Tetrahedron Vol. 48, No. 15, pp. 3021-3044, 1992
Printed in Great Britain

0040-4020/92 $5.00+.00

SYNTHESES OF SWEET TASTING DITERPENE GLYCOSIDES, BAIYUNOSIDE AND ANALOGS

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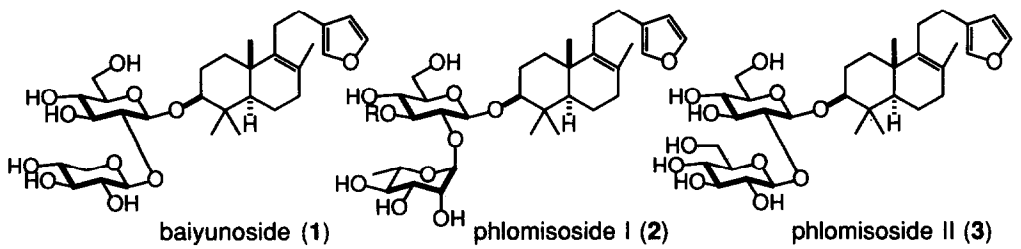
(*Received in Japan* 15 *April* 1991)

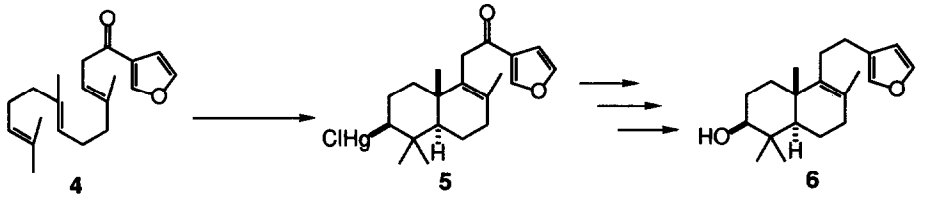
Key Words: *Total synthesis; Sweet taste; Diterpene glycosides; Glycosylation; Synthetic analogue*

Abstract: Total syntheses of sweet tasting diterpene glycosides, baiyunoside, phlomisosides I and II, as well as a variety of analogs have accomplished by means of 2'-discriminated glycosylation followed by Noyori's glycosylation from racemic baiyunol. Sweet tastes of these synthetic glycosides have evaluated qualitatively.

Sweet tasting terpene glycosides are distributed widely in nature, and intensive studies have been carrying out in order to develop much effective sweeteners.[1-5] However the most of investigations have been done based on materials originated in nature, and total synthesis of such type compounds have not yet been investigated probably due to the structural complexity. We have been interesting a sweet tasting diterpene glycoside, baiyunoside (**1**), and related glycosides phlomisosides I (**2**) and II (**3**),[6,7] on the basis of modern synthetic organic chemistry. Recently we have reported the total synthesis of the common aglycon, (±)-baiyunol (**6**),[8,9] by means of controlled biomimetic olefin cyclization using mercury(II) triflate/*N*, *N*-dimethylaniline complex.[10] Herein disclosed are the synthesis of baiyunoside (**1**)[11] as well as 23 kinds of related glycosides. Qualitative analyses of their sweet tastes have also carried out by our own tongue.



Total synthesis of (±)-baiyunol (**6**) has achieved as seen in the following scheme. Mercury (II) triflate/*N*,*N*-dimethylaniline complex induced biomimetic cyclization of 13-oxoambliofuran (**4**) affording organomercuric product **5** and which was efficiently converted to (±)-baiyunol (**6**) in total 45% yield.[9] By repeating this synthetic route, we have prepared 15 g of (±)-**6**. Thus we focussed glycosylation chemistry.

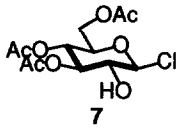


4 **5** **6**

In order to synthesize not only baiyunoside (**1**) but also a variety of synthetic analogs including phlomisosides **2** and **3**, we choose a stepwise introduction of two kinds of sugars into (±)-**6**. We are interested to taste many synthetic analogs such as stereoisomers or diastereomers with the normal and the ent-type aglycon. The first problem to be solved is how to prepare the 2'-discriminated glycoside such as **8p** or **9p**.

Glycosylation of (±)-baiyunol (**6**) with 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride (**7**)[12] under Koenigs-Knorr condition using silver triflate and tetramethylurea[13] took place smoothly but in a non-stereoselective manner to give the desired 2' discriminated glycosides **8p**, **9p**, **10p**, and **11p** in 29:20:25:26 ratio in total 60% yield.[5] These isomers were separated by HPLC and fully characterized by spectral analysis. For example, the NMR spectra of **8p** showed characteristic β-glycosidic feature (δ 4.44, d, J = 7.8 Hz for 1' proton and δ 104.9, d, $J_{C1\text{-}H1}$ = 159.9 Hz for C-1' in $CDCl_3$) without acetyl moiety at 2' (δ 3.62, 1H, br t, J = 7.8 Hz, H-2'; δ 5.16, t, J = 9.2 Hz, H-3'; δ 5.04, t, J = 9.2 Hz, H-4'). The absolute configurations of β-glycosides **8p** and **10p** were determined by ^{13}C NMR chemical shift analogy with a related class of natural products, namely glycosylation shift.[14-16] The absolute configurations of α-glycosides were definitely established by converting **11p** into ent-baiyunol, $[\alpha]_D^{16}$ -27.5° (*c* 0.04, $CHCl_3$), via basic hydrolysis (CH_3ONa / CH_3OH) followed by an enzymic hydrolysis with α-glucosidase. Thus the α-glycoside **9p** has the normal type and **11p** has the ent-type diterpene moieties. During this novel 2' discriminated glycosylation no trace of oligosaccharide formation was detected due to the increased steric bulk of 2' hydroxyl groups of generated glycosides, **8p**-**11p**.

The difficulty to prepare 1,2-*O*-disaccharide linkage has been argued based on the steric bulkiness.[17,18] Indeed, **8p** was entirely inert against a variety of glycosyl halides under Koenigs-Knorr conditions. However, a novel glycosylation condition based upon a strong affinity between silicon and fluorine atoms, developed by Noyori and co-workers,[19] was successfully applied to our synthesis. Trimethylsilyl triflate (0.1 equiv) catalyzed condensation of silyl ether **8s** with 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl fluoride (**12**)[20] in toluene at 0 °C gave rise to disaccharides **1p** and **15p** in 62:38 ratio. Stereochemistry of purified disaccharides were easily characterized since protecting groups of glucosyl and xylosyl moieties were clearly discriminated to be acetyl and benzyl groups, respectively. Thus the major isomer was assigned to be β-xyloside **1p** and the minor product was assigned to be α-xyloside **15p** based upon NMR analysis. Benzyl groups of **1p** were cleaved by lithium ammonia reduction and following methanolysis of acetyl groups with lithium methoxide afforded baiyunoside (**1**). The product was identified with natural baiyunoside in every respect including the sweet taste.



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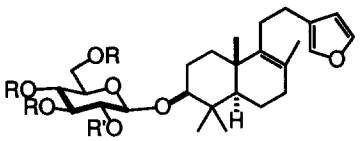
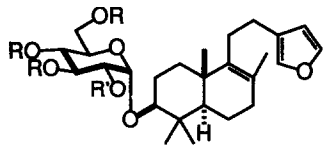
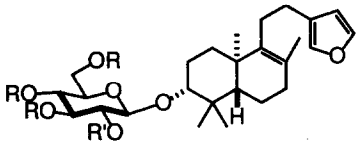


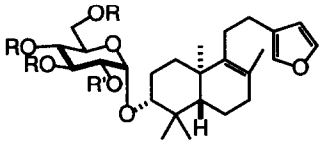
8p: R = Ac, R' = H
8s: R = Ac, R' = $SiMe_3$
8: R = R' = H



9p: R = Ac, R' = H
9s: R = Ac, R' = $SiMe_3$
9: R = R' = H

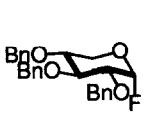


10p: R = Ac, R' = H
10s: R = Ac, R' = $SiMe_3$
10: R = R' = H



11p: R = Ac, R' = H
11s: R = Ac, R' = $SiMe_3$
11: R = R' = H

The minor xylosylation product **15p** was also subjected to deprotection and disaccharide **15** was obtained in good yield. Analogous xylosylation of α-glucoside **9s** followed by deprotection afforded α,β-disaccharide **16** selectively in overall 33% yield. The β-glycoside with ent-type aglycon **10p** was converted into **17** and **18**, and α-glucoside **11p** afforded α,β-isomer **19**.



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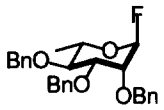

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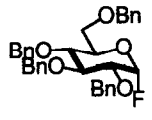

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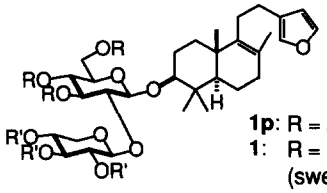
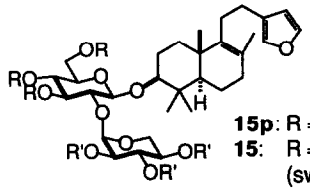
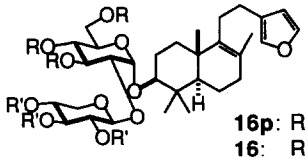


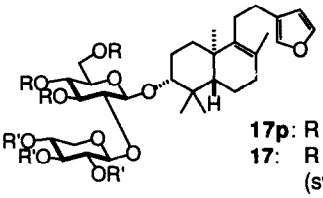
1p: R = Ac, R' = Bn
1: R = R' = H
(sweet, sweet)



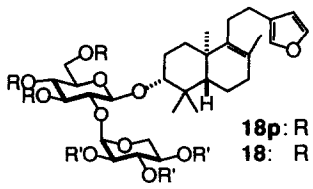
15p: R = Ac, R' = Bn
15: R = R' = H
(sweet)



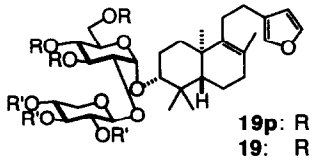
16p: R = Ac, R' = Bn
16: R = R' = H



17p: R = Ac, R' = Bn
17: R = R' = H
(sweet)

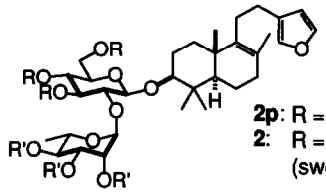


18p: R = Ac, R' = Bn
18: R = R' = H

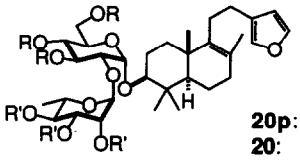


19p: R = Ac, R' = Bn
19: R = R' = H
(bitter)

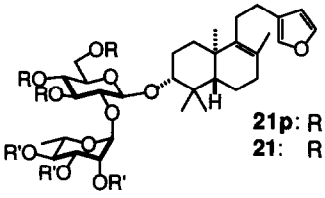
Syntheses of phlomisosides I (**2**) and II (**3**) were also achieved via analogous rhamnosylation of **8s** with rhamnosyl fluoride **13** or glucosylation of **8s** with glucosyl fluoride **14**, respectively, and following deprotections. Artificial disaccharides with glc-rha linkages **20**, **21**, and **22**, and glc-glc linkages **23**, **24**, **25**, **26**, **27**, **28**, and **29** were also derived from **8p**-**11p** by the same operations. Monoglycosides **8**-**11** were simply derived from the original glycosylation products **8p**-**11p** by methanolysis with sodium methoxide.



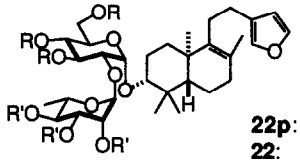
2p: R = Ac, R' = Bn
2: R = R' = H
(sweet, sweet)



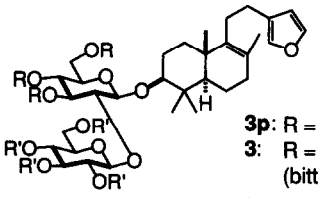
20p: R = Ac, R' = Bn
20: R = R' = H



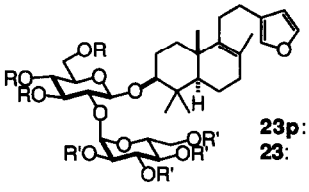
21p: R = Ac, R' = Bn
21: R = R' = H



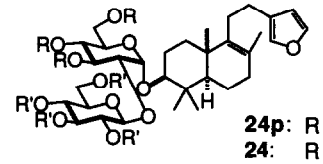
22p: R = Ac, R' = Bn
22: R = R' = H



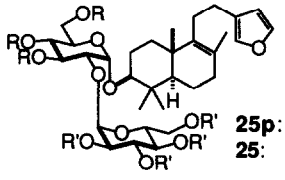
3p: R = Ac, R' = Bn
3: R = R' = H
(bitter, bitter)



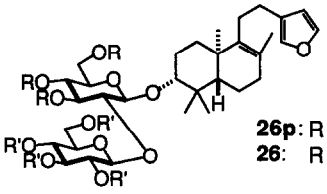
23p: R = Ac, R' = Bn
23: R = R' = H
(sweet, sweet, sweet)



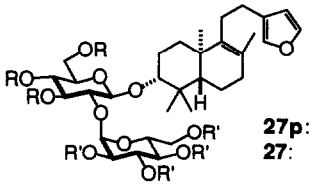
24p: R = Ac, R' = Bn
24: R = R' = H
(sweet)



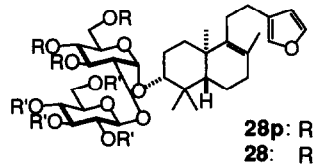
25p: R = Ac, R' = Bn
25: R = R' = H



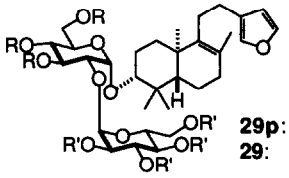
26p: R = Ac, R' = Bn
26: R = R' = H



27p: R = Ac, R' = Bn
27: R = R' = H

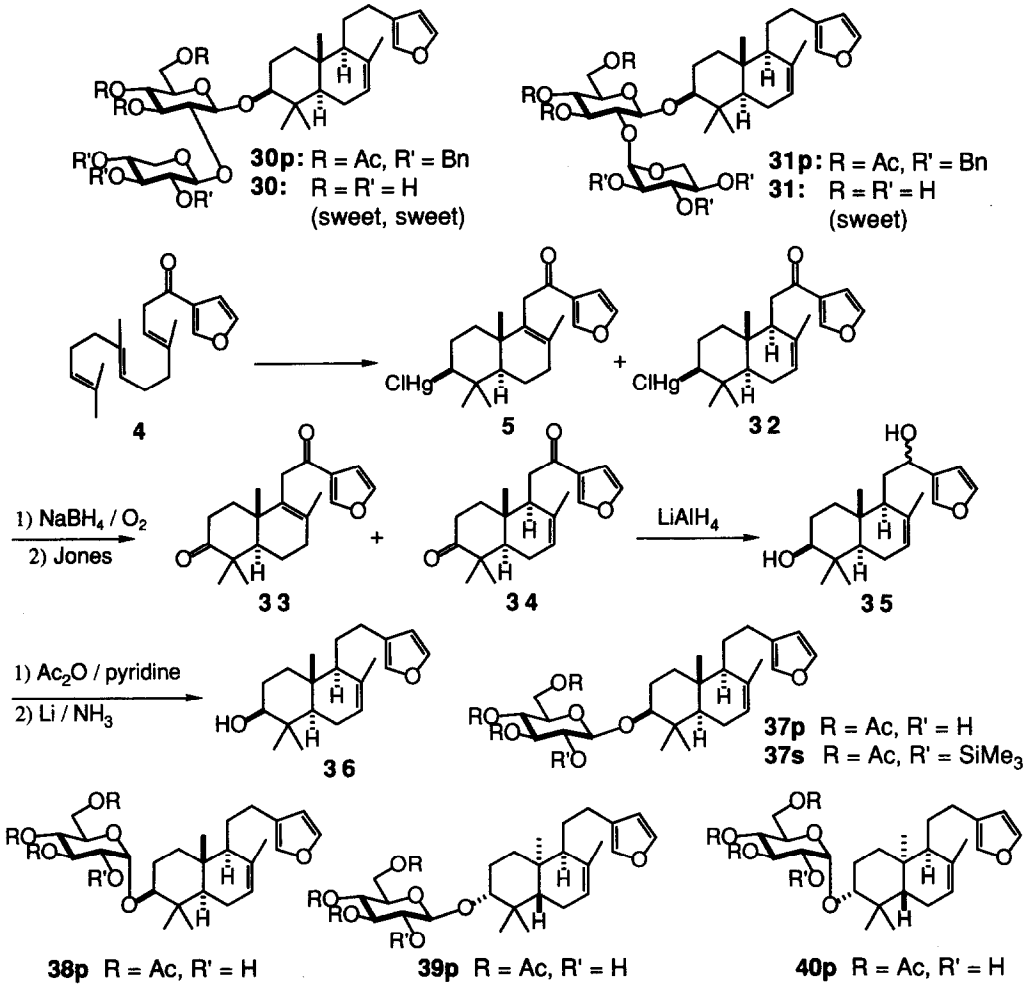


28p: R = Ac, R' = Bn
28: R = R' = H



29p: R = Ac, R' = Bn
29: R = R' = H

$\Delta^{7,8}$-Baiyunoside (**30**) and its stereoisomer **31** were prepared as follows. Mercury(II) triflate/*N*,*N*-dimethylaniline complex induced cyclization of (±)-**4** afforded major cyclization product (±)-**5** (68% yield) along with minor product (±)-**32** (8% yield).[6] Although the separation of (±)-**5** and (±)-**32** in preparative scale is difficult, diketones (±)-**33** and (±)-**34**, derived by hydroxylative demercuration and following Jones oxidation, were separated nicely by the combination of recrystallization and column chromatography. LAH reduction of diketone (±)-**34** afforded diastereomeric mixture of diols (±)-**35**, and Li/NH_3 reduction of the derived acetates gave rise to (±)-**36**. 2'-Discriminated glucosylation of (±)-**36** with glucosyl chloride **7** in the presence of AgOTf and TMU gave glucosides **37p-40p**. These glucosides were separated by HPLC and characterized by NMR analysis. Introduction of xylose moiety into **37p** was accomplished via trimethylsilylether **37s** to give **30p** and **31p**. Following deprotection afforded **30** and **31**.



