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Nuclear Magnetic Resonance Study on Glycosyl Esters: Glycosyl Esters of 3-*O*-Acetyloleanolic Acid and Octanoic Acid

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α-L-Rhamnosyl, α-L-arabinosyl, 2′-*O*-β-D-glucosyl-α-L-arabinosyl and 2′-*O*-α-L-rhamnosyl-α-L-arabinosyl esters of octanoic acid and β-D-xylosyl, α-L-rhamnosyl, α-L-arabinosyl, 2′-*O*-β-D-glucosyl-α-L-arabinosyl and 2′-*O*-α-L-rhamnosyl-α-L-arabinosyl esters of 3-*O*-acetyloleanolic acid were synthesized. The nuclear magnetic resonance spectra of sugar moieties of the esters of 3-*O*-acetyloleanolic acid, which is a representative sterically hindered carboxylic acid, were compared with those of the corresponding less-hindered glycosyl esters of octanoic acid. In the case of rhamnose and arabinose, the displacements of sugar carbon signals on acylation of the anomeric hydroxyl group are similar to those already observed for fatty acid glucosyl esters regardless of the steric hindrance of the acyl group. However, the 2-*O*-glycosylation shifts of 1-*O*-acyl-α-L-arabinopyranose were found to depend upon the steric hindrance of the acyl groups. The anomalous 2′-*O*-glycosylation shifts of arabinosyl carbon signals of α-L-arabinosyl 3-*O*-acetyloleanolate were not observed in the case of α-L-arabinosyl octanoate.

Keywords——glycosyl ester synthesis; reducing terminal protecting group; *tert*-butyl glycoside; glycosyl octanoate; glycosyl 3-*O*-acetyloleanolate; NMR glycosylation shift; 1-*O*-acyl-2-*O*-glycosyl-α-L-arabinose NMR; 2-*O*-glycosyl-arabinopyranoside ring conformation

Introduction

To expand the applicability of carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrometry to glycoside chemistry, α- and β-anomeric pairs of D-glucosides,[1,2] L-rhamnosides, D-mannosides,[3] and L-arabinosides (pyranoside form)[4] were synthesized and the carbon signal displacements of the sugar and aglycone moieties on glycoside formation, the so-called "^{13}C-NMR glycosylation shifts" were studied. Such shifts have been effectively utilized in the structure elucidation of a number of natural glycosides.

Tori *et al.*[5] reported an extensive study on anomalous glycosylation shifts for a variety of 28-(2′-*O*-α-L-rhamnopyranosyl)-α-L-arabinopyranosyl esters of oleanane-type triterpenes with or without a 16α-hydroxyl group (in pyridine-d_5) and their acetates (in $CDCl_3$), these data are valuable for studies on the configuration and conformation of arabinosyl esters of this type. In connection with their work, we have been engaged in NMR studies on the conformation of 2-linked α- and β-L-arabinopyranosides. It was found that in the case of 2-*O*-glycosyl-α-L-arabinopyranosides of aliphatic alcohols, the ring conformation of the arabinopyranoside moiety depends upon the type of the 2-*O*-glycosyl group.[6] As a continuation of these studies, the present paper deals with an NMR study on glycosyl esters of 3-*O*-acetyloleanolic acid (**1**) as a representative of hindered carboxylic acids in comparison with those of less-hindered octanoic acid (**2**). All of the glycoside units in this report are in the pyranoside form.

α-L-Rhamnosyl and α-L-Arabinosyl Esters

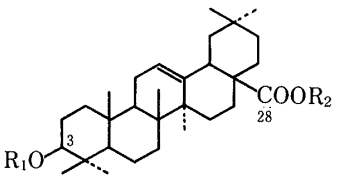
α-L-Rhamnosyl and α-L-arabinosyl esters (**3**, **4**) of **2** were prepared by the procedure used for the preparation of 1-*O*-fattyacyl-D-glucoses by Yoshimoto *et al.*[7] β-D-Xylosyl, α-L-rhamnosyl and α-L-arabinosyl esters (**5**, **6**, **7**) of **1** were prepared[8,9] from **1** by condensation of the respective acetobromosugar in the presence of Ag_2CO_3 followed by mild deacetylation with BaO in MeOH. The β-D-glucosyl ester (**8**) of oleanolic acid (**9**) was isolated from *Hemsleya* spp. as described in the previous paper.[10]

Assignments of sugar-carbon chemical shifts of these glycosyl esters are listed in Table I. Because of the unexpected glycosylation shift (*vide infra*), identification of sugar carbon resonances of **6** was confirmed by means of a two-dimensional correlation procedure (2D NMR); first, the sugar proton signals of methyl α-L-rhamnoside (**10**) and **6** were assigned by H–H 2D NMR as shown in Table II and then the carbon chemical shifts of the sugar moiety of **6** were identified by C–H 2D NMR as shown in Table I.

