR spectrum of **1**, the signals assigned to the triterpene moiety, and the oligosaccharide moieties at C-3 and C-28, were superimposable with those of **10** within ± 0.1 ppm, except for the signals of the glycosylated monoterpene moiety. The ^{13}C -NMR spectrum of **3** was very similar to those of the monoterpene glycoside moiety of the saponin G (**1**). The signals attributable to C-3, C-4 and C-5 of the arabinose at δ 83.9, 69.1 and 66.6, respectively, in **10**, were found to be shifted -2.7 , $+2.6$ and -2.4 ppm, respectively, in the saponin G(**1**). The five prominent signals at δ 176.7, 41.2, 27.0, 11.5 and

TABLE II. Carbon-13 NMR Chemical Shifts (δ) of the Monoterpene Glycoside Moiety and Sugars at C-28 in Pyridine- d_5 ^{a)}

Carbon	3' ^{b)}	12	10 $\Delta\delta$ 10-12	1 $\Delta\delta$ 1-10	Carbon	10	1 $\Delta\delta$ 1-10
					C-28 glc		
1	168.4	171.2	167.8 (-3.4)	167.8 (± 0)	1	95.0	95.0 (± 0)
2	127.7	129.6	128.5 (-1.1)	128.6 (+0.1)	2	78.9	78.9 (± 0)
3	143.0	141.5	142.3 (+0.8)	142.2 (-0.1)	3	77.8	77.9 (+0.1)
4	23.6	23.7	23.6 (-0.1)	23.6 (± 0)	4	71.3	71.4 (+0.1)
5	40.3	40.6	40.4 (-0.2)	40.3 (-0.1)	5	76.6	76.5 (-0.1)
6	79.8	79.7	79.7 (± 0)	79.9 (+0.2)	6	66.8	66.8 (± 0)
7	143.0	144.0	144.0 (± 0)	143.7 (-0.3)	rham		
8	115.2	115.0	115.1 (+0.1)	115.2 (+0.1)	1	101.4	101.4 (± 0)
9	12.4	12.9	12.7 (-0.2)	12.7 (± 0)	2	71.7	71.8 (+0.1)
10	23.7	23.7	23.7 (± 0)	23.7 (± 0)	3	72.4	72.4 (± 0)
ara					4	84.1	84.1 (± 0)
1	99.7	99.9	99.9 (± 0)	99.8 (-0.1)	5	68.3	68.2 (-0.1)
2	71.7	71.5	71.5 (± 0)	71.7 (+0.2)	6	18.6	18.6 (± 0)
3	81.4	84.0	83.9 (-0.1)	81.2 (-2.7)	xyl		
4	71.6	69.1	69.1 (+0)	71.7 (+2.6)	1	106.3	106.2 (-0.1)
5	64.1	66.6	66.6 (+0)	64.2 (-2.4)	2	75.0	74.9 (-0.1)
glc					3	87.7	87.7 (± 0)
1	106.1	106.0	106.0 (± 0)	106.1 (+0.1)	4	68.9	68.9 (± 0)
2	75.5	75.6	75.6 (± 0)	75.6 (± 0)	5	67.1	67.1 (± 0)
3	78.4	78.6	78.5 (-0.1)	78.3 (-0.2)	xyl		
4	71.5	71.5	71.5 (± 0)	71.6 (+0.1)	1	105.9	106.0 (+0.1)
5	78.2	78.2	78.2 (± 0)	78.2 (± 0)	2	75.1	75.1 (± 0)
6	62.9	62.6	62.6 (± 0)	63.0 (+0.4)	3	78.1	78.1 (± 0)
2-Methylbutyroyl					4	70.7	70.7 (± 0)
1	176.7			176.6	5	67.3	67.2 (-0.1)
2	41.2			41.2	rham		
3	27.0			27.0	1	102.0	101.9 (-0.1)
4	11.5			11.5	2	72.0	72.0 (± 0)
5	16.5			16.5	3	72.6	72.6 (± 0)
					4	73.9	73.9 (± 0)
					5	69.6	69.6 (± 0)
					6	18.6	18.6 (± 0)

a) Measured with TMS as an internal standard, at 75.0 MHz, on a Varian XL 300. b) Methyl ester of **3** (diazomethane).