Some of the glycosylation of **8s-11s** with glycosyl fluorides **12**, and **13** under Noyori's conditions using toluene as solvent occurred stereoselectively, particularly the rhamnosylation reaction with **13** always afforded only α-isomer, and are summarized in table I.

Table 1. Synthesis of disaccharides under Noyori's condition.[a]

run	donor	acceptor	products	yield(%)[b]	α/β ratio[c]
1	**12**	**8s**	**1p, 15p**	51	38 : 62
2	**12**	**9s**	**16p**	45	0 : 100
3	**12**	**10s**	**17p, 18p**	56	71 : 29
4	**12**	**11s**	**19p**	68	0 : 100
5	**13**	**8s**	**2p**	55	100 : 0
6	**13**	**9s**	**20p**	91	100 : 0
7	**13**	**10s**	**21p**	35	100 : 0
8	**13**	**11s**	**22p**	31	100 : 0
9	**14**	**8s**	**3p, 23p**	62	23 : 77
10	**14**	**9s**	**24p, 25p**	43	53 : 47
11	**14**	**10s**	**26p, 27p**	34	63 : 37
12	**14**	**11s**	**28p, 29p**	38	67 : 33
13	**12**	**37s**	**30p, 31p**	31	49 : 51

[a]Coupling reactions were carried out in the presence of trimethylsilyl triflate (0.1 equiv) in toluene. [b]Isolation yield after silica gel column chromatography. [c]Determined by HPLC analysis using RI detector.

Thus 24 kinds of glycosides in hand, a qualitative taste analysis of each synthetic glycoside was carried out using 0.1% aqueous solution by comparing with the taste of baiyunoside (**1**), which is represented as SWEET SWEET. A disaccharide **15**, showed moderate sweet taste which is represented as SWEET. Corresponding α,β-isomer **16** did not gave any taste. Among the glc-xyl series of (-)-baiyunol derivatives, β-glc-β-xyl derivative **17** showed moderate sweet taste, **18** was not sweet at all, and **19** was moderately bitter. Among the four rhamnose derivatives, phlomisoside I (**2**) showed strong sweet taste as sweet as baiyunoside (**1**), and other three stereoisomers were not sweet at all. Although phlomisoside II (**3**), (+)-baiyunol with β-glc-β-glc, showed strong bitter taste represented as BITTER BITTER, corresponding β-glc-α-glc derivative **23** showed very strong sweet taste represented as SWEET SWEET SWEET! (+)-Baiyunol with α-glc-β-glc derivative **24** was moderately sweet and α-glc-α-glc derivative **25** did not give any taste. Glucose-glucose derivatives of (-)-baiyunol **26**, **27**, **28**, and **29**, did not give any taste. $\Delta^{7,8}$-Baiyunoside (**30**) was as sweet as baiyunoside (**1**) and the stereoisomeric **31** was moderately sweet. Four kinds of monosaccharides **8**, **9**, **10**, and **11** did not have any taste. Therefore, we have prepared 24 kinds of glycosides, one of the synthetic analog of baiyunoside, (+)-baiyunol with β-glc-α-glc linkage **23**, showed the strongest sweet taste. This is the sweet taste of our recommendation but very expensive.

EXPERIMENTAL SECTION

General. Reactions were run under a positive pressure of argon unless otherwise noted and performed in flame-dried glassware which was cooled under argon. Anhydrous solvents were transferred by an oven-dried syringe. Solvents were distilled before use. After workup the organic layers were dried over anhydrous magnesium sulfate. The term "in vacuo" refers to solvent removal via rotary evaporator at water aspirator pressure, followed by evacuation of the flask at 0.1 mmHg for a few hours. Analytical thin-layer chromatography (TLC) was performed on precoated glass plates (5 × 1.5 cm) with silica gel (Merck Kieselgel 60 F_{254} for ordinary phase and Merck RP-18 F_{254} for reverse phase). Column chromatography was performed by using silica gel of Fuji-Devison

(BW-820, 60-200 mesh). High performance liquid chromatography (HPLC) was performed on a JASCO 880PU instrument with Gilson 131 refractive index (RI) detector using a Develosil 30-3 column (4 × 250 or 10 × 250 mm for ordinary phase) or a Develosil ODS-5 column (4 × 250 or 10 × 250 mm for reverse phase) supplied from Nomura Chemicals. Retention time of HPLC were reported with T*r* (min). Melting points were obtained on a Yanagimoto apparatus and are uncorrected. Optical rotation values were determined on JASCO PIP-140 in indicated solvent. Infrared spectra (IR) were determined in the indicated solvents in sodium chloride cavity cells on a HITACHI 260-10 spectrophotometer and reported in ν_{max} values. Proton nuclear magnetic resonance (^{1}H NMR) spectra were determined on JEOL GX-400 (400 MHz) or FX-90 (90 MHz) instruments. Chemical shifts are reported in δ units downfield from tetramethylsilane (TMS). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. Coupling constants (*J*) are reported in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were determined on JEOL GX-400 (100 MHz) or FX-90 (22.5 MHz) instruments. Chemical shifts are reported as s, singlet; d, doublet; t, triplet; and q, quartet. Mass spectra (MS) were obtained on a JEOL HX-100 instrument at an ionization voltage of 70 eV.

2'-Discriminated glucosylation of (±)-baiyunol (6) with glucosyl chloride 7 (Preparation of 8p, 9p, 10p and 11p). To a stirred solution of (±)-baiyunol (**6**) (582 mg, 1.92 mmol), 3,4,6-tri-*O*-acetyl-β-D-glucopyransyl chloride (**7**) (935 mg, 2.88 mmol), and TMU (357 mg, 3.07 mmol) in dry dichloromethane (10 ml) was added silver triflate (705 mg, 2.88 mmol) in one portion, and the mixture was stirred for 3 h at room temperature under dark. A filtrated solution through a cotton-Celite pad was poured into water. A concentrated chloroform extract was subjected to column chromatography on silica gel (30 g) using hexane-ethyl acetate (5:2) as eluant to give a mixture of glucosides (683 mg, 60% yield) along with (±)-**6** (60.3 mg, 10%). The crude glycosides were separated by HPLC with a column of Develosil ODS-7 (10 × 250 mm) eluted with methanol-water (6:1) in flow rate of 2.5 ml/min to give pure **8p**: mp 146-147°C; $[\alpha]_D^{15}$ +27.6° (*c* 6.29, $CHCl_3$); IR ($CHCl_3$) 3620-3300, 2950, 2880, 2830, 1750, 1500, 1455, 1440, 1370, 1210, 1160, 1130, 1080, 1060, 1030, 990, 905, 875, 720, 655, 595 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) 0.85 (3H, s), 0.97 (3H, s), 1.03 (3H, s), 1.61 (3H, s), 2.03 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 3.19 (1H, dd, *J* = 11.7, 4.4 Hz), 3.62 (1H, br t, *J* = 7.6 Hz), 3.68 (1H, ddd, *J* = 9.9, 5.1, 2.5 Hz), 4.10 (1H, dd, *J* = 12.1, 2.6 Hz), 4.29 (1H, dd, *J* = 12.1, 5.3 Hz), 4.44 (1H, d, *J* = 7.8 Hz), 5.02 (1H, t, *J* = 9.7 Hz), 5.13 (1H, t, *J* = 9.5 Hz), 6.29 (1H, dd, *J* = 1.7, 1.0 Hz), 7.23 (1H, br s), 7.35 (1H, t, *J* = 1.7 Hz); ^{13}C NMR (100 MHz in $CDCl_3$) 16.8 q, 18.9 t, 19.7 q, 20.4 q, 20.9 q, 20.0 q, 21.1 q, 26.0 t, 26.6 t, 28.5 q, 29.0 t, 33.9 t, 35.3 t, 37.8 s, 39.3 s, 51.5 d, 62.5 t, 68.7 d, 71.7 d, 72.8 d, 74.5 d, 90.4 d, 104.9 d (*J* = 160 Hz), 110.6 d, 125.2 s, 126.5 s, 138.1 d, 139.1 s, 142.4 d, 169.2 s, 170.2 s, 170.3 s; HRMS (EI) *m/z* 590.3105 (found), calcd for $C_{32}H_{46}O_{10}$ 590.3091; Anal. found, C, 64.82%, H, 7.76%, calcd for $C_{32}H_{46}O_{10}$, C, 65.07%, H, 7.85%, **11p**: $[\alpha]_D^{18}$ +67.5° (*c* 2.28, $CHCl_3$); IR ($CHCl_3$) 3650-3200, 2950, 1750, 1370, 1200, 1150, 1035, 870, 720, 660, 600 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) 0.89 (3H, s), 0.99 (3H, s), 1.03 (3H, s), 1.61 (3H, s), 2.04 (3H, s), 2.08 (3H, s), 2.09 (3H, s), 3.23 (1H, dd, *J* = 11.8, 4.5 Hz), 3.69 (1H, dt, *J* = 10.5, 3.7 Hz), 4.08 (1H, dd, *J* = 12.0, 2.2 Hz), 4.11 (1H, ddd, *J* = 9.7, 4.6, 2.2 Hz), 4.25 (1H, dd, *J* = 12.1, 4.5 Hz), 5.01 (1H, t, *J* = 9.9 Hz), 5.03 (1H, d, *J* = 4.2 Hz), 5.22 (1H, t, *J* = 9.7 Hz), 6.28 (1H, dd, *J* = 1.7, 1.0 Hz), 7.22 (1H, br s), 7.35 (1H, t, *J* = 1.7 Hz); ^{13}C NMR (100 MHz in $CDCl_3$) 17.0 q, 18.9 t, 19.7 q, 20.4 q, 20.9 q, 21.0 q, 21.2 q, 22.9 q, 26.0 t, 26.3 t, 28.6 q, 29.0 t, 33.9 t, 35.3 t, 38.6 s, 39.4 s, 51.4 d, 62.2 t, 67.8 d, 68.3 d, 71.6 d, 73.6 d, 89.8 d, 100.4 d ($J_{C1\text{-}H1}$ = 169 Hz), 110.6 d, 125.2 s, 126.7 s, 138.1 d, 138.9 s, 142.4 d, 162.9 s, 170.1 s, 170.8 s; HRMS (EI) *m/z* 590.3124 (found), calcd for $C_{32}H_{46}O_{10}$ 590.3091, and a mixture of **9p** and **10p**. The latter mixture of was subjected to ordinary phase HPLC with a Develosil 30-3 column (4.6 × 250 mm) with a mixture of hexane and 2-propanol

(10:1) as an eluant in a flow rate of 1 ml/min to give pure **9p**: $[\alpha]_D^{18}$ +115.1° (*c* 4.83, $CHCl_3$); IR ($CHCl_3$) 3650-3300, 2950, 2890, 2840, 1750, 1500, 1455, 1365, 1210, 1150, 1080, 1070, 1020, 980, 870, 720, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.85 (3H, s), 0.98 (3H, s), 1.06 (3H, s), 1.61 (3H, s), 2.05 (3H, s), 2.08 (3H, s), 2.09(3H, s), 3.20 (1H, dd, *J*= 11.7, 4.4 Hz), 3.69 (1H, td, *J*= 10.0, 4.2 Hz), 4.08 (1H, dd, *J*= 12.0, 2.2 Hz), 4.13 (1H, ddd, *J*= 10.0, 4.6, 2.2 Hz), 4.25 (1H, dd, *J*= 12.0, 4.6 Hz), 5.03 (1H, t, *J*= 9.4 Hz), 5.08 (1H, d, *J*= 4.2 Hz), 5.17 (1H, t, *J*= 9.7 Hz), 6.28 (1H, dd, *J*= 1.7, 1.0 Hz), 7.23 (1H, br, s), 7.35 (1H, t, *J*= 1.7 Hz); ^{13}C NMR (100 MHz in $CDCl_3$) 16.9 q, 19.1 t, 19.7 t, 20.4 q, 20.9 q, 21.0 q, 21.2 q, 23.6 t, 26.0 t, 29.0 t, 29.1 q, 33.9 t, 35.0 t, 38.8 s, 38.9 s, 51.6 d, 62.2 t, 68.1 d, 68.4 d, 70.8 d, 73.6 d, 85.4 d, 95.4d ($J_{C1\text{-}H1}$ = 172 Hz), 110.6 d, 125.2 s, 126.7 s, 138.1 d, 139.0 s, 142.4 d, 169.2 s, 170.2 s, 170.2 s; HRMS (EI) *m/z* 590.3105 (found), calcd for $C_{32}H_{46}O_{10}$ 590.3091, and **10p**: $[\alpha]_D^{18}$ -18.7° (*c* 2.75, $CHCl_3$); IR ($CHCl_3$) 3650-3200, 2950, 2880, 2840, 1750, 1500, 1450, 1370, 1210, 1160, 1130, 1060, 1030, 990, 980, 870, 720, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.81 (3H, s), 0.98 (3H, s), 1.01 (3H, s), 1.61 (3H, s), 2.03 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 3.28 (1H, dd, *J*= 11.7, 4.6 Hz), 3.55 (1H, br t, *J*= 8.4 Hz), 3.63 (1H, ddd, *J*= 12.0, 5.1, 2.7 Hz), 4.11 (1H, dd, *J*= 12.2, 2.7 Hz), 4.23 (1H, dd, *J*= 12.0, 5.1 Hz), 4.42 (1H, d, *J*= 7.8 Hz), 5.03 (1H, t, *J*= 9.7 Hz), 5.14 (1H, t, *J*= 9.4 Hz), 6.29 (1H, br s), 7.23 (1H, br s), 7.35 (1H, t, *J*= 1.7 Hz), ^{13}C NMR (100 MHz in $CDCl_3$) 16.7 q, 19.1 t, 19.8 q, 20.4 q, 20.9 q, 21.0 q, 21.1 q, 24.1 t, 26.0 t, 28.3 q, 29.0 t, 34.0 t, 35.1 t, 38.4 s, 38.8 s, 51.8 d, 62.4 t, 69.0 d, 71.7 d, 72.2 d, 74.5 d, 85.5 d, 100.2d ($J_{C1\text{-}H1}$ = 157 Hz), 110.7 d, 125.2 s, 126.7 s, 138.1 d, 139.0 s, 142.4 d, 169.3 s, 169.3 s, 170.2 s; HRMS (EI) *m/z* 590.3101 (found), calcd for $C_{32}H_{46}O_{10}$ 590.3091. The ratio of these four isomeric glycosides **8p**, **9p**, **10p**, and **11p** was established through HPLC analysis to be 29:20:25:26, respectively.