It is known that on acylation of aliphatic alcohols, a carbinyl carbon is generally deshielded and signals due to carbons vicinal to the carbinyl carbon are displaced upfield, while other carbon signals remain almost unshifted. However, the ^{13}C-NMR acylation shift of an anomeric hydroxyl group of carbohydrates is evidently different from the above case;[11] the C-1 and -2 signals are both displaced upfield as indicated in Table I. Further, Yoshimoto *et al.* reported an unexpected downfield shift by about 1 ppm of the C-5 signal of D-glucose on acylation of the anomeric hydroxyl group for 1-*O*-acyl-β-D-glucose (equatorial 1-*O*-acyl) and by about 3 ppm for 1-*O*-acryl-α-D-glucose (axial 1-*O*-acyl).[12] This anomalous shift was explained in terms of a decrease of electron density on C-5 due to the change of anomeric effect by acylation. In the present study, a similar characteristic acylation shift of the C-5 signal was observed for all of the glycosyl esters of **1**, **2**, and **9**; it was slight for equatorial 1-*O*-acyl esters, **4**, **5**, **7** and **8**, but evident for axial 1-*O*-acyl esters, **3** and **6** (Table I). This indicated that the acylation shift of the C-5 signal is also characteristic of xylosyl, arabinosyl and rhamnosyl esters regardless of the structure (steric hindrance) of the carboxyl groups.

2-Linked α-L-Arabinosyl Esters

2-*O*-Glycosyl-L-arabinoses are important intermediates in the syntheses of 2-linked-α-L-arabinosyl esters. For the preparation of these glycobioses, an appropriate protecting group for the reducing terminal of arabinose is required, that can be removed after 2-*O*-glycosylation without cleavage of the intersaccharide linkage. It has been reported that the glycoside linkages of tertiary alkyl glycosides are rather unstable.[13] For instance, glycosyl linkages of tertiary alcohols such as Ginseng saponins[14] and Stevia sweet glycosides[15] are



$CH_3(CH_2)_6COOR$

1: R_1=Ac R_2=H
5: R_1=Ac R_2=β-D-Xyl*p*
6: R_1=Ac R_2=α-L-Rha*p*
7: R_1=Ac R_2=α-L-Ara*p*
8: R_1=H R_2=β-D-Glc*p*
9: R_1=H R_2=H
19: R_1=Ac R_2=β-D-Glc*p*-(1→2)-α-L-Ara*p*
20: R_1=Ac R_2=α-L-Rha*p*-(1→2)-α-L-Ara*p*

2: R=H
3: R=α-L-Rha*p*
4: R=α-L-Ara*p*
27: R=β-D-Glc*p*-(1→2)-α-L-Ara*p*
28: R=α-L-Rha*p*-(1→2)-α-L-Ara*p*