16.6 in **1** correspond to the 2-methylbutyroyl group of **3**.²⁾ On the basis of the acylation shift rule,⁶⁾ it was concluded that the 2-methylbutyroyl group was located at C-4 of the arabinose, as in **3**.

Based on all of the above results, the structure of gymnocladus saponin G (**1**) was characterized as 2 β ,23-dihydroxy-3-*O*-[β -D-xylopyranosyl-(1 $\rightarrow$ 2)- α -L-arabinopyranosyl-(1 $\rightarrow$ 6)- β -D-glucopyranosyl]-21-*O*-{(6*S*)-2-*trans*-2,6-dimethyl-6-[3-*O*-(β -D-glucopyranosyl)-4-*O*-(2-methylbutyroyl)- α -L-arabinopyranosyloxy]-2,7-octadienoyl}acacic acid 28-*O*- β -D-xylopyranosyl-(1 $\rightarrow$ 3)- β -D-xylopyranosyl-(1 $\rightarrow$ 4)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-[α -L-rhamnopyranosyl-(1 $\rightarrow$ 6)]- β -D-glucopyranoside.

Experimental

Unless otherwise stated, ¹H-NMR spectra were measured on a Varian XL-300 NMR spectrometer in CDCl₃ at 300 MHz with tetramethylsilane (TMS) as an internal standard. UV spectra were measured on a Shimadzu UV 240 spectrometer in 95% EtOH. HPLC were carried out on μ -Bondapak C-18 (Waters Ltd.), 7.8 mm $\times$ 30 cm, solvent flow rate 1.6 ml/min. Conditions of TLC and gas liquid chromatography (GLC) for identification of methylated

monosaccharides were reported in the previous papers.^{3,5)}

Purification and Properties of Gymnocladus Saponin G (1)—The crude saponin fraction³⁾ was chromatographed repeatedly on silica gel columns with $\text{CHCl}_3 : \text{MeOH} : \text{H}_2\text{O} = 65 : 35 : 10$ (lower layer). The major fraction was subjected to gel filtration on Sephadex LH20 with MeOH, and purified by preparative HPLC with $\text{MeOH} : \text{H}_2\text{O} = 68 : 32$ to afford **1** as a hygroscopic white powder (Yield: 0.015% from the dried fruits). $[\alpha]_D^{27} - 4.8^\circ$ ($c = 1.20$, MeOH). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400—3600 (OH), 1680, 1730 (COOR). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 217 (18000). ^{13}C -NMR: Tables I and II. Anal. Calcd for $\text{C}_{100}\text{H}_{160}\text{O}_{53} \cdot \text{H}_2\text{O}$: C, 53.90; H, 7.33. Found: C, 53.74; H, 7.50.

Hydrolysis of 1 with 10% H_2SO_4 —A solution of **1** (100 mg) in EtOH (10 ml) and 10% H_2SO_4 (10 ml) was refluxed for 2.5 h and neutralized with Amberlite IRA 450. The reaction mixture was concentrated to half the initial volume *in vacuo*, and then extracted with EtOAc. The organic layer was evaporated, and the residue was recrystallized from MeOH– H_2O to afford $2\beta,23$ -dihydroxyacacic acid lactone (**8**, 20 mg) as colorless needles (mp 187 — 189°C); this product was identical with an authentic sample obtained from gymnocladus saponin A (**4**)³⁾ on the basis of TLC, IR and ^1H -NMR comparisons and mixed melting point determination. From the water layer, glucose, xylose, rhamnose and arabinose were identified by paper partition chromatography (PPC).