Baiyunyl 2-*O*-trimethylsilyl-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (8s). To mixture of **8p** (158 mg, 0.268 mmol) and 2,6-lutidine (201 mg, 1.876 mmol) in dichloromethane (2 ml) was added trimethylsilyl triflate (298 mg, 1.338 mmol) at 0° C, and the mixture was stirred for 10 h at room temperature. Concentrated residue was directly subjected to column chromatography on silica gel (10 g) with a mixture of hexane and ethyl acetate (5:2) as eluant affording silyl ether **8s** (161 mg, 91% yield): $[\alpha]_D^{23}$ +28.6° (*c* 4.24, $CHCl_3$); IR ($CHCl_3$) 2960, 1750, 1585, 1500, 1460, 1370, 1255, 1230, 1170, 1105, 1040, 990, 875, 845, 700, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.14 (9H, s), 0.87 (3H, s), 0.97 (3H, s), 1.03 (3H, s), 1.60 (3H, s), 2.00 (3H, s), 2.05 (3H, s), 2.06 (3H, s), 3.12 (1H, dd, *J*= 11.7, 4.4 Hz), 3.66 (2H, m), 4.08 (1H, dd, *J*= 11.7, 2.2 Hz), 4.29 (1H, dd, *J*= 12.5, 5.9 Hz), 4.41 (1H, d, *J*= 7.3 Hz), 4.95 (1H, t, *J*= 9.5 Hz), 5.09 (1H, t, *J*= 9.5 Hz), 6.28 (1H, br s), 7.22 (1H, br s), 7.34 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 0.4 q, 16.3 q, 18.4 t, 19.2 q, 20.0 q, 20.4 q, 20.5 q, 20.9 q, 25.6 t, 26.4 t, 27.8 q, 28.7 t, 33.6 t, 35.2 t, 38.3 s, 39.0 s, 51.4 d, 62.2 t, 69.1 d, 71.1 d, 72.8 d, 75.6 d, 89.9 d, 105.5 d, 110.6 d, 125.2 s, 126.4 s, 138.2 d, 139.3 s, 142.5 d, 169.5 s, 169.9 s, 170.3 s; HRMS *m/z* 662.3489 (found), calcd for $C_{35}H_{54}O_{10}Si$ 662.3486.

Baiyunyl 2-*O*-trimethylsilyl-3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (9s). By the same operation described above, **9p** (123.6 mg, 0.209 mmol) was converted to **9s** (136.7 mg, 100% yield): $[\alpha]_D^{21}$ +107.5° (*c* 4.45, $CHCl_3$); IR ($CHCl_3$) 2950, 1750, 1500, 1455, 1440, 1365, 1210, 1160, 1120, 1020, 875, 840, 720, 660, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.12 (9H, s), 0.89 (3H, s), 0.99 (3H, s), 1.04 (3H, s), 1.61 (3H, s), 2.03 (6H, s), 2.08 (3H, s), 3.17 (1H, dd, *J*= 11.7, 4.4 Hz), 3.77 (1H, dd, *J*= 9.8, 3.9 Hz), 4.06 (1H, dd, *J*= 12.2, 2.0 Hz), 4.20 (1H, m), 4.27 (1H, dd, *J*= 12.2, 4.9 Hz), 4.87 (1H, d, *J*= 3.9 Hz), 4.96 (1H, t, *J*= 9.8 Hz), 5.25 (1H, t, *J*= 9.8 Hz), 6.30 (1H, br s), 7.24 (1H, br s), 7.35 (1H, br s); ^{13}C NMR (22.5 MHz in $CDCl_3$) 0.2 q, 16.7 q, 18.9 t, 19.5 q, 20.2 q, 20.7 q, 20.7 q, 21.0 q, 23.8 t, 25.8 t, 28.8 q, 28.8

t, 33.8 t, 35.0 t, 38.8 s, 38.8 s, 51.5 d, 62.4 t, 67.9 d, 69.1 d, 70.9 d, 71.1 d, 86.7 d, 97.5 d, 110.8 d, 125.6 s, 126.8 s, 138.4 d, 139.5 s, 142.7 d, 170.0 s, 170.0 s, 170.7 s.

Ent-baiyunyl 2-*O*-trimethylsilyl-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside (10s). According to the same operation described above, **10p** (175 mg, 0.296 mmol) was converted to **10s** (174.2 mg, 90% yield): $[\alpha]_D^{21}$ -28.0° (*c* 4.73, $CHCl_3$); IR ($CHCl_3$) 2960, 2900, 2875, 2840, 1750, 1500, 1450, 1365, 1210, 1160, 1110, 1040, 990, 905, 875, 840, 720, 655, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.11 (9H, s), 0.83 (3H, s), 0.98 (3H, s), 1.00 (3H, s), 1.60 (3H, s), 2.01 (3H, s), 2.05 (3H, s), 2.06 (3H, s), 3.23 (1H, dd, *J*= 11.7, 4.4 Hz), 3.56 (1H, dd, *J*= 8.8, 7.8 Hz), 3.61 (1H, ddd, *J*= 9.8, 4.9, 2.4 Hz), 4.11 (1H, dd, *J*= 12.2, 2.4 Hz), 4.22 (1H, dd, *J*= 12.2, 4.9 Hz), 4.36 (1H, d, *J*= 7.3 Hz), 4.98 (1H, t, *J*= 9.8 Hz), 5.08 (1H, t, *J*= 9.8 Hz), 6.29 (1H, br s), 6.23 (1H, br s), 7.36 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 0.5 q, 16.7 q, 18.8 t, 19.4 q, 20.2 q, 20.7 q, 20.8 q, 21.0 q, 23.6 t, 25.7 t, 28.1 q, 28.8 t, 33.8 t, 35.0 t, 38.2 s, 38.7 s, 51.8 d, 62.3 t, 69.2 d, 71.2 d, 72.8 d, 75.8 d, 85.4 d, 100.7 d, 110.8 d, 125.5 s, 126.8 s, 138.4 d, 139.4 s, 142.7 d, 169.8 s, 170.2 s, 170.7 s.

Ent-baiyunyl 2-*O*-trimethylsilyl-3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (11s). According to the same operation described above, **11p** (135 mg, 0.229 mmol) as a stating material to give **11s** (73 mg, 47% yield): $[\alpha]_D^{21}$ +57.8° (*c* 3.63, $CHCl_3$); IR ($CHCl_3$) 2960, 2840, 1750, 1500, 1440, 1365, 1210, 1160, 1120, 1030, 880, 845, 720, 660, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.10 (9H, s), 0.89 (3H, s), 0.98 (3H, s), 1.15 (3H, s), 1.60 (3H, s), 2.03 (6H, s), 2.09 (3H, s), 3.08 (1H, dd, *J*= 11.7, 4.4 Hz), 3.75 (1H, dd, *J*= 9.8, 3.9 Hz), 4.06 (1H, dd, *J*= 12.2, 2.4 Hz), 4.17 (1H, ddd, *J*= 10.3, 4.4, 2.0 Hz), 4.28 (1H, dd, *J*= 12.2, 4.4 Hz), 4.83 (1H, d, *J*= 3.9 Hz), 4.96 (1H, t, *J*= 9.3 Hz), 5.29 (1H, t, *J*= 9.3 Hz), 6.28 (1H, br s), 7.22 (1H, br s), 7.35 (1H, dd, *J*= 2.0, 1.5 Hz); ^{13}C NMR (22.5 MHz in $CDCl_3$) 0.2 q, 16.6 q, 18.9 t, 19.7 q, 20.3 q, 20.9 q, 20.9 q, 21.2 q, 26.1 t, 26.2 t, 28.2 q, 29.0 t, 34.0 t, 35.4 t, 38.7 s, 39.6 s, 51.6 d, 62.6 t, 67.6 d, 69.4 d, 71.4 d, 73.3 d, 90.7 d, 101.7 d, 111.0 d, 125.7 s, 127.0 s, 138.6 d, 139.7 s, 142.9 d, 170.1 s, 170.3 s, 170.8 s; MS (EI) *m/z* 662 (M^+), 377, 361, 317, 285, 241, 203, 119, 95, 81, 43.

Baiyunyl β-D-glucopyranoside (8). To a solution of **8p** (19 mg, 0.0322 mmol) in dry methanol (1 ml) was added a solution of sodium methoxide in methanol (0.158 M solution, 20.4 ml, 0.00322 mmol), and the mixture was stirred for 15 h at room temperature. The mixture was neutralized by the addition of Amberlite IR-120B, and stirred for additional 5 min. A filtrate through cotton-Celite pad was concentrated and the residue was subjected to column chromatography on silica gel using chloroform-methanol (6:1) as an eluant affording **8** as a colorless syrup (13.1 mg, 88% yield): $[\alpha]_D^{21}$ +17.4° (*c* 0.57, CH_3OH); IR ($CHCl_3$) 3400, 2940, 2870, 1680, 1450, 1360, 1200, 1155, 1075, 1020, 875, 715, 635, 595 cm^{-1}; ^1H NMR (400 MHz in C_5D_5N) 0.95 (3H, s), 1.05 (3H, s), 1.37 (3H, s), 1.60 (3H, s), 3.49 (1H, dd, *J*= 11.8, 4.3 Hz), 4.02 (1H, m), 4.07 (1H, br t, *J*= 7.6 Hz), 4.25-4.31 (2H, m), 4.45 (1H, dd, *J*= 11.5, 4.9 Hz), 4.59 (1H, br d, *J*= 11.5 Hz), 5.00 (1H, d, *J*= 7.8 Hz), 6.54 (1H, br s), 7.56 (1H, br s), 7.65 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 17.6, 19.6, 20.1, 20.9,26.6, 27.8, 28.9, 29.7, 34.5, 35.8, 39.3, 40.1, 52.0, 63.4, 72.1, 76.2, 78.7, 79.1, 89.4, 107.2, 111.7, 126.3, 126.7, 139.2, 140.0, 143.4; HRMS (FAB) *m/z* 487.2670 (found), calcd for $C_{26}H_{40}O_7Na$ 487.2671.

Baiyunyl α-D-glucopyranoside (9). According to the same operation described above, **9p** (18.7 mg, 0.0317 mmol) was transferred to **9** (14.1 mg, 96% yield) as colorless syrup: $[\alpha]_D^{21}$ +124.4° (*c* 0.30, CH_3OH);

IR ($CHCl_3$) 3400, 2950, 2880, 1450, 1370, 1200, 1145, 1045, 1020, 875, 720, 660, 595 cm^{-1}; ^1H NMR (400 MHz in C_5D_5N) 0.91 (3H, s), 0.96 (3H, s), 1.22 (3H, s), 1.59 (3H, s), 3.54 (1H, dd, J= 11.6, 4.3 Hz), 4.20 (1H, dd, J=9.7, 3.8 Hz), 4.26 (1H, t, J= 9.2 Hz), 4.46 (1H, dd, J= 11.2, 5.1 Hz), 4.52-4.64 (3H, m), 5.53 (1H, d, J= 3.7 Hz), 6.55 (1H, s), 7.61 (1H, s), 7.66 (1H, s); ^{13}C NMR (100 MHz in C_5D_5N) 17.5 q, 19.6 t, 20.1 q, 20.8 q, 23.9 t, 26.6 t, 29.6 q, 29.7 t, 34.5 t, 35.5 t, 39.5 s, 39.5 s, 52.0 d, 63.5 t, 72.8 d, 74.2 d, 75.2 d, 75.8 d, 83.9 d, 97.5 d, 111.7 d, 126.2 s, 126.8 s, 139.2 d, 139.9 d, 143.4 d; HRMS (FAB) *m/z* 487.2633 (found), calcd for $C_{26}H_{40}O_7Na$ 487.2671.

(-)-Baiyunyl β-D-glucopyranoside (10). According to the same operation described above, **10p** (23.6 mg, 0.040 mmol) was converted to **10** (18.6 mg, 100% yield): $[\alpha]_D^{21}$ -30.2° (*c* 0.76, CH_3OH); IR ($CHCl_3$) 3400, 2950, 2880, 1450, 1375, 1200, 1150, 1070, 1015, 870, 710, 595 cm^{-1}; ^1H NMR (400 MHz in C_5D_5N) 0.93 (3H, s), 0.95 (3H, s), 1.24 (3H, s), 1.61 (3H, s), 3.59 (1H, dd, J= 11.7, 4.4 Hz), 4.06 (2H, m), 4.26 (1H, t, J= 8.9 Hz), 4.32 (1H, t, J= 8.8 Hz), 4.43 (1H, dd, J= 11.5, 5.6 Hz), 4.63 (1H, dd, J= 11.6, 2.6 Hz), 4.97 (1H, d, J= 7.8 Hz), 6.56 (1H, s), 7.61 (1H, s), 7.66 (1H, s); ^{13}C NMR (100 MHz in C_5D_5N) 17.6 q, 19.7 t, 20.1 q, 20.8 q, 24.8 t, 26.7 t, 29.1 q, 29.8 t, 34.5 t, 35.6 t, 39.1 s, 39.4 s, 52.1 d, 63.7 t, 72.5 d, 75.6 d, 78.7 d, 79.1 d, 85.2 d, 102.7 d, 111.7 d, 126.2 s, 126.7 s, 139.2 d, 139.9 d, 143.4 d; HRMS (FAB) *m/z* 487.2684 (found), calcd for $C_{26}H_{40}O_7Na$ 487.2671.

Ent-baiyunyl α-D-glucopyranoside (11). According to the same operation described above, **11p** (26.4 mg, 0.0447 mmol) was converted to **11** (15.8 mg, 76% yield): $[\alpha]_D^{21}$ +48.0° (*c* 0.63, CH_3OH); IR ($CHCl_3$) 3400, 2950, 1500, 1450, 1375, 1200, 1145, 1045, 1020, 910, 875, 715, 595 cm^{-1}; ^1H NMR (400 MHz in C_5D_5N) 0.98 (3H, s), 1.00 (3H, s), 1.36 (3H, s), 1.59 (3H, s), 3.34 (1H, dd, J= 11.7, 4.4 Hz), 4.18 (1H, dd, J=11.7, 4.4 Hz), 4.23 (1H, t, J= 9.0 Hz), 4.46 (1H, dd, J= 11.1, 5.0 Hz), 4.53-4.60 (2H, m), 4.64 (1H, t, J= 9.3 Hz), 5.46 (1H, d, J= 3.7 Hz), 6.54 (1H, s), 7.59 (1H, s), 7.66 (1H, s); ^{13}C NMR (100 MHz in C_5D_5N) 17.4 q, 19.6 t, 20.1 q, 20.8 q, 26.6 t, 27.1 t, 28.8 q, 29.7 t, 34.5 t, 35.8 t, 39.2 s, 40.3 s, 52.0 d, 63.6 t, 73.0 d, 74.7 d, 74.7 d, 75.6 d, 89.8 d, 103.7 d, 111.7 d, 126.2 s, 126.7 s, 139.2 d, 140.0 s, 143.4 d; HRMS (FAB) *m/z* 487.2657 (found), calcd for $C_{26}H_{40}O_7Na$ 487.2671.

Ent-baiyunol. To a stirred suspension of **11** (12.7 mg, 0.027 mmol) in phosphate buffer (pH 5, 0.7 ml) was added α-glucosidase (18 mg, 1350 units), and the mixture was stirred at 35° C for 3 h. To the mixture was added powdered NaCl, and the filtrate through cotton-Celite pad was extracted with chloroform. The concentrated extract was subjected to column chromatography on silica gel (3 g) using a mixture of hexane and ethyl acetate (4:1) followed by a mixture of methanol and chloroform (2:5) as eluants to give Ent-baiyunol (0.8 mg, 10% yield): $[\alpha]_D^{16}$ -27.5° (*c* 0.04, $CHCl_3$), along with the starting material **11** (0.9 mg, 7% yield). Spectral data of Ent-baiyunol was indistinguishable from those of baiyunol.