Chart 1

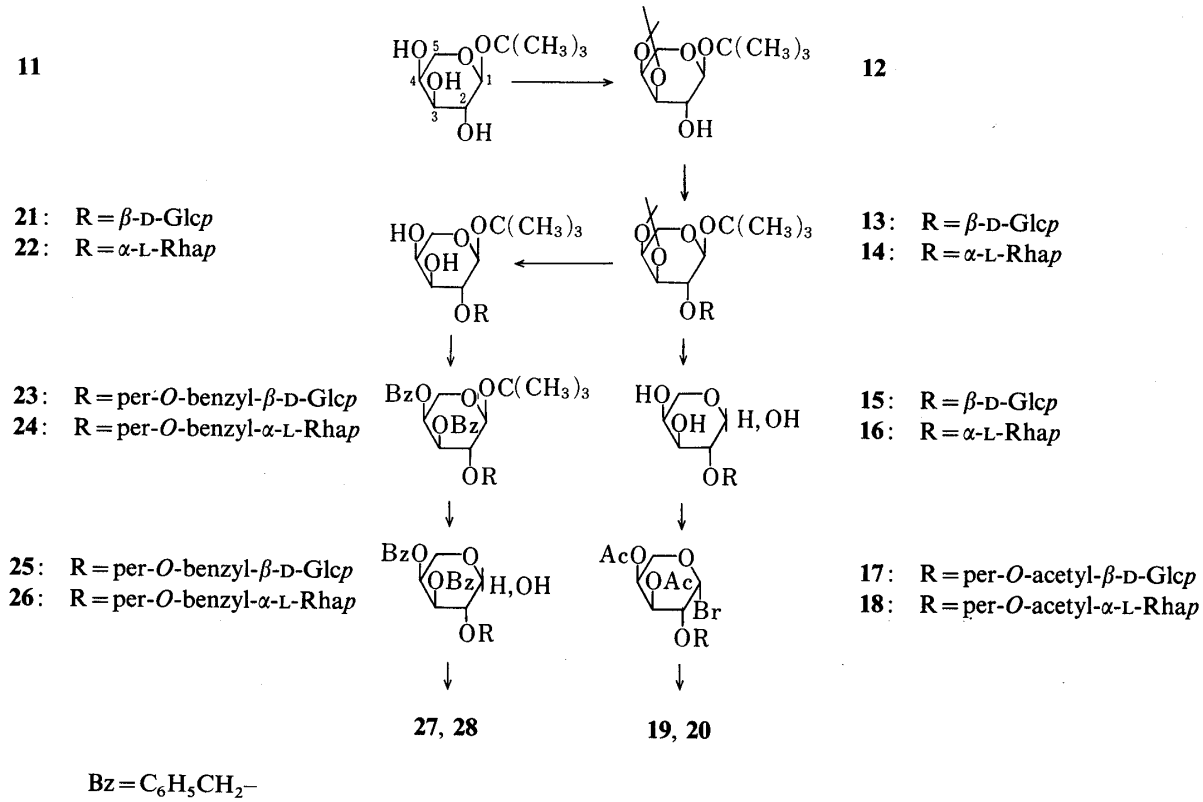


Chart 2

TABLE I. Carbon-13 Chemical Shifts of Sugar Moieties, Glycosylation Shifts and Coupling Constants of Ester Glycosides (**3**—**8**)

Compd.	δC-1 (Δδ)[a]	δC-2 (Δδ)	δC-3 (Δδ)	δC-4 (Δδ)	δC-5 (Δδ)	δC-6 (Δδ)	$^1J_{C1,H1}$ (Hz)	$^3J_{H1,H2}$ (Hz)	δH-1
3	95.4 (−7.2)	71.1 (−1.0)	72.3 (−0.4)	73.3 (−0.5)	72.3 (+2.8)	18.5 (−0.1)	173	Singlet	6.83
4	96.3 (−9.5)	71.1 (−1.0)	74.1 (−0.1)	68.8 (−0.2)	67.5 (+1.0)		164	7.0	6.20
5	96.2 (−9.7)	73.6 (−1.0)	78.2 (+0.2)	70.8 (0)	67.6 (+0.8)		164	c)	6.18
6	95.1 (−7.5)	71.5 (−0.6)	72.9 (+0.2)	73.4 (−0.4)	72.6 (+3.1)	18.8 (+0.2)	173	1.5	6.79
7	95.9 (−9.9)	71.4 (−0.7)	74.1 (−0.1)	68.1 (−0.9)	66.3 (−0.2)		162	5.8	6.28
8	95.6 (−9.9)	74.0 (−0.9)	78.8[b] (+0.5)	71.1 (−0.5)	79.1[b] (+0.8)	62.2 (−0.5)	164	7.3	6.21

a) $\Delta\delta = \delta C$ of ester glycoside-δC of corresponding methyl glycoside. *b*) These assignments may be reversed in each row. *c*) Virtual coupling.

readily hydrolyzed even by heating with acetic acid to give the oligosaccharide. In the present study, the tertiary-butyl group was found to be suitable for the synthesis of 2-linked α-L-arabinoses. As illustrated in Chart 2, *tert*-butyl α-L-arabinoside (**11**) prepared by our reported procedure[4] was converted into the 3,4-*O*-isopropylidene derivative (**12**). Glycosylation of **12** with acetobromoglucose or acetobromorhamnose followed by deacetylation gave the corresponding *tert*-butyl 3,4-*O*-isopropylidene-glycobiosides (**13**, **14**). Heating of **13** and **14** with

TABLE II. Proton Chemical Shifts and Coupling Constants of Sugar Moieties of **10** and **6**