Hydrolysis of 1 with 2% NaHCO_3 —A solution of **1** (160 mg) in EtOH (30 ml) and 2% NaHCO_3 (30 ml) was refluxed for 1.5 h. The reaction mixture was neutralized with Dowex 50W $\times 8$, and evaporated to dryness *in vacuo*. The residue showed two major spots on TLC (R_f : 0.20 and 0.15) ($\text{CHCl}_3 : \text{MeOH} : \text{H}_2\text{O} = 65 : 35 : 10$, lower layer). The mixture was separated and purified by HPLC ($\text{MeOH} : \text{H}_2\text{O} = 7 : 3$) to give 40 mg of **1** (R_f 0.20) and 80 mg of **10** (R_f 0.15) as a hygroscopic white powder. $[\alpha]_D^{26} - 23.2^\circ$ ($c = 0.64$, MeOH). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400—3600 (OH), 1680, 1720 (COOR). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 216. ^{13}C -NMR: Tables I and II. Anal. Calcd for $\text{C}_{95}\text{H}_{152}\text{O}_{52} \cdot 3\text{H}_2\text{O}$: C, 52.32; H, 7.30. Found: C, 52.11; H, 7.48.

Hydrolysis of 1 with 10% KOH—A solution of **1** (500 mg) in EtOH (15 ml) and KOH (15 ml) was refluxed for 3 h, and neutralized with Dowex 50W $\times 8$. The solution was evaporated to half the initial volume, and extracted with *n*-BuOH saturated with H_2O . The organic layer was evaporated to dryness to give a brown oily residue (280 mg). The residue showed three major spots on TLC (R_f : 0.55, 0.45 and 0.21, $\text{CHCl}_3 : \text{MeOH} : \text{H}_2\text{O} = 65 : 35 : 10$, lower layer). The mixture was subjected to chromatography on a silica gel column ($\text{CHCl}_3 : \text{MeOH} : \text{H}_2\text{O} = 8 : 3 : 1$, lower layer) to afford three major fractions, and each fraction was purified by HPLC ($\text{MeOH} : \text{H}_2\text{O} = 66 : 34$) to give 45 mg of **6**, corresponding to the product of R_f 0.55. This product was identified with an authentic sample of gymnocladus saponin C on the basis of TLC, IR and ^{13}C -NMR, comparisons. From the second fraction, **12** (35 mg) was obtained as a white amorphous powder. $[\alpha]_D^{26} - 4.8^\circ$ ($c = 0.81$, MeOH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm: 215. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400—3500 (OH), 1680 (COOR). ^{13}C -NMR: Table II. This product was identical with an authentic sample of deacyl monoterpene glycoside (**12**) obtained from **3** on the basis of TLC, IR and ^{13}C -NMR²⁾ comparisons. From the third fraction, compound **11** (110 mg) corresponding to the product of R_f 0.21 was obtained as a white powder. $[\alpha]_D^{26} - 1.5^\circ$ ($c = 0.74$, MeOH). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400—3500 (OH), 1680 (COOH). ^{13}C -NMR: Table I. Anal. Calcd for $\text{C}_{46}\text{H}_{74}\text{O}_{20} \cdot 2\text{H}_2\text{O}$: C, 56.20; H, 8.00. Found: C, 56.49; H, 8.09.