Xylosylation of 8s with 12 (Preparation of 1p and 15p). To a solution of **8s** (71 mg, 0.108 mmol) and 2,3,4,6-tetra-*O*-benzyl-α-D-xylopyranosyl fluoride (**12**) (68.4 mg, 0.162 mmol) in dry toluene (1.5 ml) was added trimethylsilyl triflate (2.4 mg, 0.0108 mmol), and the mixture was stirred at 0° C for 80 min. The reaction mixture was poured into saturated aqueous sodium bicarbonate solution, and extracted with chloroform. The concentrated extract was subjected to column chromatography on silica gel with a mixture of hexane and ethyl acetate (4:1 and then 2:1) as eluant to afford a mixture of disaccharides (54.4 mg, 51% yield, **1p**:**15p** = 64:36), along with **8p** (18.1 mg, 28% yield). The crude disaccharides were purified by HPLC with Develosil

ODS-5 column (4.6 × 250 mm) with a mixture of acetone and water (5:1) as an eluant in a flow rate of 1.5 ml/min to give **1p** as a colorless solid: T*r*, 12.7 min; $[\alpha]_D^{18}$ +38.5° (*c* 1.22, $CHCl_3$); IR ($CHCl_3$) 3010, 2955, 2880, 1755, 1500, 1455, 1365, 1205, 1170, 1070, 1025, 995, 905, 875, 695, 595 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.83 (3H, s), 0.97 (3H, s), 1.00 (3H, s), 1.57 (3H, s), 1.97 (3H, s), 2.00 (3H, s), 2.05 (3H, s), 3.09 (1H, dd, *J* = 12.0, 4.4 Hz), 3.13 (1H, dd, *J* = 11.5, 9.8 Hz), 3.29 (1H, t, *J* = 8.2 Hz), 3.50 (1H, t, *J* = 8.8 Hz), 3.55 (1H, m), 3.71 (1H, ddd, *J* = 9.8, 4.7, 2.6 Hz), 3.78 (1H, dd, *J* = 8.6, 7.6 Hz), 3.91 (1H, dd, *J* = 11.5, 4.9 Hz), 4.12 (1H, dd, *J* = 12.0, 2.4 Hz), 4.24 (1H, dd, *J* = 12.1, 4.8 Hz), 4.46 (1H, d, *J* = 9.0 Hz), 4.48 (1H, d, *J* = 9.0 Hz), 4.59 (1H,d, *J* = 11.2 Hz), 4.61 (1H, d, *J* = 11.5 Hz), 4.71 (1H, d, *J* = 11.5 Hz), 4.79 (1H, d, *J* = 13.0 Hz), 4.79 (1H, d, *J* = 11.0 Hz), 4.83 (1H, d, *J* = 11.0 Hz), 4.97 (1H, t, *J* = 9.8 Hz), 5.25 (1H, t, *J* = 9.4 Hz), 6.28 (1H, dd, *J* = 1.7, 1.0 Hz), 7.22 (1H, br s), 7.22-7.33 (15H, m), 7.34 (1H, t, *J* = 2.0, 1.5 Hz); ^{13}C NMR (100 MHz in $CDCl_3$) 15.9 q, 18.7 t, 19.5 q, 20.1 q, 20.1 q, 20.7 q, 20.8 q, 25.8 t, 26.6 t, 27.6 q, 28.9 t, 33.8 t, 35.3 t, 38.6 s, 39.5 s, 51.5 d, 62.4 t, 63.7 t, 69.1 d, 71.3 d, 73.3 d, 75.1 d, 75.2 t, 75.7 t, 78.3 d, 82.0 d, 84.0 d, 91.3 d, 103.9 d, 104.1 d, 110.8 d, 125.5 s, 126.7 s, 127.5-128.5 (many d), 138.2 s, 138.4 s, 138.5 d, 138.6 s, 139.6 s, 142.7 d, 169.8 s, 170.2 s, 170.7 s; MS (FD) *m/z* 993 (M^++1), and **15p** as a colorless solid: T*r* 11.6 min; $[\alpha]_D^{19}$ +51.4° (*c* 0.77, $CHCl_3$); IR ($CHCl_3$) 3020, 2995, 2880, 1755, 1500, 1445, 1365, 1205, 1070, 1165, 1030, 990, 875, 720, 695, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.80 (3H, s), 0.94 (3H, s), 0.97 (3H, s), 1.58 (3H, s), 1.99 (3H, s), 2.01 (3H, s), 2.07 (3H, s), 3.15 (1H, dd, *J* = 11.7, 4.4 Hz), 3.43 (1H, dd, *J* = 9.8, 3.2 Hz), 3.52-3.63 (3H, m), 3.68 (1H, ddd, *J* = 10.0, 5.4, 2.4 Hz), 3.75-3.82 (2H, m), 4.09 (1H, dd, *J* = 12.0, 2.4 Hz), 4.28 (1H, dd, *J* = 12.0, 5.4 Hz), 4.57 (1H, d, *J* = 11.5 Hz), 4.59 (1H, d, *J* = 7.6 Hz), 4.68 (1H, d, *J* = 12.7 Hz), 4.72 (1H, d, *J* = 11.5 Hz), 4.76 (1H, d, *J* = 12.0 Hz), 4.79 (1H, d, *J* = 11.0 Hz), 4.82 (1H, d, *J* = 11.0 Hz), 4.98 (1H, t, *J* = 9.8 Hz), 5.25 (1H, t, *J* = 9.3 Hz), 5.28 (1H, d, *J* = 3.2 Hz), 6.28 (1H, dd, *J* = 1.7, 0.7 Hz), 7.23 (1H, br s), 7.24-7.33 (15H, m), 7.35 (1H, t, *J* = 1.7 Hz); ^{13}C NMR (100 MHz in $CDCl_3$) 16.4 q, 18.6 t, 19.4 q, 20.1 q, 20.7 q, 20.7 q, 20.9 q, 25.8 t, 26.5 t, 28.2 q, 28.8 t, 33.7 t, 35.4 t, 38.5 s, 39.0 s, 51.5 d, 60.6 t, 62.4 t, 69.4 d, 71.2 d, 73.4 d, 73.6 d, 73.8 t, 74.8 t, 75.6 d, 78.0 d, 79.4 d, 80.8 d, 89.5 d, 96.5 d, 104.3 d, 110.8 d, 125.5 s, 126.7 s, 127.6-128.5 (many d), 138.4 s, 138.4 d, 138.7 s, 139.5 s, 142.7 d, 169.8 s, 170.2 s, 170.6 s; MS (FD) *m/z* 992 (M^+).

Baiyunoside (1). To a stirred solution of metallic lithium (36 mg, 5.2 mg atom) in liquid ammonia (10 ml) was dropwise added a solution of **1p** (50.4 mg, 0.051 mmol) in THF at -78° C, and the mixture was stirred at -78° C for 30 min and at -33° C for an additional 1 h. To the resulting dark blue solution, isoprene (0.1 ml) was added to give white suspension. Methanol (3 ml) was added and the mixture was stirred at room temperature for 6 h. The solution was neutralized by the addition of Amberlite IR-120B, and filtrated through cotton-Celite pad. The concentrated material was subjected to column chromatography on silica gel with a mixture of methanol and chloroform (1:5) as an eluant to afford baiyunoside (**1**) (23.5 mg, 78 % yield) as a colorless semi-solid. The spectral properties were indistinguishable from those of natural product.

Disaccharide 15. According to the same procedure described above, **15p** (9.5 mg, 0.0096 mmol) was converted to **15** (4.7 mg, 82% yield) as a colorless solid: $[\alpha]_D^{19}$ +24.5° (*c* 0.40, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.93 (3H, s), 1.12 (3H, s), 1.40 (3H, s), 1.59 (3H, s), 3.53 (1H, dd, *J* = 10.7, 4.6 Hz), 3.88 (1H, m), 4.16 (1H, dd, *J* = 11.0, 5.4 Hz), 4.17-4.30 (4H, m), 4.32 (1H, t, *J* = 8.5 Hz), 4.37 (1H, dd, *J* = 11.7, 5.6 Hz), 4.56 (1H, dd, *J* = 11.5, 2.0 Hz), 4.64 (1H, t, *J* = 8.8 Hz), 5.00 (1H, d, *J* = 7.3 Hz), 5.15 (1H, t, *J* = 10.7 Hz), 6.19 (1H, d, *J* = 3.2 Hz), 6.52 (1H, br s), 7.56 (1H, br s), 7.65 (1H, br s); ^{13}C NMR (100 MHz in

C_5D_5N) 17.0 q, 18.9 t, 19.5 q, 20.2 q, 26.1 t, 27.2 t, 28.5 q, 29.0 t, 34.1 t, 35.4 t, 38.7 s, 39.4 s, 51.5 d, 62.8 t, 64.0 t, 71.8 d, 72.2 d, 74.1 d, 75.4 d, 77.0 d, 78.2 d, 78.8 d, 88.0 d, 99.3 d, 105.8 d, 111.6 d, 126.2 s, 126.6 s, 139.1 d, 140.0 s, 143.3 d.

Xylosylation of 9s with 12 (Preparation of 16p). According to the same procedure with xylosylation of **8s**, **9s** (65.0 mg, 0.0993 mmol) and **12** (70 mg, 0.165 mmol) in toluene (1 ml) was treated in the presence of trimethylsilyl triflate (2.4 mg, 0.011 mmol) to give β-xyloside **16p** (44.8 mg, 45% yield): $[\alpha]_D^{21}$ +66.2° (*c* 2.35, $CHCl_3$); ^1H NMR (400 MHz in $CDCl_3$) 0.88 (3H, s), 0.96 (3H, s), 1.03 (3H, s), 1.60 (3H, s), 1.86 (3H, s), 2.02 (3H, s), 2.06 (3H, s), 3.17 (2H, m), 3.30 (1H, dd, *J* = 8.5, 7.8 Hz), 3.52 (1H, t, *J* = 9.0 Hz), 3.58 (1H, dd, *J* = 9.8, 5.1 Hz), 3.80 (1H, dd, *J* = 10.3, 3.7 Hz), 3.92 (1H, dd, *J* = 11.7, 5.1 Hz), 4.07 (1H, br d, *J* = 10.5 Hz), 4.22 (1H, m), 4.26 (1H, dd, *J* = 11.7, 4.9 Hz), 4.43 (1H, d, *J* = 7.6 Hz), 4.62 (2H, d, *J* = 11.5 Hz), 4.71 (1H, d, *J* = 11.5 Hz), 4.79 (1H, d, *J* = 11.7 Hz), 4.83 (1H, d, *J* = 11.0 Hz), 4.86 (1H, d, *J* = 11.0 Hz), 4.96 (1H, t, *J* = 9.6 Hz), 5.07 (1H, d, *J* = 3.7 Hz), 5.45 (1H, t, *J* = 9.8 Hz), 6.30 (1H, br s), 7.25-7.35 (17H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.7 q, 18.8 t, 19.4 q, 20.1 q, 20.7 q, 20.7 q, 20.7 q, 23.8 t, 25.7 t, 28.8 q, 28.8 t, 33.8 t, 34.9 t, 38.7 s, 38.7 s, 51.5 d, 62.3 t, 63.8 t, 67.8 d, 69.1 d, 72.2 d, 73.3 t, 74.5 t, 75.8 t, 75.9 d, 77.0 d, 81.2 d, 83.7 d, 87.5 d, 97.5 d, 105.1 d, 110.9 d, 125.5 s, 126.7 s, 127.5-128.5d (many d), 138.1 s, 138.4 d, 138.4 s, 138.5 s, 139.5 s, 142.7 d, 170.0 s, 170.3 s, 170.7 s, along with **9p** (23.8 mg, 41% yield) after silica gel column chromatography.

Disaccharide 16. According to the same procedure described for the deprotection of **1p**, **16p** (17.2 mg, 0.0173 mmol) was treated to give **16** (7.5 mg, 73% yield) as a colorless syrup: $[\alpha]_D^{19}$ +74.9° (*c* 0.36, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.86 (3H, s), 0.93 (3H, s), 1.15 (3H, s), 1.56 (3H, s), 3.45 (1H, dd, *J* = 12.0, 4.4 Hz), 3.70 (1H, t, *J* = 10.0 Hz), 4.07 (1H, dd, *J* = 10.0, 3.4 Hz), 4.13 (1H, t, *J* = 8.5 Hz), 4.24-4.32 (3H, m), 4.36 (1H, dd, *J* = 11.5, 5.2 Hz), 4.31-4.54 (3H, m), 4.70 (1H, t, *J* = 9.8 Hz), 5.03 (1H, d, *J* = 7.6 Hz), 5.61 (1H, d, *J* = 3.7 Hz), 6.55 (1H, br s), 7.60 (1H, br s), 7.66 (1H, t, *J* = 1.5 Hz); ^{13}C NMR (100 MHz in C_5D_5N) 17.1 q, 19.0 t, 19.5 q, 20.1 q, 23.7 t, 26.0 t, 29.0 q, 29.1 t, 33.9 t, 35.0 t, 39.0 s, 39.0 s, 51.6 d, 62.8 t, 67.8 t, 71.0 d, 72.0 d, 74.2 d, 74.7 d, 75.4 d, 78.2 d, 82.9 d, 85.4 d, 97.6 d, 107.6 d, 111.6 d, 126.1 s, 126.6 s, 139.2 d, 140.0 s, 143.4 d; HRMS (FAB) *m/z* 619.3083 (found), calcd for $C_{31}H_{48}O_{11}Na$ 619.3014.

Xylosylation of 10s with 12 (Preparation of 17p and 18p). According to the same procedure described for the xylosylation of **8s**, **10s** (64.7 mg, 0.0988 mmol) was treated with **12** (70 mg, 0.165 mmol) and trimethylsilyl triflate (2.4 mg, 0.011 mmol) in toluene (1 ml), and a crude disaccharide (55.3 mg, 56% yield, **17p**:**18p** = 71:29) was obtained along with **10p** (18.5 mg, 32% yield). The disaccharide was subjected to HPLC with Develosil ODS-5 (4.6 × 250 mm) column using a mixture of acetonitrile and water (40:1) in a flow rate of 1.5 ml/min to give **17p** as a colorless solid: Tr 9.4 min; $[\alpha]_D^{21}$ -10.8° (*c* 0.78, $CHCl_3$); ^1H NMR (400 MHz in $CDCl_3$) 0.79 (3H, s), 0.96 (3H, s), 1.01 (3H, s), 1.61 (3H, s), 1.89 (3H, s), 2.00 (3H, s), 2.05 (3H, s), 3.22-3.28 (2H, m), 3.31 (1H, dd, *J* = 8.8, 6.8 Hz), 3.55-3.61 (2H, m), 3.68 (1H, ddd, *J* = 10.0, 4.9, 2.4 Hz), 3.81 (1H, dd, *J* = 8.8, 7.3 Hz), 3.94 (1H, dd, *J* = 12.2, 4.4 Hz), 4.12 (1H, dd, *J* = 12.0, 2.4 Hz), 4.21 (1H, dd, *J* = 12.0, 4.9 Hz), 4.53 (1H, d, *J* = 7.3 Hz), 4.61 (1H, d, *J* = 11.5 Hz), 4.63 (1H, d, *J* = 6.6 Hz), 4.65 (1H, d, *J* = 11.2 Hz), 4.69 (1H, d, *J* = 11.5 Hz), 4.76 (1H, d, *J* = 11.2 Hz), 4.79 (1H, d, *J* = 11.7 Hz), 4.82 (1H, d, *J* = 11.2 Hz), 5.03 (1H, t, *J* = 9.8 Hz), 5.24 (1H, t, *J* = 9.0 Hz), 6.30 (1H, br s), 7.24-7.36 (17H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.5 q, 18.8 t, 19.5 q, 20.2 q, 20.8 q, 20.8 q, 20.9 q, 23.3 t, 25.8 t, 28.1 q, 28.8 t, 33.8 t, 34.9 t, 38.3 s, 38.7 s, 51.7 d, 62.4 t, 63.4 t, 69.4 d, 71.1 d, 72.9 t, 74.7

t, 75.1 d, 75.3 t, 76.1 d, 78.3 d, 81.8 d, 83.3 d, 85.3 d, 99.1 d, 103.0 d, 110.8 d, 125.5 s, 126.8 s, 127.5-128.5 (many d), 138.1 s, 138.4 s, 138.4 d, 138.6 s, 139.4 s, 142.7 d, 169.8 s, 170.3 s, 170.7 s, and **18p** as a colorless solid: T*r* 10.8 min; $[\alpha]_D^{16}$ +23.0° (*c* 0.43, $CHCl_3$); IR ($CHCl_3$) 2950, 2860, 1750, 1600, 1490, 1450, 1360, 1230, 1155, 1065, 1020, 870, 690, 590 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.77 (3H, s), 0.87 (3H, s), 0.96 (3H, s), 1.61 (3H, s), 2.03 (6H, s), 2.06 (3H, s), 3.30 (1H, dd, *J* = 12.0, 4.4 Hz), 3.43 (1H, dd, *J* = 9.8, 3.4 Hz), 3.51-3.65 (4H, m), 3.77-3.81 (2H, m), 4.14 (1H, dd, *J* = 12.0, 2.7 Hz), 4.20 (1H, dd, *J* = 12.0, 4.6 Hz), 4.56 (1H, d, *J* = 11.7 Hz), 4.63 (1H, d, *J* = 7.8 Hz), 4.71 (1H, d, *J* = 11.7 Hz), 4.73 (1H, d, *J* = 12.2 Hz), 4.78 (1H, d, *J* = 12.2 Hz), 4.82 (1H, d, *J* = 11.0 Hz), 4.86 (1H, d, *J* = 11.0 Hz), 5.02 (1H, t, *J* = 9.8 Hz), 5.31 (1H, t, *J* = 9.5 Hz), 5.44 (1H, d, *J* = 3.4 Hz), 6.29 (1H, br s), 7.21-7.34 (16H, m), 7.37 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 16.6 q, 18.8 t, 19.4 q, 20.1 q, 20.7 q, 20.8 q, 20.9 q, 23.3 t, 25.7 t, 28.0 q, 28.8 t, 33.7 t, 34.7 t, 38.0 s, 38.6 s, 51.6 d, 60.4 t, 62.2 t, 69.4 d, 71.3 d, 72.5 d, 73.2 t, 73.4 t, 73.5 d, 75.7 t, 78.0 d, 79.2 d, 80.8 d, 84.0 d, 95.4 d, 99.7 d, 110.8 d, 125.5 s, 126.8 s, 127.4-128.5 (many d), 138.3 s, 138.4 d, 138.4 s, 138.7 s, 139.3 s, 142.7 d, 169.9 s, 170.2 s, 170.6 s.