Proton	Compd. **10**	Compd. **6**
1	5.09 (1H, d, J=1.2 Hz)	6.79 (1H, d, J=1.5 Hz)
2	4.48 (1H, dd, J=1.2, 3.4 Hz)	4.58 (1H, br s)
3	4.40 (1H, dd, J=3.4, 9.2 Hz)	4.52 (1H, dd, J=2.8, 8.9 Hz)
4	4.23 (1H, dd, J=9.2, 9.2 Hz)	4.39 (1H, dd, J=8.9, 8.9 Hz)
5	4.07 (1H, dq, J=9.2, 6.1 Hz)	4.34 (1H, dq, J=8.9, 5.5 Hz)
6	1.61 (3H, d, J=6.1 Hz)	1.71 (3H, d, J=5.5 Hz)

TABLE III. Carbon-13 Chemical Shifts of Sugar Moieties of 2-*O*-Glycosyl-α-L-Arabinosyl Esters (**19**, **20**, **27** and **28**)

Compd.	α-L-Arabinosyl					2-*O*-Glycosyl					
	δC-1 ($\Delta\delta$)[a]	δC-2 ($\Delta\delta$)	δC-3 ($\Delta\delta$)	δC-4 ($\Delta\delta$)	δC-5 ($\Delta\delta$)	δC-1	δC-2	δC-3	δC-4	δC-5	δC-6
19	93.6 (−2.3)	77.6 (+6.2)	71.9 (−2.2)	66.6 (−1.4)	64.7 (−1.6)	104.7	75.2	78.1	71.6	78.1	63.1
20	93.3 (−2.6)	74.9 (+3.5)	70.2 (−3.9)	66.0 (−2.1)	62.9 (−3.4)	101.2	72.1	72.4	73.7	70.2	18.4
27	94.2 (−2.1)	80.9 (+9.8)	73.0 (−1.1)	67.9 (−0.9)	66.5 (−1.0)	106.3	76.0	78.2[b]	71.4	78.6[b]	62.5
28	94.3 (−2.0)	75.2 (+4.1)	74.1 (0)	69.0 (+0.2)	67.1 (−0.4)	101.2	72.2	72.5	73.8	69.9	18.5

a) $\Delta\delta$ = δC of 2-*O*-glycosyl-α-L-arabinosyl ester − δC of corresponding α-L-arabinosyl ester. *b*) These assignments may be reversed in each row.

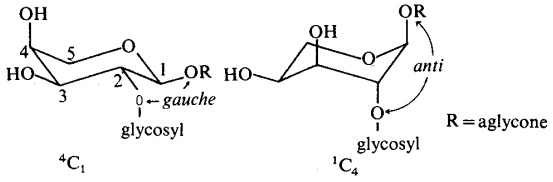


TABLE IV. C–H Coupling Constants of Anomeric Carbon Signals and H–H Coupling Constants between the Anomeric Proton and H-2 of 2-*O*-Glycosyl-α-L-arabinosyl Esters (**19**, **20**, **27** and **28**)

Compd.	α-L-Arabinosyl			2-*O*-Glycosyl		
	$^1J_{C1,H1}$ (Hz)	$^3J_{H1,H2}$ (Hz)	δH-1	$^1J_{C1,H1}$ (Hz)	$^3J_{H1,H2}$ (Hz)	δH-1
19	169	4.3	6.51	158	7.6	5.32
20	171	3.3	6.50	168	Singlet	5.90
27	168	6.2	6.37	154	7.7	5.18
28	164	7.0	6.19	171	1.1	6.13

50% acetic acid resulted in the simultaneous removal of both the protecting groups to yield 2-*O*-β-D-glucosyl-L-arabinose (**15**) and 2-*O*-α-L-rhamnosyl-L-arabinose (**16**), respectively, which were converted into the acetobromosugars (**17**, **18**) in the usual way. Glycosylation

of **1** with **17** and **18** followed by the mild deacetylation afforded 2′-*O*-β-D-glucosyl-α-L-arabinosyl 3-*O*-acetyloleanolate (**19**) and 2′-*O*-α-L-rhamnosyl-α-L-arabinosyl 3-*O*-acetyloleanolate (**20**), respectively.