Permethylation of 1 and 10—According to Hakomori's method,⁴⁾ the reagent mixture (20 ml) [prepared from NaH (2 g) and DMSO (50 ml)] was added to a solution of **1** (400 mg) in DMSO (10 ml). The mixture was stirred for 1 h at room temperature under an N_2 stream. After addition of CH_3I (25 ml), the reaction mixture was stirred for 3 h at room temperature, then poured into ice-water and extracted with Et_2O . The Et_2O layer was washed with H_2O , dried over MgSO_4 and evaporated to give a yellow oily product (505 mg). This oily product was purified by chromatography on a silica gel column (benzene : acetone = 7 : 3) to give the permethylate (**13**, 150 mg) as a colorless syrup. $[\alpha]_D^{26} - 9.5^\circ$ ($c = 0.85$, CHCl_3). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1720 (COOR), 1100 (C–O–C). ^1H -NMR δ : 0.76, 0.83, 0.92, 1.00, 1.20, 1.25 (3H, each s, $\text{CH}_3 \times 6$), 4.19 (1H, d, $J = 7.5$ Hz, anomeric H), 4.24 (1H, d, $J = 7.5$ Hz, anomeric H), 4.43 (1H, d, $J = 6.5$ Hz, anomeric H), 4.45 (1H, d, $J = 7.0$ Hz, anomeric H), 4.54 (1H, d, $J = 3.5$ Hz, anomeric H), 4.61 (1H, d, $J = 7.0$ Hz, anomeric H), 4.69 (1H, d, $J = 7.5$ Hz, anomeric H), 4.83 (1H, br s, anomeric H), 5.10 (1H, br s, anomeric H), 5.13 (1H, dd, $J = 18.0, 2.5$ Hz, $\text{H}_R\text{C}=\text{C}=\text{H}_H$), 5.20 (1H, dd, $J = 11.5, 2.5$ Hz, $\text{H}_R\text{C}=\text{C}=\text{H}_H$), 5.58 (1H, d, $J = 7.0$ Hz, anomeric H), 5.82 (1H, dd, $J = 18.0, 11.5$ Hz, $\text{H}_R\text{C}=\text{C}=\text{H}_H$). Anal. Calcd for $\text{C}_{124}\text{H}_{210}\text{O}_{53} \cdot \text{H}_2\text{O}$: C, 58.02; H, 8.32. Found: C, 57.85; H, 8.30. This permethylate (**13**) was also obtained from **10** in the same manner.

Methanolysis of 13—A solution of **13** (20 mg) in 2 N methanolic HCl (20 ml) was refluxed for 3 h, then neutralized with Ag_2CO_3 and filtered. The filtrate was evaporated and residue was examined by TLC and GLC. Nine different methylated monosaccharides, methyl 2,3,4-tri-*O*-methyl-D-xylopyranoside, methyl 2,4-di-*O*-methyl-D-xylopyranoside, methyl 2,4-di-*O*-methyl-L-arabinopyranoside, methyl 3,4-di-*O*-methyl-L-arabinopyranoside, methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside, methyl 2,3-di-*O*-methyl-L-rhamnopyranoside, methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside, methyl 2,3,4-tri-*O*-methyl-D-glucopyranoside and methyl 3,4-di-*O*-methyl-D-glucopyranoside were identified by comparison with authentic samples.

Reductive Cleavage of Permethylate (13) with LiAlH_4 —A solution of the permethylate (**13**, 200 mg) in anhydrous tetrahydrofuran (THF) (15 ml) was treated with LiAlH_4 (150 mg), and the mixture was refluxed for 3 h. The excess LiAlH_4 was decomposed with wet Et_2O and the mixture was extracted with Et_2O and EtOAc successively.