Disaccharide 17. According to the same procedure for the deprotection of **1p**, **17p** (14 mg, 0.014 mmol) was treated to give **17** (8.2 mg, 98% yield) as a colorless solid: $[\alpha]_D^{20}$ -44.3° (*c* 0.275, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 1.00 (3H, s), 1.06 (3H, s), 1.22 (3H, s), 1.61 (3H, s), 3.59 (1H, dd, *J* = 11.7, 4.4 Hz), 3.82 (1H, dd, *J* = 11.2, 9.3 Hz), 3.97 (1H, ddd, *J* = 9.5, 5.6, 2.7 Hz), 4.11-4.30 (5H, m), 4.37 (1H, t, *J* = 9.0 Hz), 4.38 (1H, dd, *J* = 12.0, 5.9 Hz), 4.54 (1H, dd, *J* = 11.7, 4.9 Hz), 4.59 (1H, dd, *J* = 11.7, 2.2 Hz), 5.05 (1H, d, *J* = 7.6 Hz), 5.27 (1H, d, *J* = 7.1 Hz), 6.57 (1H, br s), 7.62 (1H, br s), 7.66 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 16.9 q, 19.1 t, 19.5 q, 20.2 q, 23.5 t, 26.1 t, 28.5 q, 29.2 t, 34.0 t, 34.9 t, 38.5 s, 38.9 s, 51.7 d, 62.9 t, 67.4 t, 71.1 d, 71.9 d, 76.2 d, 77.4 d, 78.1 d, 78.3 d, 83.9 d, 84.1 d, 99.7 d, 106.8 d, 111.5 d, 126.1 s, 126.6 s, 139.2 d, 140.0 s, 143.4 d.

Disaccharide 18. According to the same procedure for the deprotection of **1p**, **18p** (56.4 mg, 0.086 mmol) was treated to give **18** (3.1 mg, 85% yield) as a colorless solid: $[\alpha]_D^{20}$ +0.6° (*c* 0.15, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.94 (3H, s), 1.04 (3H, s), 1.17 (3H, s), 1.60 (3H, s), 3.67 (1H, dd, *J* = 12.0, 4.2 Hz), 3.95 (1H, dd, *J* = 6.1, 5.9 Hz), 4.15-4.31 (6H, m), 4.37 (1H, dd, *J* = 11.5, 5.9 Hz), 4.59-4.64 (2H, m), 5.09-5.13 (2H, m), 6.11 (1H, d, *J* = 3.4 Hz), 6.56 (1H, br s), 7.61 (1H, br s), 7.67 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 17.1 q, 19.1 t, 19.5 q, 20.1 q, 23.3 t, 26.1 t, 28.5 q, 29.2 t, 34.0 t, 34.9 t, 38.4 s, 38.8 s, 51.6 d, 63.2 t, 63.8 t, 71.8 d, 72.5 d, 74.4 d, 75.7 d, 77.1 d, 78.4 d, 78.8 d, 83.5 d, 99.6 d, 100.6 d, 111.5 d, 126.2 s, 126.6 s, 139.2 d, 139.9 s, 143.4 d; MS (FAB) *m/z* 619 (M^++ Na).

Xylosylation of 11p with 12 (Preparation of 19p). According to the same procedure for the glycosylation of **8s**, **11s** (6.1 mg, 0.0061 mmol) was treated with **12** (60 mg, 0.147 mmol) in the presence of trimethyl triflate (2.1 mg, 0.0095 mmol) in toluene (1 ml) to give β-xyloside **19p** (9.3 mg, 11% yield) as a colorless solid: $[\alpha]_D^{21}$ +18.5° (*c* 3.32, $CHCl_3$); IR ($CHCl_3$) 3427, 3063, 3032, 2928, 1751, 1660, 1602, 1496, 1454, 1367, 1317, 1236, 1168, 1087, 1030, 914, 738, 700, 601 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.89 (3H, s), 0.98 (3H, s), 1.06 (3H, s), 1.58 (3H, s), 1.83 (3H, s), 2.02 (3H, s), 2.08 (3H, s), 3.15 (1H, dd, *J* = 12.2, 4.4 Hz), 3.17 (1H, t, *J* = 11.7 Hz), 3.29 (1H, dd, *J* = 8.3, 8.1 Hz), 3.51 (1H, t, *J* = 8.8 Hz), 3.56 (1H, dd, *J* = 9.8, 5.4 Hz), 3.79 (1H, dd, *J* = 10.3, 3.7 Hz), 3.91 (1H, dd, *J* = 11.9, 5.4 Hz), 4.07 (1H, dd, *J* = 12.2, 2.0 Hz), 4.19 (1H, ddd, *J* = 10.0, 4.6, 2.0 Hz), 4.27 (1H, dd, *J* = 12.2, 4.4 Hz), 4.42 (1H, d, *J* = 7.6 Hz), 4.58 (1H, d, *J* = 11.5 Hz), 4.62 (1H, d, *J* = 11.7 Hz), 4.72 (1H, d, *J* = 11.7 Hz), 4.80 (1H, d, *J* = 11.5

Hz), 4.83 (2H, s), 4.97 (1H, t, J= 9.8 Hz), 5.07 (1H, d, J= 3.7 Hz), 5.50 (1H, t, J= 10.0 Hz), 6.28 (1H, br s), 7.22 (1H, br s), 7.25-7.33 (15H, m), 7.35 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 16.6 q, 18.7 t, 19.5 q, 20.1 q, 20.7 q, 20.7 q, 20.8 q, 25.8 t, 26.1 t, 28.0 q, 28.8 t, 33.8 t, 35.1 t, 38.5 s, 39.4 s, 51.4 d, 62.2 t, 63.9 t, 67.3 d, 69.2 d, 72.2 d, 73.4 t, 74.9 t, 75.9 t, 76.4 d, 78.1 d, 81.9 d, 83.8 d, 90.0 d, 100.9 d, 105.2 d, 110.8 d, 125.5 s, 126.9 s, 127.5-128.5 (many d), 138.4 s, 138.4 d, 138.5 s, 138.5 s, 139.4 s, 142.7 d, 170.0 s, 170.4 s, 170.7 s, along with **11p** (34.3 mg, 68% yield).

Disaccharide 19. According to the same procedure described for the deprotection of **1p**, **19p** (9.0 mg, 0.0091 mmol) was treated to give **19** (1.5 mg, 28% yield) as a colorless solid: $[\alpha]_D^{19}$ +1.9° (c 0.065, CH_3OH); ^{1}H NMR (400 MHz in C_5D_5N) 0.73 (3H, s), 0.76 (3H, s), 1.06 (3H, s), 1.35 (3H, s), 1.94-1.99 (1H, m), 2.07-2.15 (2H, m), 2.25-2.32 (2H, m), 3.11 (1H, dd, J= 11.6, 3.9 Hz), 3.48 (1H, t, J= 10.5 Hz), 3.85 (1H, dd, J= 11.5, 3.9 Hz), 3.88 (1H, t, J= 7.7 Hz), 3.96 (1H, t, J= 8.8 Hz), 3.99-4.07 (2H, m), 4.14 (1H, dd, J = 11.0, 5.0 Hz), 4.21-4.32 (2H, m), 4.36 (1H, br d, J= 11.0 Hz), 4.48 (1H, t, J= 9.4 Hz), 4.89 (1H, d, J= 7.2 Hz), 5.36 (1H, d, J= 3.9 Hz), 6.37 (1H, br s), 7.44 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 16.8 q, 18.9 t, 19.5 q, 20.1 q, 26.0 t, 26.5 t, 28.2 q, 29.7 t, 33.9 t, 35.2 t, 38.7 s, 39.6 s, 51.6 d, 63.0 t, 67.3 t, 71.0 d, 72.2 d, 74.1 d, 74.2 d, 75.7 d, 78.4 d, 83.1 d, 89.5 d, 102.3 d, 107.4 d, 111.5 d, 126.1 s, 126.6 s, 139.1 d, 140.0 s, 143.4 d; HRMS (FAB) m/z 619.3074 (found), calcd for $C_{31}H_{48}O_{11}Na$ 619.3095.

Rhamnosylation of 8s with 13 (Preparation of 2p). To a stirred solution of **8s** (99.5 mg, 0.152 mmol) and 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl fluoride (**13**) in toluene (7 ml) was refluxed through 4A molecular sieves (5 g) for 6 h in order to remove contaminating water. After the mixture became cool to room temperature, trimethylsilyl triflate (3.3 mg, 0.015 mmol) was added, and stirring was continued for 24 h at room temperature. Aqueous work-up and the concentrated dichloromethane extract was subjected to silica gel column chromatography to give **2p** (34 mg, 22% yield) as colorless solid: $[\alpha]_D^{14}$ +6.4° (c 1.64, $CHCl_3$); IR ($CHCl_3$) 3000, 2950, 2870, 1750, 1600, 1495, 1450, 1365, 1220, 1180, 1130, 875, 690, 595 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) 0.87 (3H, s), 0.96 (3H, s), 0.97 (3H, s), 1.30 (3H, d, J= 6.1 Hz), 1.61 (3H, s), 2.01 (3H, s), 2.07 (3H, s), 2.18 (3H, s), 3.11 (1H, dd, J= 11.7, 4.4 Hz), 3.59 (1H, t, J= 9.3 Hz), 3.66 (1H, m), 3.75 (1H, br s), 3.81 (1H, m), 3.83 (1H, t, J= 8.5 Hz), 4.05 (1H, m), 4.06 (1H, dd, J=12.2, 2.3 Hz), 4.28 (1H, dd, J= 12.0, 5.4 Hz), 4.49 (1H, d, J= 7.3 Hz), 4.55-4.77 (5H, m), 4.94 (1H, d, J= 11.5 Hz), 5.00 (1H, t, J = 9.8 Hz), 5.07 (1H, br s), 5.20 (1H, t, J= 8.8 Hz), 6.29 (1H, br s), 7.23-7.35 (17H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.3 q, 17.9 q, 18.6 t, 19.4 q, 20.1 q, 20.6 q, 20.7 q, 20.9 q, 25.8 t, 26.5 t, 27.9 q, 28.8 t, 33.8 t, 35.5 t, 38.5 s, 39.1 s, 51.8 d, 62.4 t, 68.6 d, 69.2 d, 71.2 d, 72.3 t, 72.8 t, 74.3 d, 74.7 t, 74.9 d, 75.8 d, 79.6 d, 80.5 d, 90.3 d, 97.9 d (J= 172 Hz), 104.0 d (J= 161 Hz), 110.8 d, 125.4 s, 126.7 s, 127.2-128.6 (many d), 138.2 s, 138.4 d, 138.5 s, 139.0 s, 139.5 s, 142.7 d, 169.6 s, 170.1 s, 170.6 s, along with **8p** (49.4 mg, 55% yield).

Phlomisoside I (2). According to the same procedure for the deprotection of **1p**, **2p** (31.2 mg, 0.031 mmol) was converted to **2** (10.7 mg, 57% yield) as a colorless solid. The spectral properties were indistinguishable from those of natural product.

Rhamnosylation of 9s with 13 (Preparation of 20p). According to the same procedure for the rhamnosylation of **8s**, **9s** (147.6 mg, 0.255 mmol) and **13** (98 mg, 0.225 mmol) was treated with trimethylsilyl triflate (5.0 mg, 0.0225 mmol) to give **20p** (47.6 mg, 21% yield) as a colorless solid: $[\alpha]_D^{25}$ +21.0° (c 1.39,

$CHCl_3$); IR ($CHCl_3$) 3010, 2950, 2870, 1750, 1600, 1500, 1455, 1370, 1230, 1090, 1060, 1030, 875, 695, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.85 (3H, s), 0.89 (3H, s), 1.05 (3H, s), 1.30 (3H, d, J= 6.4 Hz), 1.60 (3H, s), 1.76 (3H, s), 2.02 (3H, s), 2.08 (3H, s), 3.23 (1H, dd, J= 12.0, 3.8 Hz), 3.60 (1H, t, J= 9.0 Hz), 3.65 (1H, m), 3.72-3.80 (3H, m), 4.02-4.05 (2H, m), 4.26 (1H, dd, J= 12.5, 4.4 Hz), 4.60-4.77 (5H, m), 4.82 (1H, br s), 4.95 (1H, d, J= 11.5 Hz), 4.95 (1H, t, J= 10.0 Hz), 5.12 (1H, d, J= 3.7 Hz), 5.33 (1H, t, J= 9.8 Hz), 6.26 (1H, br s), 7.21 (1H, br s), 7.25-7.36 (16H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.5 q, 17.9 q, 18.7 t, 19.4 q, 20.0 q, 20.6 q, 20.7 q, 20.7 q, 21.8 t, 25.7 t, 28.6 t, 28.8 q, 33.8 t, 34.8 t, 38.6 s, 38.7 s, 51.4 d, 62.0 t, 67.6 d, 68.7 d, 68.8 d, 72.3 t, 72.6 d, 72.7 d, 74.3 t, 74.6 d, 76.0 t, 80.0 d, 80.2 d, 82.5 d, 93.3 d, 100.3 d, 110.8 d, 125.4 s, 126.8 s, 127.1-128.4 (many d), 138.2 s, 138.3 s, 138.4 d, 139.0 s, 139.4 s, 142.7 d, 169.9 s, 169.9 s, 170.6 s, along with **9p** (44.2 mg, 33% yield).

Disaccharide 20. According to the same procedure for the deprotection of **1p**, **20p** (26.6 mg, 0.026 mmol) was converted to **20** (13.8 mg, 87% yield) as a colorless solid: $[\alpha]_D^{20}$ +47.2° (*c* 0.57, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.92 (3H, s), 1.00 (3H, s), 1.18 (3H, s), 1.59 (3H, s), 1.74 (3H, d, J= 6.1 Hz), 3.65 (1H, dd, J= 11.7, 3.7 Hz), 4.22 (1H, t, J= 9.0), 4.28 (1H, dd, J= 9.8, 3.7 Hz), 4.35 (1H, t, J= 9.3 Hz), 4.43-4.54 (3H, m), 4.58-4.60 (2H, m), 4.72 (1H, t, J= 9.3 Hz), 4.78 (1H, br s), 5.70 (1H, d, J= 3.7 Hz), 6.00 (1H, s), 6.52 (1H, s), 7.61 (1H, s), 7.66 (1H, s); ^{13}C NMR (22.5 MHz in C_5D_5N) 17.0, 18.7, 18.7, 19.5, 20.3, 22.4, 26.0, 28.9, 29.0, 33.9, 34.9, 39.0, 51.4, 63.1, 70.1, 72.2, 72.5, 72.8, 73.9, 74.5, 74.7, 79.6, 81.7, 94.9, 103.9, 111.5, 126.1, 126.6, 139.2, 140.0, 143.3; MS (FAB) *m/z* 633 (M^++ Na).

Rhamnosylation of 10s with 13 (Preparation of 21p). According to the same procedure for the rhamnosylation of **8s**, **10s** (174 mg, 0.266 mmol) was treated with **13** (116 mg, 0.226 mmol) and trimethyl triflate (5.9 mg, 0.0226 mmol) in toluene (5 ml) to give **21p** (81.6 mg, 30% yield): $[\alpha]_D^{20}$ -18.8° (*c* 5.49, $CHCl_3$); IR ($CHCl_3$) 2950, 2890, 1750, 1500, 1460, 1370, 1230, 1090, 1055, 1040, 880, 700, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.71 (3H, s), 0.77 (3H, s), 0.96 (3H, s), 1.28 (3H, d, J= 6.1 Hz), 1.59 (3H, s), 1.95 (3H, s), 2.00 (3H, s), 2.06 (3H, s), 3.13 (1H, dd, J= 11.7, 4.6 Hz), 3.55-3.60 (2H, m), 3.76-3.79 (2H, m) 3.81 (1H, dd, J= 8.6, 8.3 Hz), 4.08 (1H, dd, J= 12.2, 2.7 Hz), 4.19-4.23 (2H, m), 4.34 (1H, d, J = 7.8 Hz), 4.51 (1H, d, J= 12.2 Hz), 4.59 (1H, d, J= 12.2), 4.63 (1H, d, J= 11.2 Hz), 4.68 (1H, d, J= 12.5 Hz), 4.72 (1H, d, J= 12.7 Hz), 4.95 (1H, d, J= 12.0 Hz), 4.97 (1H, t, J= 9.3 Hz), 4.99 (1H, br s), 5.19 (1H, t, J= 9.3 Hz), 6.30 (1H, br s), 7.18-7.36 (17H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.7 q, 18.2 q, 18.8 t, 19.4 q, 19.8 q, 20.6 q, 20.8 q, 20.9 q, 23.7 t, 25.7 t, 28.1 q, 28.8 t, 33.8 t, 34.9 t, 38.1 s, 38.6 s, 51.8 d, 62.3 t, 68.1 d, 69.2 d, 71.2 d, 71.5 t, 72.5 t, 72.8 d, 74.5 d, 75.2 t, 76.3 d, 79.1 d, 80.6 d, 86.7 d, 97.2 d (J= 170 Hz), 99.7 d (J= 162 Hz), 110.8 d, 125.5 s, 126.7 s, 127.2-128.4 (many d), 138.2 s, 138.4 s, 138.5 s, 139.0 d, 139.4 s, 142.8 d, 169.6 s, 170.1 s, 170.6 s, along with **10p** (55.6 mg, 35% yield).