Treatment of **13** and **14** with oxalic acid afforded *tert*-butyl 2-*O*-β-D-glucosyl-α-L-arabinoside (**21**) and *tert*-butyl 2-*O*-α-L-rhamnosyl-α-L-arabinoside (**22**), respectively, which were converted into the corresponding perbenzyl ethers (**23**, **24**). The selective cleavage of the *tert*-butyl α-L-arabinoside linkage of both **23** and **24** was achieved by heating in acetic acid, affording **25** and **26**, respectively. Acylation of **25** and **26** with octanoyl chloride followed by catalytic desbenzylation afforded 2′-*O*-β-D-glucosyl-α-L-arabinosyl octanoate (**27**) and 2′-*O*-α-L-rhamnosyl-α-L-arabinosyl octanoate (**28**), respectively.

It has been reported[6] that β-D-glucosyl, β-D-xylosyl and α-L-arabinosyl substitution at the 2-hydroxyl group of α-L-arabinosides of a variety of alcohols resulted in anomalous glycosylation shifts of the signals of the 2-linked arabinoside moiety: decrease of $^3J_{H1,H2}$, increase of $^1J_{C1,H1}$ and significant shielding of C-3, -4 and -5, as well as the expected glycosylation shifts of the C-1 and -2 signals. These unusual displacements can be explained in terms of the release from the strong steric hindrance of the 2-linked α-L-arabinoside ring in the $^4C_1$ form by increase in the population of the $^1C_4$ form. In these cases, the 1,2-*gauche* interaction between the 1-*O*-aglycone and 2-*O*-glycosyl group as the $^4C_1$ form was relieved by conversion into the $^1C_4$ form in which the relative orientation of the 1-*O*- and 2-*O*-substituents is *anti*.

The assignments of carbon signals of 2-linked α-L-arabinosyl esters are summarized in Table III. It was found that the 2′-*O*-β-D-glucosylation of the oleanolate (from **7** to **19**) resulted in significant shielding of C-3′, -4′ and -5′ as well as a decrease of $^3J_{H1,H2}$ and increase of $^1J_{C1,H1}$ similar to those observed for alkyl α-L-arabinosides.[6] In the case of the octanoyl ester (from **4** to **27**), the magnitude of this unusual glycosylation shift was found to be less than in the case of the oleanolate. This indicates that the degree of contribution of the $^1C_4$ ring conformation in 2′-*O*-β-D-glucosyl-α-L-arabinosyl esters depends upon the steric hindrance of the carboxyl group.

Tori *et al.*[5] reported a remarkable contribution of the $^1C_4$ conformation of the arabinosyl ring in 28-(2′-*O*-α-L-rhamnosyl)-α-L-arabinosyl esters (in pyridine-d_5) such as saponins of *Platycodon grandiflorum* based on an NMR study. However, our previous study[6] revealed that for the alkyl 2-*O*-α-L-rhamnosyl-α-L-arabinosides, no unusual glycosylation shift was observed and the ring conformation of the arabinoside ring must be mostly the $^4C_1$ form as in the case of usual α-L-arabinosides.[4] The extremely unusual glycosylation shifts of C-3′, -4′ and -5′ signals (Table III) and $^3J_{H1,H2}$ and $^1J_{C1,H1}$ (Table IV) of the arabinosyl moiety which were found in 2′-*O*-α-L-rhamnosyl-α-L-arabinosyl esters of oleanolic acid homologues (in pyridine-d_5), such as **20** and saponins of *Platycodon grandiflorum*, were not observed on 2′-*O*-α-L-rhamnosylation of α-L-arabinosyl octanoate (**4**). On going from **4** to **28**, glycosylation shift of the arabinosyl moiety was observed only at C-1′ and -2′ and no significant change was found in the chemical shifts of C-3′, -4′ and -5′ or in $^1J_{C1,H1}$ and $^3J_{H1,H2}$, as in the case of 2-*O*-α-L-rhamnosylation of alkyl α-L-arabinosides[6] mentioned above. It follows that the preferential $^1C_4$ ring conformation of the 2-*O*-α-L-rhamnosylated α-L-arabinoside moiety in pyridine-d_5 reported by Tori *et al.*[5] must be restricted to the case of the glycosyl esters of sterically hindered carboxylic groups such as triterpene carboxylic acids.

The present results should prove useful for structural elucidation of natural glycosyl esters such as physiologically active bisdesmosides of triterpenes.