The Et₂O extract was chromatographed on a silica gel column (benzene : acetone = 7 : 3), and purified by preparative TLC (benzene : acetone = 5 : 4) to give 30 mg of **14** as a colorless syrup. $[\alpha]_D^{25} + 17.1^\circ$ ($c = 1.70$, CHCl₃). IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 3500 (OH), 1100 (C—O—C). ¹H-NMR δ : 0.98 (3H, d, $J = 1.9$ Hz, CH₃), 1.32 (3H, s, CH₃), 3.36, 3.44, 3.52, 3.58, 3.62, 3.63 (3H, each s, OCH₃ × 6), 4.26 (1H, d, $J = 7.1$ Hz, anomeric H), 4.44 (1H, d, $J = 6.8$ Hz, anomeric H), 5.15 (1H, dd, $J = 18.0$, 2.0 Hz, $\text{H}_R\text{C}=\text{C}\text{H}_H$), 5.21 (1H, dd, $J = 11.2$, 2.0 Hz, $\text{H}_R\text{C}=\text{C}\text{H}_H$), 5.84 (1H, dd, $J = 18.0$, 11.2 Hz, $\text{H}_R\text{C}=\text{C}\text{H}_H$). From the second fraction, a triterpenoid glycoside alcohol (**15**, 35 mg) was obtained as an amorphous powder. IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 3450 (OH), 1100 (C—O—C). ¹H-NMR δ : 0.87, 0.91, 0.94, 0.96, 1.22, 1.29 (3H, each s, CH₃ × 6), 3.23, 3.31, 3.35, 3.41, 3.45, 3.47, 3.53, 3.58, 3.61, 3.62, 3.63 (3H, each s, OCH₃ × 11), 4.19 (1H, d, $J = 8.0$ Hz, anomeric H), 4.43 (1H, d, $J = 7.3$ Hz, anomeric H), 4.53 (1H, d, $J = 4.8$ Hz, anomeric H), 5.28 (1H, t like, C-12-H), 4.12 (1H, dd, $J = 15.0$, 7.3 Hz, C-18-H). The EtOAc extract was purified by preparative TLC (benzene : acetone = 9 : 10) to give an oligosaccharide alcohol (**16**, 15 mg) as a colorless oil. $[\alpha]_D^{25} - 67.4^\circ$ ($c = 1.40$, CHCl₃). IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 3450 (OH), 1100 (C—O—C). ¹H-NMR δ : 1.30, 1.32 (3H, each d, $J = 6.3$ Hz, CH₃ × 2), 3.45, 3.46, 3.48, 3.49 (3H, each s, OCH₃ × 4), 3.50 (6H, s, OCH₃ × 2), 3.51, 3.55, 3.75, 3.61 (3H, each s, OCH₃ × 4), 3.62 (6H, s, OCH₃ × 2), 4.59 (1H, d, $J = 8.0$ Hz, anomeric H), 4.70 (1H, d, $J = 8.3$ Hz, anomeric H), 4.88 (1H, d, $J = 2.1$ Hz, anomeric H), 5.06 (1H, d, $J = 3.2$ Hz, anomeric H).

Methanolysis of 15—A solution of **15** (10 mg) in 2N methanolic HCl (10 ml) was refluxed for 3 h. The reaction mixture was treated in the same manner as described above, to give three different methylated monosaccharides and a triterpene alcohol (**17**, 5 mg). **17** was identical with the corresponding alcohol, olean-12-ene-2 β ,16 β ,23-tri-*O*-methyl-3 β ,21 β ,28-triol, obtained from gymnocladus saponin D (**7**) in the same manner, on the basis of TLC, IR and ¹H-NMR¹⁾ comparisons.

Partial Methanolysis of 16—A solution of **16** (90 mg) in 2N methanolic HCl (30 ml) was allowed to stand at room temperature for 24 h. After being neutralized with Ag₂CO₃, the mixture was filtered, the filtrate was evaporated and the residue was purified by preparative TLC (benzene : acetone = 5 : 4) to give **18** and **19** as colorless syrups. These methylated oligosaccharides were identical with the previously reported samples.⁵⁾

Methanolysis of 16—A solution of **16** in methanolic HCl was refluxed for 2 h, and treated in the usual manner as described above. All of the methylated monosaccharides were identical with authentic samples on the basis of TLC and GLC comparisons.⁵⁾

Acknowledgement The authors are grateful to Mr. Y. Fujiwara, Kyoto Pharmaceutical University, for ¹H- and ¹³C-NMR measurements, and to Miss M. Takahashi of Kyoto Pharmaceutical University for MS measurements. They are also indebted to the members of the Analytical Center of Kyoto University for microanalysis.

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