Disaccharide 21. According to the same procedure for the deprotection of **1p**, **21p** (77.7 mg, 0.077 mmol) was converted to **21** (23.7 mg, 50% yield) as a colorless solid: $[\alpha]_D^{20}$ -55.0° (*c* 0.48, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 1.04 (3H, s), 1.16 (3H, s), 1.24 (3H, s), 1.61 (3H, s), 1.74 (3H, d, J= 6.1 Hz), 3.47 (1H, dd, J= 11.7, 3.9 Hz), 3.96 (1H, m), 4.16 (1H, m), 4.32-4.40 (5H, m), 4.58 (1H, dd, J= 11.2, 2.2 Hz), 4.66 (1H, dd, J= 9.3, 3.4 Hz), 4.83 (1H, br s), 4.88 (1H, d, J= 6.1 Hz), 4.95 (1H, m), 6.60 (1H, s), 7.66 (1H, s), 7.69 (1H, t, J= 1.5 Hz); ^{13}C NMR (100 MHz in C_5D_5N) 17.4 q, 19.0 q, 19.1 t, 19.5 q, 20.1 q, 24.2 t, 26.0 t, 28.5 q, 29.2 t, 34.0 t, 35.0 t, 38.5 s, 38.9 s, 51.8 d, 63.0 t, 69.0 d, 72.1 d, 72.4 d, 72.6 d, 74.2 d, 75.8 d, 78.2 d, 80.2 d, 86.0 d, 101.0 d, 101.1 d, 111.5 d, 126.2 s, 126.5 s, 139.2 s, 139.9 s, 143.4 s; HRMS (FAB) *m/z* 633.3240 (found), calcd for $C_{32}H_{50}O_{11}$ 633.3255.

Rhamnosylation of 11s with 13 (Preparation of 22p). According to the same procedure for the rhamnosylation of **8s**, **11s** (117 mg, 0.179 mmol) was treated with **13** (78 mg, 0.179 mmol) and trimethylsilyl triflate (4.0 mg, 0.0179 mmol) in toluene (5 ml) to give **22p** (41.5 mg, 23% yield) as a colorless solid: $[\alpha]_D^{23}$ +4.6° (*c* 0.60, $CHCl_3$); IR ($CHCl_3$) 2950, 2870, 1750, 1605, 1500, 1455, 1370, 1230, 1090, 1060, 1025, 875, 695, 595 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.87 (3H, s), 0.98 (3H, s), 1.05 (3H, s), 1.29 (3H, d, *J* = 6.1 Hz), 1.61 (3H, s), 1.79 (3H, s), 2.02 (3H, s), 2.08 (3H, s), 3.10 (1H, dd, *J* = 12.0, 4.4 Hz), 3.59 (1H, t, *J* = 9.3 Hz), 3.67-3.70 (2H, m), 3.78 (1H, dd, *J* = 10.3, 3.4 Hz), 3.82 (1H, dd, *J* = 9.0, 2.9 Hz), 4.06 (1H, br d, *J* = 12.2 Hz), 4.13 (1H, m), 4.27 (1H, dd, *J* = 12.2, 4.4 Hz), 4.59 (1H, d, *J* = 10.0 Hz), 4.60 (1H, d, *J* = 10.0 Hz), 4.64 (1H, d, *J* = 11.7 Hz), 4.67 (1H, d, *J* = 12.7 Hz), 4.72 (1H, d, *J* = 12.7 Hz), 4.89 (1H, br s), 4.93 (1H, d, *J* = 4.9 Hz), 4.95 (1H, t, *J* = 9.5 Hz), 4.96 (1H, d, *J* = 12.0 Hz), 5.37 (1H, t, *J* = 9.8 Hz), 6.28 (1H, br s), 7.22 (1H, br s), 7.26-7.30 (15H, m), 7.35 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 16.6 q, 18.0 q, 18.6 t, 19.4 q, 20.1 q, 20.7 q, 20.7 q, 20.7 q, 25.6 t, 25.7 t, 28.5 q, 28.8 t, 33.7 t, 35.0 t, 38.4 s, 39.1 s, 51.2 d, 62.1 t, 67.5 d, 68.8 d, 69.0 d, 72.5 t, 72.5 d, 72.8 t, 74.6 t, 74.8 d, 75.7 d, 79.6 d, 80.1 d, 90.7 d, 99.9 d (*J* = 170 Hz), 100.3 d (*J* = 172 Hz), 110.8 d, 125.5 s, 126.9 s, 127.3-128.4 (many d), 138.2 s, 138.4 d, 138.4 s, 139.0 s, 139.3 s, 142.7 d, 169.9 s, 170.1 s, 170.7 s, along with **11p** (33.3 mg, 31% yield).

Disaccharide 22. According to the same procedure for the deprotection of **1p**, **22p** (11.3 mg, 0.011 mmol) was converted to **22** (5.4 mg, 80% yield) as a colorless solid: $[\alpha]_D^{23}$ +2.4° (*c* 0.22, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.90 (3H, s), 0.95 (3H, s), 1.33 (3H, s), 1.61 (3H, s), 1.74 (3H, d, *J* = 5.9 Hz), 3.30 (1H, dd, *J* = 11.7, 3.7 Hz), 4.22 (1H, t, *J* = 9.5 Hz), 4.33 (1H, dd, *J* = 10.3, 3.7 Hz), 4.35 (1H, t, *J* = 9.5 Hz), 4.43-4.52 (3H, m), 4.57 (1H, d, *J* = 11.7 Hz), 4.60 (1H, dd, *J* = 9.5, 2.9 Hz), 4.72 (1H, t, *J* = 9.5 Hz), 4.79 (1H, br s), 5.49 (1H, d, *J* = 2.9 Hz), 6.16 (1H, br s), 6.56 (1H, br s), 7.62 (1H, br s), 7.66 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 16.8, 18.7, 18.9, 19.5, 20.1, 26.0, 26.3, 28.8, 29.2, 33.8, 35.1, 38.6, 39.5, 51.3, 62.9, 70.1, 72.2, 72.4, 72.6, 74.0, 74.6, 74.8, 78.7, 90.1, 102.2, 103.6, 111.5, 126.6, 139.2, 143.4; MS (EI) *m/z* 310 (M^+), 503, 429, 355, 341, 279.

Glucosylation of 8s with 14 (Preparation of 3p and 23p). To a stirred solution of **8s** (83.3 mg, 0.127 mmol) and 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl fluoride (**14**) (103.6 mg, 0.191 mmol) in toluene (1 ml) was added trimethylsilyl triflate (2.8 mg, 0.0127 mmol), and the mixture was stirred for 2 h at room temperature. The mixture was poured into saturated aqueous sodium bicarbonate solution, and extracted with chloroform. The concentrated extract was subjected to column chromatography on silica gel (5 g) using a mixture of hexane and ethyl acetate (4:1 and then 5:2) as eluant to afford glycosides (87.2 mg, 62% yield, **3p**:**23p** = 23:77) along with **8p** (28.7 mg, 38% yield). The crude disaccharide was subjected to HPLC with Develosil ODS-7 (10 × 250 mm) column using a mixture acetone and water (5:1) in a flow rate of 7 ml/min to give **3p**: *Tr* 11.7 min; $[\alpha]_D^{21}$ +23.4° (*c* 0.80, $CHCl_3$); IR ($CHCl_3$) 3020, 2955, 2880, 1750, 1600, 1500, 1455, 1365, 1230, 1175, 1065, 1025, 905, 875, 695, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.83 (3H, s), 0.91 (3H, s), 1.03 (3H, s), 1.60 (3H, s), 2.01 (3H, s), 2.01 (3H, s), 2.07 (3H, s), 3.10 (1H, dd, *J* = 11.7, 4.4 Hz), 3.36 (1H, t, *J* = 8.3 Hz), 3.43 (1H, m), 3.55 (1H, t, *J* = 8.8 Hz), 3.57 (1H, t, *J* = 7.8 Hz), 3.67 (1H, dd, *J* = 10.8, 4.9 Hz), 3.74 (1H, ddd, *J* = 10.3, 4.9, 2.4 Hz), 3.80 (1H, dd, *J* = 10.7, 2.0 Hz), 3.97 (1H, dd, *J* = 9.3, 7.8 Hz), 4.11 (1H, dd, *J* = 12.2, 2.1 Hz), 4.32 (1H, dd, *J* = 12.2, 4.9 Hz), 4.49 (1H, d, *J* = 7.8 Hz), 4.54 (1H, d, *J* = 12.2 Hz), 4.57 (1H, d, *J* = 10.7 Hz), 4.58 (1H, d, *J* = 12.2 Hz), 4.58 (1H, d, *J* = 11.7 Hz), 4.58 (1H, d, *J* = 7.3 Hz), 4.74 (1H, d, *J* = 10.7 Hz), 4.81 (1H, d, *J* = 10.7 Hz), 4.83 (1H, d, *J* = 11.2 Hz),

4.84 (1H, d, J = 10.7 Hz), 4.98 (1H, t, J = 9.3 Hz), 5.28 (1H, t, J = 9.3 Hz), 6.28 (1H, t, J = 1.0 Hz), 7.16-7.38 (22H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.3 q, 18.6 t, 19.5 q, 20.1 q, 20.7 q, 20.8 q, 20.8 q, 25.8 t, 26.5 t, 27.7 q, 28.9 t, 33.8 t, 35.2 t, 38.5 s, 39.5 s, 51.4 d, 62.4 t, 69.0 d, 69.3 t, 71.3 d, 73.5 t, 75.0 t, 75.0 d, 75.1 t, 75.2 d, 75.6 d, 75.8 t, 78.3 d, 82.3 d, 84.9 d, 91.2 d, 103.1 d, 104.2 d, 110.8 d, 125.5 s, 126.7 s, 127.4-128.5 (many d), 138.1 s, 138.4 s, 138.4 s, 138.4 s, 138.4 d, 138.5 s, 138.5 s, 142.7 d, 169.8 s, 170.1 s, 170.7 s, and **23p**: Tr 10.0 min; $[\alpha]_D^{21}$ +50.7° (c 2.65, $CHCl_3$); IR ($CHCl_3$) 3000, 2950, 2860, 1750, 1495, 1450, 1360, 1200, 1150, 1060, 1030, 1020, 870, 715, 690, 660, 590 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) 0.80 (3H, s), 0.94 (3H, s), 0.95 (3H, s), 1.59 (3H, s), 1.92 (3H, s), 2.00 (3H, s), 2.06 (3H, s), 3.15 (1H, dd, J = 11.7, 4.4 Hz), 3.55 (1H, dd, J = 9.8, 3.4 Hz), 3.64 (1H, dd, J = 9.8, 3.4 Hz), 3.67-3.72 (3H, m), 3.82 (1H, dd, J = 9.8, 7.8 Hz), 3.88 (1H, t, J = 8.8 Hz, overlap 1H, m), 4.08 (1H, dd, J = 12.2, 2.4 Hz), 4.28 (1H, dd, J = 11.7, 5.4 Hz), 4.42 (1H, d, J = 10.7 Hz), 4.45 (1H, d, J = 12.2 Hz), 4.59 (1H, d, J = 7.8 Hz), 4.62 (1H, d, J = 12.2 Hz), 4.71 (1H, d, J = 11.7 Hz), 4.74 (1H, d, J = 10.7 Hz), 4.75 (1H, d, J = 11.7 Hz), 4.78 (1H, d, J = 11.5 Hz), 4.86 (1H, d, J = 11.2 Hz), 4.97 (1H, t, J = 9.8 Hz), 5.24 (1H, t, J = 9.3 Hz), 5.42 (1H, d, J = 3.4 Hz), 6.28 (1H, br s), 7.05-7.07 (2H, m), 7.23-7.35 (21H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.6, 18.6, 19.4, 20.1, 20.7, 20.8, 20.8, 25.8, 26.5, 28.3, 28.8, 33.7, 35.4, 38.5, 39.1, 51.5, 62.5, 67.9, 69.4, 70.8, 71.2, 73.6, 73.6, 74.0, 74.6, 74.9, 75.6, 77.2, 79.7, 81.6, 89.4, 96.6, 104.4, 110.8, 125.5, 126.7, 127.5-128.4, 138.3, 138.4, 138.5, 138.5, 138.7, 139.4, 142.7, 169.8, 170.3, 170.3.

Phlomisoside II (3). According to the same procedure for the deprotection of **1p**, **3p** (16 mg, 0.014 mmol) was converted to phlomisoside II (**3**) (1.5 mg, 24% yield). The spectral properties were indistinguishable from those of natural product.

Disaccharide 23. According to the same procedure for the deprotection of **1p**, **23p** (52 mg, 0.047 mmol) was converted to **23** (7.7 mg, 26% yield): $[\alpha]_D^{19}$ +55.1° (c 0.39, CH_3OH); ^{1}H NMR (400 MHz in C_5D_5N) 0.95 (3H, s), 1.14 (3H, s), 1.40 (3H, s), 1.60 (3H, s), 3.54 (1H, dd, J = 11.7, 4.4 Hz), 3.87 (1H, m), 4.14-4.22 (3H, m), 4.31-4.36 (2H, m), 4.39 (1H, t, J = 9.8 Hz), 4.49 (1H, dd, J = 11.5, 4.6 Hz), 4.53-4.57 (2H, m), 4.70 (1H, t, J = 9.0 Hz), 5.00 (1H, d, J = 8.1 Hz), 5.29 (1H, m), 6.21 (1H, d, J = 4.0 Hz), 6.53 (1H, br s), 7.66 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 17.1 q, 19.0 t, 19.6 q, 20.3 q, 26.2 t, 27.3 t, 28.6 q, 29.1 t, 34.1 t, 35.5 t, 38.8 s, 39.5 s, 51.7 d, 62.8 t, 62.9 t, 72.1 d, 72.2 d, 73.6 d, 74.3 d, 75.7 d, 77.3 d, 78.2 d, 79.3 d, 88.0 d, 99.4 d, 105.8 d, 111.6 d, 126.2 s, 126.7 s, 139.2 d, 140.1 s, 143.4 d.