Experimental

^{13}C-NMR spectra were recorded with a JEOL JNM-PFT-100 spectrometer at 25 °C for 0.05—0.3 M solutions in

C_5D_5N at 25.15 MHz, with Me_4Si as an internal standard. The following conditions were used for proton-decoupled FT measurement: spectral width, 4 or 5 kHz; pulse flipping angle, 90°; acquisition time, 0.4 s; number of data points, 4096; transient time, 1.0 s; number of transients, 1200—2000. Conditions for measurement of $^1J_{C1,H1}$ by gated decoupling were: spectral width, 4 or 5 kHz; pulse flipping angle, 90°; acquisition time, 0.4 s; number of data points, 4096; transient time, 1.0 s; number of transients, 2400—9600.

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded in the FT mode, with a JEOL GX-270 or JEOL FX-270 spectrometer for 0.05—0.1 M solutions in C_5D_5N at 270 MHz, with Me_4Si as an internal standard. Two-dimensional correlation NMR spectra were recorded with a JEOL GX-270 instrument for solutions in C_5D_5N, and the data size of the time-domain for COSYP or CHSHF spectra was a 1024×256 or 2048×128 matrix, respectively.

Melting points were determined on a micro hot-stage and are uncorrected. Optical rotations were measured with a Union automatic digital polarimeter for solutions in C_5H_5N. For column chromatography, silica gel (Kieselgel 60; Merck) was used. High performance liquid chromatography (HPLC) was carried out on an HLC-803D (Toyo Soda) with an RI-8 differential refractometer (Toyo Soda) as a detector.

Because **3**, **22**, **27** and **28** were obtained only in a highly hygroscopic syrupy state and could not be subjected to elemental analysis, their purity and structure were substantiated by thin-layer chromatography (TLC), HPLC and NMR analysis.

Synthesis of 3 and 4[7,16]——Benzyl chloride (6 ml) was added dropwise to a mixture of methyl α-L-rhamnoside (**10**, 1 g) or methyl α-L-arabinoside (**29**, 1 g) and powdered KOH (5 g) in dry dioxane (3 ml) with stirring at 130 °C. The mixture was further stirred for 3 h at 130 °C, diluted with H_2O and then extracted with $CHCl_3$. After being washed with H_2O, the $CHCl_3$ layer was dried over Na_2SO_4 and concentrated to afford a syrupy residue. Benzyl alcohol and dibenzyl ether in this mixture were removed by distillation under reduced pressure at 130 °C. The resulting residue was purified by chromatography on silica gel. Elution with n-C_6H_{14} and then C_6H_6–Me_2CO (50 : 1) gave methyl 2,3,4-tri-*O*-benzyl-α-L-rhamnoside (**30**) or methyl 2,3,4-tri-*O*-benzyl-α-L-arabinoside (**31**) as a syrup in a yield of 85—94% from **10** or **29**, respectively. A solution of **30** or **31** in 2 N HCl–AcOH (1 : 2, 30 ml) was refluxed for 1 h. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried over Na_2SO_4 and concentrated to dryness. The residue was purified by chromatography on silica gel with C_6H_6–Me_2CO (30 : 1) to give 2,3,4-tri-*O*-benzyl-L-rhamnose (**32**) or 2,3,4-tri-*O*-benzyl-L-arabinose (**33**) as a white powder in a yield of 64—70% from **30** or **31**, respectively.

A solution of **32** (500 mg) in C_5H_5N (2 ml) and CH_2Cl_2 (5 ml) was mixed with octanoyl chloride (0.2 ml) at 0 °C, and the mixture was stirred for 12 h at room temperature then poured into H_2O. The whole was extracted with $CHCl_3$ and the $CHCl_3$ layer was washed with H_2O, dried over Na_2SO_4 and concentrated to dryness. The residue was chromatographed on silica with C_6H_6–Me_2CO (70 : 1) to give an anomeric mixture of 2,3,4-tri-*O*-benzyl-L-rhamnosyl octanoate. This anomeric mixture was hydrogenated over Pd–black (50 mg) in EtOH (50 ml) for 12 h. The catalyst was filtered off and the filtrate was concentrated to dryness. The crude product was separated by chromatography on silica gel with $CHCl_3$–MeOH (12 : 1) to give **3** in a yield of 25% from **32**. **3**; colorless syrup, $[\alpha]_D^{15}$ −61.4° (c = 0.89).

A mixture of **33** (500 mg) and $(Bu_3Sn)_2O$ (0.7 ml) in dry toluene (10 ml) was refluxed for 30 min and then a half of the solvent was distilled off. Then C_5H_5N (1 ml) and octanoyl chloride (0.2 ml) were added and the mixture was treated by the same procedure as used for the synthesis of **3**. The resulting anomeric mixture was separated by chromatography on silica gel with $CHCl_3$–MeOH (10 : 1) to give **4** in a yield of 32% from **33**. **4**, colorless needles, mp 90.0—92.5 °C (from $CHCl_3$–n-C_6H_{14}), $[\alpha]_D^{15}$ +37.8° (c = 1.07). *Anal.* Calcd for $C_{13}H_{24}O_6$: C, 56.50; H, 8.76. Found: C, 56.07; H, 8.68.

Synthesis of 5, 6 and 7[8]——Oleanolic acid (**9**) prepared from saponins of *Panax japonicus* C.A. Meyer[17] was acetylated in the usual way to give **1**.

A mixture of **1** (200 mg), acetobromosugar [prepared from D-xylose, L-rhamnose or L-arabinose (each 400 mg)] and Ag_2CO_3-celite (600 mg) in CH_2ClCH_2Cl (40 ml) was refluxed for 4—5 h. After removal of the precipitate by filtration through a celite column, the filtrate was concentrated to dryness. The residue was deacetylated in 0.5 N BaO–dry MeOH for 20 min with stirring at room temperature and the resulting precipitate was removed by filtration. The filtrate was de-ionized with Amberlite MB-3 resin, and concentrated to dryness. The residue was purified by chromatography on silica gel with C_6H_6–Me_2CO (gradient elution, from a ratio of 4 : 1, 5 : 2 to 1 : 1) to give **5**, **6** or **7** respectively, which was crystallized from EtOH–H_2O in a yield of 65—70% from **1**. **5**, colorless needles, mp 185.0—187.0 °C (from EtOH–H_2O), $[\alpha]_D^{25}$ +27.8° (c = 0.67). *Anal.* Calcd for $C_{37}H_{58}O_8 \cdot 1/3H_2O$: C, 70.06; H, 9.35. Found: C, 69.78; H, 9.27. **6**, colorless needles, mp 210.0—211.5 °C (from EtOH–H_2O), $[\alpha]_D^{25}$ +20.3° (c = 1.13). *Anal.* Calcd for $C_{38}H_{60}O_8 \cdot 1/2H_2O$: C, 69.59; H, 9.28. Found: C, 69.80; H, 9.40. **7**, colorless needles, mp 215.0—216.0 °C (from EtOH–H_2O), $[\alpha]_D^{25}$ +57.9° (c = 0.57). *Anal.* Calcd for $C_{37}H_{58}O_8 \cdot 1/2H_2O$: C, 69.38; H, 9.20. Found: C, 69.45; H, 9.29.

Synthesis of 19 and 20——According to the method described in the previous paper,[6] **12** prepared from **11** was condensed with acetobromosugar prepared from D-glucose or L-rhamnose, and the product was deacetylated to give **13** or **14** in a yield of 50—58% from **11**. A solution of **13** or **14** (5 mmol) in 50% AcOH (70 ml) was refluxed for 1 h and concentrated at 40 °C. The residue was purified by chromatography on silica gel with $CHCl_3$–MeOH–H_2O

(65 : 35 : 10, lower phase) to give **15** or **16** in a yield of 55—60% from **13** or **14**. A solution of **15** or **16** (each 500 mg) in Ac_2O–C_5H_5N (1 : 1, 10 ml) was stirred for 12 h at room temperature then concentrated to dryness. A solution of the dried residue in $CHCl_3$ (10 ml) was treated with 25% HBr–AcOH (10 ml) at 0 °C and the mixture was stirred for 4 h at 0 °C. The reaction mixture was poured into ice-water, and extracted with $CHCl_3$ and the $CHCl_3$ layer was washed repeatedly with a saturated aqueous solution of $NaHCO_3$ and then with H_2O. After being dried over Na_2SO_4, the $CHCl_3$ layer was concentrated to dryness at 40 °C to give the corresponding per-*O*-acetylglycobiosyl bromide (**17** or **18**) in a yield of 70—80% from **15** or **16**.