Glucosylation of 9s with 14 (Preparation of 24p and 25p). According to the same procedure for the glycosylation of **8s**, **9s** (116 mg, 0.177 mmol) was treated with **14** (96 mg, 0.177 mmol) and trimethylsilyl triflate (3.9 mg, 0.0177 mmol) in toluene (4 ml) to give a mixture of disaccharides (84.3 mg, 43% yield, **24p**:**25p** = 47:53) along with **9p** (26.7 mg, 26% yield) after silica gel column chromatography. The crude disaccharides was separated by HPLC with Develosil ODS-5 (10 × 250 mm) column using a mixture of acetone and water (5:1) in a flow rate of 7.0 ml/min to give **24p**: Tr 12.7 min; $[\alpha]_D^{20}$ +70.0° (c 0.53, $CHCl_3$); IR ($CHCl_3$) 3000, 2940, 2860, 1750, 1600, 1495, 1450, 1360, 1220, 1150, 1060, 1020, 870, 690, 595 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) 0.90 (3H, s), 0.96 (3H, s), 1.01 (3H, s), 1.61 (3H, s), 1.85 (3H, s), 2.03 (3H, s), 2.11 (3H, s), 3.21 (1H, dd, J = 11.7, 4.2 Hz), 3.38-3.44 (2H, m), 3.58-3.71 (4H, m), 3.85 (1H, dd, J = 10.3, 3.9 Hz), 4.09 (1H, d, J = 10.7 Hz), 4.22-4.31 (2H, m), 4.47 (1H, d, J = 12.0 Hz), 4.51 (1H, d, J = 7.8 Hz), 4.54 (1H, d, J = 11.0 Hz), 4.61 (1H, d, J = 12.0 Hz), 4.66 (1H, d, J = 11.5 Hz), 4.79 (1H, d, J = 10.8 Hz), 4.81 (1H, d, J = 10.5 Hz), 4.83 (1H, d, J = 11.7 Hz), 4.93 (1H, d, J = 10.5 Hz), 4.99 (1H, t, J = 9.8

Hz), 5.22 (1H, d, J= 3.7 Hz), 5.48 (1H, t, J= 9.8 Hz), 6.29 (1H, br s), 7.15-7.34 (22H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.7 q, 18.8 t, 19.5 q, 20.1 q, 20.7 q, 20.7 q, 20.8 q, 23.7 t, 25.8 t, 28.7 t, 28.8 q, 33.8 t, 34.9 s, 38.7 s, 38.7 s, 51.4 d, 62.4 t, 67.7 d, 68.9 t, 69.1 d, 72.1 d, 73.6 t, 74.4 t, 74.8 d, 75.0 t, 75.9 t, 76.2 d, 77.8 d, 81.6 d, 84.5 d, 87.2 d, 97.4 d, 104.5 d, 110.9 d, 125.5 s, 126.7 s, 127.5-128.4 (many d), 138.1 s, 138.4 s, 138.4 s, 138.4 s, 139.6 s, 142.7 d, 170.0 s, 170.4 s, 170.7 s, and **25p**: Tr 10.0 min; $[\alpha]_D^{14}$ +97.7° (c 0.69, $CHCl_3$); IR ($CHCl_3$) 3010, 2950, 2880, 1750, 1650, 1500, 1455, 1370, 1220, 1160, 1090, 1060, 1040, 1025, 875, 695, 600 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) 0.86 (3H, s), 0.87 (3H, s), 1.01 (3H, s), 1.58 (3H, s), 1.94 (3H, s), 2.03 (3H, s), 2.08 (3H, s), 3.18 (1H, dd, J= 11.7, 4.4 Hz), 3.52-3.55 (2H, m), 3.69-3.73 (3H, m), 3.81 (1H, br d, J= 10.0 Hz), 3.94 (1H, t, J= 9.3 Hz), 4.07 (1H, br d, J= 11.0 Hz), 4.18 (1H, dd, J= 11.0, 4.9 Hz), 4.25 (1H, dd, J= 12.0, 4.9 Hz), 4.44 (1H, d, J= 12.2 Hz), 4.46 (1H, d, J = 11.2 Hz), 4.57 (1H, d, J= 12.0 Hz), 4.67 (1H, d, J= 11.7 Hz), 4.75 (1H, d, J= 11.2 Hz), 4.77 (1H, d, J = 10.5 Hz), 4.81 (1H, d, J= 11.0 Hz), 4.88 (1H, d, J= 11.0 Hz), 4.92 (1H, d, J= 3.2 Hz), 4.96 (1H, t, J= 9.8 Hz), 5.15 (1H, d, J= 3.7 Hz), 5.36 (1H, t, J= 9.8 Hz), 6.15 (1H, br s), 7.09-7.12 (2H, m), 7.21-7.32 (20H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.7 q, 18.8 t, 19.4 q, 20.1 t, 20.7 q, 20.8 q, 21.0 q, 23.8 t, 25.7 t, 28.7 t, 28.7 q, 33.8 t, 34.8 s, 38.6 s, 38.6 s, 51.3 d, 62.3 t, 67.6 d, 67.8 t, 68.9 d, 71.4 d, 72.1 d, 73.4 t, 73.5 t, 74.8 t, 75.7 t, 77.3 d, 78.1 d, 80.0 d, 82.1 d, 86.5 d, 95.2 d, 99.3 d, 110.7 d, 125.4 s, 126.7 s, 127.5-128.5 (many d), 137.8 s, 138.2 d, 138.3 s, 138.6 s, 138.6 s, 139.4 s, 142.6 d, 169.9 s, 170.3 s, 170.7 s.

Disaccharide 24. According to the same procedure for the deprotection of **1p**, **24p** (10.3 mg, 0.0093 mmol) was converted to **24** (3.8 mg, 65% yield): $[\alpha]_D^{20}$ +56.3° (c 0.19, CH_3OH); ^{1}H NMR (400 MHz in C_5D_5N) 0.89 (3H, s), 0.93 (3H, s), 1.22 (3H, s), 1.57 (3H, s), 3.47 (1H, dd, J= 11.7, 4.2 Hz), 4.04 (1H, m), 4.14-4.21 (3H, m), 4.27 (1H, t, J= 8.8 Hz), 4.29 (1H, t, J= 8.8 Hz), 4.41 (1H, dd, J= 11.5, 5.4 Hz), 4.48 (1H, dd, J= 11.2, 4.9 Hz), 4.55-4.58 (2H, m), 4.60 (1H, dd, J= 12.0, 1.5 Hz), 4.74 (1H, t, J= 9.5 Hz), 5.33 (1H, d, J= 7.6 Hz), 5.72 (1H, d, J= 3.4 Hz), 6.53 (1H, br s), 7.65 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 17.1 q, 19.0 t, 19.5 q, 20.1 q, 23.4 t, 26.0 t, 29.1 q, 29.1 t, 33.9 t, 34.5 t, 38.9 s, 38.9 s, 51.5 d, 62.9 t, 63.0 t, 71.9 d, 71.9 d, 74.2 d, 74.6 d, 75.7 d, 78.5 d, 78.6 d, 82.8 d, 84.9 d, 97.4 d, 106.6 d, 111.6 d, 126.1 s, 126.5 s, 139.2 d, 140.0 s, 143.4 d; MS (EI) m/z 610 (M^+) .

Disaccharide 25. According to the same procedure for the deprotection of **1p**, **25p** (13.1 mg, 0.012 mmol) was converted to **25** (6.9 mg, 92% yield): $[\alpha]_D^{20}$ +57.4° (c 0.32, CH_3OH); ^{1}H NMR (400 MHz in C_5D_5N) 0.90 (3H, s), 0.92 (3H, s), 1.18 (3H, s), 1.58 (3H, s), 3.61 (1H, dd, J= 11.5, 3.9 Hz), 4.18 (1H, dd, J= 9.5, 3.9 Hz), 4.20 (1H, t, J= 9.5 Hz), 4.32 (1H, t, J= 9.5 Hz), 4.34 (1H, dd, J= 5.8, 3.7 Hz), 4.37-4.51 (3H, m), 4.56 (1H, dd, J= 10.0, 2.4 Hz), 4.60 (1H, m), 4.61 (1H, t, J= 9.5 Hz), 4.67 (1H, t, J= 9.0 Hz), 4.97 (1H, m), 5.67 (1H, d, J= 3.7 Hz), 5.75 (1H, d, J= 3.4 Hz), 6.55 (1H, br s), 7.60 (1H, br s), 7.67 (1H, t, J= 1.5 Hz); ^{13}C NMR (100 MHz in C_5D_5N) 17.0 q, 19.0 t, 19.5 q, 20.2 q, 22.5 t, 26.0 t, 29.0 q, 29.1 t, 33.9 t, 34.8 t, 38.9 s, 38.9 s, 51.4 d, 62.7 t, 63.1 t, 71.9 d, 72.3 d, 73.4 d, 74.1 d, 74.2 d, 74.7 d, 75.7 d, 78.8 d, 82.2 d, 93.2 d, 98.7 d, 111.6 d, 126.6 s, 129.5 s, 139.2 d, 139.8 s, 143.4 d; HRMS (FAB) m/z 649.3107 (found), calcd for $C_{32}H_{50}O_{12}Na$ 649.3200.

Glucosylation of 10s with 14 (Preparation of 26p and 27p). According to the same procedure for the glycosylation of **8s**, **10s** (111 mg, 0.619 mmol) was treated with **14** (92 mg, 0.169 mmol) in toluene (2 ml) to give a mixture of **26p** and **27p** (69.4 mg, 34% yield, **26p**:**27p** = 37:63) along with **10** (32.7 mg, 33% yield). The mixture of disaccharides were separated by HPLC with Develosil ODS-5 (10 × 250 mm)

column using a mixture of acetone and water (5:1) in a flow rate of 7.0 ml/min to give **26p**: T*r* 14.7 min; $[\alpha]_D^{20}$ -3.9° (*c* 0.90, $CHCl_3$); IR ($CHCl_3$) 3010, 2950, 2870, 1750, 1495, 1455, 1365, 1220, 1150, 1060, 1025, 875, 695, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.79 (3H, s), 0.84 (3H, s), 1.02 (3H, s), 1.60 (3H, s), 1.97 (3H, s), 2.00 (3H, s), 2.06 (3H, s), 3.23 (1H, dd, *J* = 11.7, 4.2 Hz), 3.38 (1H, t, *J* = 8.3 Hz), 3.42 (1H, m), 3.59 (1H, t, *J* = 9.0 Hz), 3.66 (1H, t, *J* = 9.3 Hz), 3.70-3.76 (3H, m), 3.88 (1H, dd, *J* = 8.5, 7.3 Hz), 4.10 (1H, dd, *J* = 12.0, 2.4 Hz), 4.25 (1H, dd, *J* = 11.8, 5.1 Hz), 4.52 (1H, d, *J* = 12.0 Hz), 4.54 (1H, d, *J* = 6.4 Hz), 4.55 (1H, d, *J* = 10.7 Hz), 4.58 (1H, d, *J* = 10.7 Hz), 4.60 (1H, d, *J* = 7.8 Hz), 4.65 (1H, d, *J* = 11.2 Hz), 4.78 (1H, d, *J* = 10.7 Hz), 4.80 (1H, d, *J* = 12.0 Hz), 4.85 (1H, d, *J* = 11.2 Hz), 4.86 (1H, d, *J* = 10.7 Hz), 5.04 (1H, t, *J* = 9.8 Hz), 5.26 (1H, t, *J* = 9.0 Hz), 6.30 (1H, br s), 7.14 (1H, br s), 7.16 (1H, br d, *J* = 3.2 Hz), 7.24-7.36 (20H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 16.5 q, 18.8 t, 19.4 q, 20.1 q, 20.7 q, 20.8 q, 20.8 q, 23.6 t, 25.7 t, 28.1 q, 28.8 t, 33.8 t, 34.9 t, 38.3 s, 38.6 s, 51.6 d, 62.5 t, 69.2 t, 69.3 d, 71.1 d, 73.5 t, 75.0 t, 75.0 t, 75.3 d, 75.7 t, 76.2 d, 78.0 d, 82.4 d, 85.0 d, 86.2 d, 99.6 d, 102.8 d, 110.9 d, 125.5 s, 126.7 s, 127.5-128.4 (many d), 138.1 s, 138.3 s, 138.4 s, 138.4 d, 138.5 s, 139.5 s, 142.7 d, 169.8 s, 170.1 s, 170.7 s, and **27p**: T*r* 13.7 min; $[\alpha]_D^{20}$ +23.5° (*c* 1.55, $CHCl_3$); IR ($CHCl_3$) 3100, 2950, 2870, 1750, 1495, 1455, 1365, 1220, 1150, 1070, 1030, 1020, 875, 695, 595 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.79 (3H, s), 0.82 (3H, s), 1.06 (3H, s), 1.58 (3H, s), 1.96 (3H, s), 2.01 (3H, s), 2.06 (3H, s), 3.29 (1H, dd, *J* = 11.7, 4.4 Hz), 3.55 (1H, dd, *J* = 9.8, 3.2 Hz), 3.63 (1H, m), 3.65-3.69 (3H, m), 3.82 (1H, dd, *J* = 9.8, 8.1 Hz), 3.89 (1H, t, *J* = 9.5 Hz overlapping with 1H, m), 4.12 (1H, dd, *J* = 12.2, 2.4 Hz), 4.21 (1H, dd, *J* = 12.2, 4.9 Hz), 4.43 (1H, d, *J* = 11.0 Hz), 4.48 (1H, d, *J* = 12.2 Hz), 4.62 (1H, d, *J* = 8.3 Hz), 4.63 (1H, d, *J* = 11.7 Hz), 4.75 (1H, d, *J* = 12.2 Hz), 4.76 (1H, d, *J* = 10.7 Hz), 4.79 (1H, d, *J* = 12.2 Hz), 4.81 (1H, d, *J* = 11.0 Hz), 4.90 (1H, d, *J* = 10.7 Hz), 5.01 (1H, t, *J* = 9.8 Hz), 5.30 (1H, t, *J* = 9.5 Hz), 5.55 (1H, d, *J* = 3.2 Hz), 6.29 (1H, br s), 7.05-7.08 (2H, m), 7.19-7.34 (19H, m), 7.38 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 16.7 q, 18.8 t, 19.4 q, 20.1 q, 20.7 q, 20.8 q, 20.8 q, 23.3 t, 25.7 t, 28.0 q, 28.7 t, 33.7 t, 34.6 t, 38.0 s, 38.5 s, 51.6 d, 62.2 t, 68.1 t, 69.5 d, 70.6 d, 71.3 d, 72.4 d, 73.1 t, 73.5 d, 73.5 t, 74.8 t, 75.6 t, 79.4 d, 81.6 d, 84.4 d, 95.5 d, 100.1 d, 110.8 d, 125.5 s, 126.8 s, 127.3-128.4 (many d), 137.9 s, 138.2 s, 138.4 s, 138.6 d, 139.3 s, 142.7 d, 169.8 s, 170.1 s, 170.6 s.

Disaccharide 26. According to the same procedure for the deprotection of **1p**, **26p** (20.1 mg, 0.018 mmol) was converted to **26** (10.9 mg, 97% yield): $[\alpha]_D^{20}$ -32.9° (*c* 0.51, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 1.06 (3H, s), 1.10 (3H, s), 1.21 (3H, s), 1.59 (3H, s), 3.59 (1H, dd, *J* = 8.1, 7.8 Hz), 3.93-4.09 (2H, m), 4.13-4.23 (3H, m), 4.30 (1H, t, *J* = 9.0 Hz), 4.34-4.42 (3H, m), 4.49 (1H, dd, *J* = 11.7, 4.4 Hz), 4.57-4.61 (2H, m), 5.06 (1H, d, *J* = 7.6 Hz), 5.23 (1H, d, *J* = 7.6 Hz), 6.54 (1H, br s), 7.66 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 16.9 q, 19.1 t, 19.4 q, 20.2 q, 23.5 t, 26.0 t, 28.5 q, 29.2 t, 34.0 t, 34.9 t, 38.5 s, 38.9 s, 51.6 d, 62.6 t, 62.9 t, 71.5 d, 72.0 d, 77.4 d, 77.7 d, 77.9 d, 78.2 d, 79.0 d, 83.9 d, 84.3 d, 99.8 d, 106.7 d, 111.5 d, 126.1 d, 126.4 s, 139.1 d, 140.0 s, 143.3 d; HRMS (FAB) *m/z* 649.3176 (found), calcd for $C_{32}H_{50}O_{12}Na$ 649.3200.

Disaccharide 27. According to the same procedure for the deprotection of **1p**, **27p** (29 mg, 0.026 mmol) to give **27** (4.9 mg, 30% yield): $[\alpha]_D^{20}$ +6.1° (*c* 0.23, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.95 (3H, s), 1.07 (3H, s), 1.20 (3H, s), 1.61 (3H, s), 3.67 (1H, dd, *J* = 11.7, 4.6 Hz), 3.95 (1H, m), 4.10-4.24 (4H, m), 4.34 (1H, dd, *J* = 11.5, 6.1 Hz), 4.38 (1H, t, *J* = 9.5 Hz), 4.49 (1H, dd, *J* = 11.7, 4.6 Hz), 4.58 (1H, dd, *J* = 11.7, 2.2 Hz), 4.61 (1H, dd, *J* = 11.7, 2.2 Hz), 4.66 (1H, t, *J* = 8.8 Hz), 5.08 (1H, d, *J* = 7.1 Hz), 5.22 (1H, m), 6.07 (1H, d, *J* = 3.9 Hz), 6.57 (1H, br s), 7.62 (1H, br s), 7.67 (1H, br s); ^{13}C NMR (100 MHz in

C_5D_5N) 17.2 q, 19.1 t, 19.5 q, 20.1 q, 23.3 t, 26.1 t, 28.5 q, 29.2 t, 33.9 t, 34.9 t, 38.4 s, 38.8 s, 51.6 d, 62.6 t, 63.2 t, 72.0 d, 72.4 d, 73.7 d, 74.4 d, 75.6 d, 77.2 d, 78.3 d, 79.6 d, 83.5 d, 100.0 d, 100.4 d, 111.5 d, 126.2 s, 126.6 s, 139.2 d, 139.9 d, 143.4 d.