As described for the synthesis of **5**—**7**, compound **17** or **18** was condensed with **1** in the presence of Ag_2CO_3-celite in CH_2ClCH_2Cl. After deacetylation with BaO–MeOH in the usual way, the crude product was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (70 : 10 : 1, homogeneous) and further subjected to HPLC on a reverse phase column (TSKgel ODS-120A, 21.5 i.d. × 300 mm, Toyo Soda; detection, refractive index; solvent, 90% MeOH) to give **19** or **20** in a yield of 60—65% from **1**. **19**; a white powder, $[\alpha]_D^{15}$ +13.0° (c=0.71). *Anal.* Calcd for $C_{43}H_{68}O_{13}\cdot 3/2H_2O$: C, 62.98; H, 8.27. Found: C, 63.04; H, 8.53. **20**; a white powder, $[\alpha]_D^{15}$ −4.7° (c=1.02). *Anal.* Calcd for $C_{43}H_{68}O_{12}\cdot H_2O$: C, 64.96; H, 8.88. Found: C, 64.97; H, 9.02.

Synthesis of 27 or 28——A solution of **13** or **14** (7 mmol) in 5 mM oxalic acid–H_2O (50 ml) was refluxed for 10 min. The reaction mixture was neutralized with Amberlite MB-3 resin and then concentrated to dryness. The residue was purified by chromatography on silica gel with $CHCl_3$–MeOH (4 : 1) for **21** or $CHCl_3$–MeOH (5 : 1) for **22** to give **21** or **22** in a yield of 78—80% from **13** or **14**. **21**; a white powder, $[\alpha]_D^{15}$ −3.8° (c=0.67). ^{13}C-NMR: δ 97.1 (Ara-1), 82.3 (Ara-2), 73.5 (Ara-3), 68. 3 (Ara-4), 65.1 (Ara-5), 106.4 (Glc-1), 76.3 (Glc-2), 78.0 (Glc-3 or -5), 71.4 (Glc-4), 78.4 (Glc-5 or -3), 62.5 (Glc-6), 75.4 (–C–), 28.7 ($-CH_3\times 3$). ^{1}H-NMR: δ 5.03 (1H, d, J=5.1 Hz, anomeric proton of Ara), 5.05 (1H, d, J=7.2 Hz, anomeric proton of Glc), 1.40 (9H, s, $-CH_3\times 3$). *Anal.* Calcd for $C_{15}H_{28}O_{10}\cdot 2/3H_2O$: C, 47.36; H, 7.77. Found: C, 47.16; H, 7.82. **22**; colorless syrup, $[\alpha]_D^{15}$ −21.1° (c=2.15). ^{13}C-NMR: δ 95.7 (Ara-1), 75.8 (Ara-2), 75.4 (Ara-3), 69.2 (Ara-4), 66.4 (Ara-5), 101.7 (Rha-1), 72.4 (Rha-2), 72.7 (Rha-3), 74.2 (Rha-4), 70.1 (Rha-5), 18.5 (Rha-6), 75.4 (–C–), 29.0 ($-CH_3\times 3$). ^{1}H-NMR: δ 4.79 (1H, d, J=6.4 Hz, anomeric proton of Ara), 6.06 (1H, s, anomeric proton of Rha), 1.55 (3H, d, J=6.1 Hz, $-CH_3$ of Rha), 1.38 (9H, s, $-CH_3\times 3$).

Compound **21** or **22** was treated with KOH and benzyl chloride by the same procedure as used for the synthesis of **30** or **31** ot give the corresponding per-*O*-benzyl ether (**23** or **24**), which was purified by chromatography on silica gel with *n*-C_6H_{14} and C_6H_6–Me_2CO (50 : 1). A solution of **23** or **24** (3 mmol) in AcOH (50 ml) was refluxed for 4 h and concentrated to dryness. The residue was purified by chromatography on silica gel with C_6H_6–Me_2CO (20 : 1) to give **25** or **26** in a yield of 40—50% from **21** or **22**, respectively. Compound **25** or **26** was treated by the same procedure as used for the synthesis of **4** to give an anomeric mixture of per-*O*-benzyl-glycobiosyl octanoate, which was separated by HPLC on silica gel (LiChrosorb Si 60 5 μm, 7.8 i.d. × 300 mm, Merck; detection, refractive index; solvent, C_6H_6–Me_2CO (100 : 1)), and then hydrogenated over Pd–black by the above procedure. The crude product was purified by chromatography on silica gel with $CHCl_3$–MeOH (5 : 1) for **27** or $CHCl_3$–MeOH (6 : 1) for **28** to give **27** or **28** in a yield of 20—24% from **25** or **26**, respectively. **27**; colorless syrup, $[\alpha]_D^{15}$ −3.4° (c=0.59). **28**; colorless syrup, $[\alpha]_D^{15}$ −31.8° (c=3.28).

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