Glucosylation of 11s with 14 (Preparation of 28p and 29p). According to the same procedure for the glycosylation of **8s**, **11s** (110 mg, 0.168 mmol) was treated with **14** (91 mg, 0.168 mmol) and trimethylsilyl triflate (3.7 mg, 0.0168 mmol) in toluene (4 ml) to give a mixture of **28p** and **29p** (70.6 mg, 38% yield, **28p**:**29p** = 33:67) along with **11p** (33 mg, 34% yield). The crude disaccharides were separated by HPLC with Develosil ODS-5 (10 × 250 mm) column using a mixture of acetone and water (5:1) in a flow rate of 7.0 ml/min to give pure **28p**: T*r* 12.7 min; $[\alpha]_D^{24}$ +19.5° (*c* 0.30, $CHCl_3$); IR ($CHCl_3$) 3010, 2940, 2870, 1750, 1600, 1500, 1455, 1365, 1230, 1060, 1025, 875, 695, 595 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.89 (3H, s), 0.97 (3H, s), 1.05 (3H, s), 1.61 (3H, s), 1.81 (3H, s), 2.02 (3H, s), 2.08 (3H, s), 3.14 (1H, dd, *J* = 12.0, 4.4 Hz), 3.38 (1H, dd, *J* = 9.0, 7.6 Hz). 3.44 (1H, m), 3.59-3.61 (2H, m), 3.71-3.74 (2H, m), 3.82 (1H, dd, *J* = 10.0, 3.9 Hz), 4.08 (1H, dd, *J* = 12.2, 2.2 Hz), 4.21 (1H, m), 4.30 (1H, dd, *J* = 12.2, 4.4 Hz), 4.49 (1H, d, *J* = 11.7 Hz), 4.49 (1H, d, *J* = 8.1 Hz), 4.57 (1H, d, *J* = 11.0 Hz), 4.61 (2H, d, *J* = 11.5 Hz), 4.78 (1H, d, *J* = 10.5 Hz), 4.81 (1H, d, *J* = 10.7 Hz), 4.82 (1H, d, *J* = 11.7 Hz), 4.91 (1H, d, *J* = 10.7 Hz), 4.99 (1H, t, *J* = 9.8 Hz), 5.22 (1H, d, *J* = 3.9 Hz), 5.50 (1H, t, *J* = 9.8 Hz), 6.28 (1H, br s), 7.17-7.32 (21H, m), 7.35 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 16.6 q, 18.6 t, 19.4 q, 20.1 q, 20.8 q, 20.8 q, 21.1 q, 25.6 t, 25.8 t, 28.6 q, 28.8 t, 33.7 t, 35.0 t, 38.4 s, 39.1 s, 51.3 d, 62.3 t, 67.3 d, 67.8 t, 69.1 d, 71.5 d, 72.2 d, 73.5 t, 73.6 t, 74.5 t, 75.5 t, 77.2 d, 79.7 d, 80.2 d, 81.7 d, 89.3 d, 98.9 d, 100.2 d, 110.8 d, 125.5 s, 126.8 s, 127.3-128.5 (many d), 137.8 s, 138.3 s, 138.4 s, 138.8 s, 138.8 s, 139.3 d, 142.7 d, 169.9 s, 170.4 s, 170.7 s, and **29p**: T*r* 10.0 min; $[\alpha]_D^{23}$ +61.2° (*c* 0.78, $CHCl_3$); IR ($CHCl_3$) 3010, 2950, 2880, 1750, 1600, 1500, 1460, 1365, 1220, 1155, 1090, 1040, 880, 695, 600 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.88 (3H, s), 0.96 (3H, s), 1.10 (3H, s), 1.60 (3H, s), 1.95 (3H, s), 2.05 (3H, s), 2.11 (3H, s), 3.13 (1H, dd, *J* =11.7, 4.3 Hz), 3.50-3.53 (1H, m), 3.52 (1H, dd, *J* = 10.0, 3.2 Hz), 3.65 (1H, dd, *J* = 10.0, 3.4 Hz), 3.70 (1H, t, *J* = 9.0 Hz), 3.70 (1H, d, *J* = 11.0 Hz), 3.79 (1H, d, *J* = 10.0 Hz), 3.94 (1H, t, *J* = 9.3 Hz), 4.07 (1H, dd, *J* = 12.2, 2.0 Hz), 4.17 (1H, ddd, *J* = 10.3, 4.4, 2.2 Hz), 4.25 (1H, dd, *J* = 12.2, 4.6 Hz), 4.42 (1H, d, *J* = 12.0 Hz), 4,47 (1H, d, *J* = 11.5 Hz), 4.54 (1H, d, *J* = 12.0 Hz), 4.62 (1H, d, *J* = 11.7 Hz), 4.74 (1H, d, *J* = 10.5 Hz), 4.77 (1H, d, *J* = 11.5 Hz), 4.82 (1H, d, *J* = 11.5 Hz), 4.84 (1H, d, *J* = 10.8 Hz), 4.88 (1H, d, *J* = 3.4 Hz), 4.94 (1H, t, *J* = 9.8 Hz), 5.09 (1H, d, *J* = 3.4 Hz), 5.40 (1H, t, *J* = 9.5 Hz), 6.28 (1H, t, *J* = 0.73 Hz), 7.16 (1H, d, *J* = 1.95 Hz), 7.23-7.35 (20H, m), 7.35 (1H, t, *J* = 1.47 Hz); ^{13}C NMR (100 MHz in $CDCl_3$) 16.6 q, 18.6 t, 19.5 q, 20.1 q, 20.7 q, 20.7 q, 20.8 q, 25.7 t, 26.0 t, 28.1 q, 28.8 t, 33.7 t, 35.1 t, 38.5 s, 39.3 s, 51.2 d, 62.3 t, 67.2 d, 69.1 t, 69.2 d, 72.1 d, 73.5 t, 74.7 t, 74.8 d, 75.1 t, 75.9 t, 77.0 d, 77.8 d, 82.1 d, 84.5 d, 90.0 d, 100.9 d, 104.6 d, 110.8 d, 125.5 s, 126.8 s, 127.4-128.4 (many d), 138.1 s, 138.2 s, 138.4 s, 138.4 s, 138.4 d, 139.4 s, 142.7 d, 169.9 s, 170.5 s, 170.7 s.

Disaccharide 28. According to the same procedure for the deprotection of **1p**, **28p** (4.8 mg, 0.0043 mmol) was converted to **28** (2.4 mg, 89% yield): $[\alpha]_D^{20}$ +22.5° (*c* 0.12, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.94 (3H, s), 0.97 (3H, s), 1.29 (3H, s), 1.60 (3H, s), 3.30 (1H, dd, *J* = 12.0, 3.9 Hz), 4.02 (1H, m), 4.08 (1H, dd, *J* = 10.0, 3.9 Hz), 4.13(1H, dd, *J* = 7.8, 2.1 Hz), 4.16 (1H, m), 4.23 (1H, t, *J* = 8.8 Hz), 4.27 (1H, t, *J* = 8.5 Hz), 4.36 (1H, dd, *J* = 11.9, 6.4 Hz), 4.44-4.53 (2H, m), 4.57 (1H, d, *J* = 10.7 Hz), 4.63 (1H, dd, *J* = 11.2, 1.9 Hz), 4.69 (1H, t, *J* = 9.3 Hz), 5.22 (1H, d, *J* = 7.8 Hz), 5.72 (1H, d, *J* = 3.66 Hz), 6.55 (1H, br s), 7.60 (1H, br s), 7.66 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 16.8 q, 18.9 t, 19.5 q, 20.1 q, 26.0 t, 26.4 t,

28.3 q, 29.2 t, 33.9 t, 35.1 t, 38.7 s, 39.5 s, 51.6 d, 63.0 t, 63.3 t, 72.2 d, 72.2 d, 74.1 d, 74.1 d, 75.8 d, 78.4 d, 78.4 d, 83.1 d, 89.4 d, 102.4 d, 106.6 d, 111.5 d, 126.1 s, 126.5 s, 139.2 d, 140.0 s, 143.4 d; MS (FAB) *m/z* 649 (M^++ Na).

Disaccharide 29. According to the same procedure for the deprotection of **1p**, **29p** (14.9 mg, 0.013 mmol) to give **29** (5.5 mg, 68% yield): $[\alpha]_D^{20}$ +66.7° (*c* 0.29, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.91 (3H, s), 0.93 (3H, s), 1.32 (3H, s), 1.58 (3H, s), 3.33 (1H, dd, *J*= 12.2, 4.6 Hz), 4.17-4.26 (4H, m), 4.37 (1H, dd, *J*= 11.4, 5.9 Hz), 4.40 (1H, dd, *J*= 10.3, 5.4 Hz), 4.52-4.63 (3H, m), 4.66 (1H, t, *J*= 9.5 Hz), 4.69 (1H, t, *J*= 9.3 Hz), 4.91 (1H, m), 5.61 (1H, d, *J*= 3.41), 5.68 (1H, d, *J*= 3.7 Hz), 6.50 (1H, br s), 7.60 (1H, br s), 7.66 (1H, t, *J*= 1.2 Hz); ^{13}C NMR (100 MHz in C_5D_5N) 16.8 q, 18.9 t, 19.5 q, 20.1 q, 26.0 t, 26.1 t, 28.8 q, 29.2 t, 33.9 t, 35.1 t, 38.6 s, 39.4 s, 51.5 d, 62.8 t, 63.2 t, 72.2 d, 72.2 d, 73.9 d, 74.1 d, 74.2 d, 74.7 d, 75.1 d, 82.3 d, 89.0 d, 100.2 d, 100.7 d, 111.5 d, 126.1 s, 126.5 s, 139.2 d, 140.0 s, 143.4 d; HRMS (FAB) *m/z* 649.3107 (found), calcd for $C_{32}H_{50}O_{12}Na$ 649.3198.

Synthesis of $\Delta^{7,8}$-baiyunol (36). To a suspension of lithium aluminum hydride (411 mg, 10.8 mmol) in THF (30 ml) was added a solution of diketone **34** (1.36 g, 4.32 mmol) in THF (10 ml) at 0° C, and the mixture was stirred for 10 min at 0° C then stirred for additional 80 min at room temperature. To the resulting gray suspension was added ether (150 ml) and ethyl acetate (10 ml). Water (5 ml) was then dropwise added and the stirring was continued until the grey color turned into white. To this was added anhydrous magnesium sulfate, and the mixture was stirred for an additional 10 min. A filtrate through cotton-Celite pad was concentrated to give diol **35** as a diastereomeric mixture. To a solution of **35** in pyridine (15 ml) was added acetic anhydride (3 ml), and this mixture was stirred for 3 days at room temperature. Excess pyridine and acetic anhydride was evaporated under vacuo, and the residue was subjected to column chromatography on silica gel with a mixture of hexane and ethyl acetate (4:1) as eluant to give diacetate as a mixture of diastereomers (1.58 g, 91% yield). To a stirred solution of lithium metal (0.7 g, 106 mg atom) in liquid ammonia (50 ml) was dropwise added a solution of diacetate (1.42 g, 3.53 mmol) in THF (10 ml) at -78° C, and the mixture was stirred at -33° C for an additional 30 min. To the resulting dark blue solution methanol (40 ml) was added and the mixture was stirred at room temperature for 10 h. To the solution was added 1N-hydrochloric acid and the mixture was extracted with ether. The concentrated extract was subjected to column chromatography on silica gel (30 g) with a mixture of hexane and ethyl acetate (15:1, and then 4:1) as an eluant to afford (±)-$\Delta^{7,8}$-baiyunol (**36**) (414 mg, 39 % yield) as a colorless semi-solid: ^1H NMR (400 MHz, $CDCl_3$) 0.76 (3H, s), 0.85 (3H, s), 0.97 (3H, s), 1.04 (1H, td, *J*= 13.1, 5.1 Hz), 1.18 (1H, dd, *J*= 10.5, 6.3 Hz), 1.46 (1H, m), 1.52-1.77 (4H, m), 1.73 (3H, br s), 1.38 (1H, dt, *J*= 13.4, 3.4 Hz), 1.94-2.01 (2H, m), 2.36 (1H, ddd, *J*= 15.7, 10.0, 6.8 Hz), 2.62 (1H, ddd, *J*= 14.9, 10.5, 4.4 Hz), 3.22 (1H, dd, *J*= 10.5, 4.9 Hz), 5.42 (1H, br s), 6.27 (1H, s), 7.21 (1H, s), 7.35 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) 13.6 q, 15.0 q, 22.0 q, 23.4 t, 26.9 t, 27.3 t, 27.7 t, 27.9 q, 36.4 s, 37.2 t, 38.6 s, 49.5 d, 54.1 d, 79.1 d, 111.0 d, 122.3 d, 125.2 s, 134.9 s, 138.7 s, 142.7 s, along with stating diacetate (133 mg, 9% yield) and diol **35** (506 mg, 45% yield).

2'-Discriminated glucosylation of (±)-$\Delta^{7,8}$-baiyunol (37) with glucosyl chloride 7 (Preparation of 37p, 38p, 39p and 40p). To a stirred solution of (±)-$\Delta^{7,8}$-baiyunol (**37**) (291 mg, 0.962 mmol), 3,4,6-tri-*O*-acetyl-β-D-glucopyransyl chloride (**7**) (468 mg, 1.44 mmol), and TMU (201 mg, 1.73 mmol) in dry dichloromethane (10 ml) was added silver triflate (377 mg, 1.54 mmol) in one portion, and the mixture was stirred for 16 h at room temperature under dark. A filtrate through a cotton-Celite pad was concentrated, and the

residue was subjected to column chromatography on silica gel using hexane and ethyl acetate (4:1, and then 5:2) as eluant to give a mixture of glucosides (298 mg, 52% yield) along with starting alcohol **37** (52 mg, 18%). The crude glycosides were separated by HPLC with a column of Develosil ODS-5 (10 × 250 mm) eluted with methanol and water (6:1) in flow rate of 5.0 ml/min to give pure **37p**: Tr 12.2 min; $[\alpha]_D^{23}$ +11.3° (*c* 3.52, $CHCl_3$); IR ($CHCl_3$) 3650-3200, 2960, 2850, 1750, 1500, 1460, 1440, 1370, 1230, 1160, 1080, 1030, 995, 905, 875, 595 cm^{-1}; ^1H NMR (400 MHz in $CDCl_3$) 0.76 (3H, s), 0.89 (3H, s), 0.97 (3H, s), 1.73 (3H, s), 2.03 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 3.17 (1H, dd, *J*= 12.0, 3.4 Hz), 3.61 (1H, ddd, *J*= 9.5, 7.8, 2.7 Hz), 3.68 (1H, ddd, *J*= 10.0, 5.4, 2.7 Hz), 4.10 (1H, dd, *J*= 12.2, 2.7 Hz), 4.28 (1H, dd, *J*= 12.2, 5.4 Hz), 4.42 (1H, d, *J*= 7.8 Hz), 5.01 (1H, t, *J*= 9.8 Hz), 5.12 (1H, t, *J*= 9.5 Hz), 5.41 (1H, br s), 6.27 (1H, br s), 7.22 (1H, br s), 7.35 (1H, br s); ^{13}C NMR (100 MHz in $CDCl_3$) 13.6 q, 16.2 q, 20.7 q, 20.8 q, 20.8 q, 22.1 q, 23.3 t, 26.0 t, 26.8 t, 27.8 t, 28.1 q, 36.2 s, 37.2 t, 38.9 s, 49.8 d, 53.9 d, 62.4 t, 68.7 d, 71.7 d, 72.8 d, 74.4 d, 90.6 d, 104.9 d, 111.1 d, 122.2 d, 125.2 s, 135.0 s, 138.8 d, 142.8 d, 169.7 s, 170.7 s, 170.8 s; HRMS (FAB) *m/z* 613.2966 (found), calcd for $C_{32}H_{46}O_{10}Na$ 613.2989, **40p**: Tr 13.9 min; $[\alpha]_D^{23}$ +72.1° (*c* 3.74, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 0.77 (3H, s), 0.93 (3H, s), 0.99 (3H, s). 1.73 (3H, s), 2.04 (3H, s), 2.08 (6H, s), 3.20 (1H, dd *J*= 11.7, 3.9 Hz), 3.69 (1H, m), 4.05-4.11 (2H, m), 4.24 (1H, dd, *J*= 12.2, 5.1 Hz), 5.00 (1H, t, *J*= 10.0), 5.02 (1H, d, *J*= 3.7 Hz), 5.20 (1H, t, *J*= 9.8 Hz), 5.42 (1H, br s), 6.26 (1H, br s), 7.21 (1H, br s), 7.35 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) 13.6 q, 16.3 q, 20.7 q, 20.7 q, 20.9 q, 22.0 q, 23.2 t, 25.5 t, 26.7 t, 27.7 t, 28.1 q, 36.1 s, 37.1 t, 39.0 s, 49.7 d, 53.7 d, 62.2 t, 67.7 d, 68.2 d, 71.6 d, 73.6 d, 89.9 d, 100.3 d, 111.0 d, 122.2 d, 125.0 s, 134.9 s, 138.8 d, 142.8 d, 169.6 s, 170.6 s, 171.3 s; MS (FAB) *m/z* 613 (M^++Na), and a mixture of **38p** and **39p**: Tr 13.3 min. The latter mixture of was subjected to ordinary phase HPLC with a Develosil ODS-5 column (10 × 250 mm) with a mixture of acetone and water (5:2) as an eluant in a flow rate of 5 ml/min to give pure **38p**: Tr 12.7 min; $[\alpha]_D^{23}$ +115° (*c* 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 0.78 (3H, s), 0.93 (3H, s), 1.01 (3H, s), 1.74 (3H, s), 2.04 (3H, s), 2.07 (3H, s), 2.08 (3H, s), 3.27 (1H, dd, *J*= 11.7, 3.7 Hz), 3.69 (1H, ddd, *J*= 11.2, 10.0, 3.9 Hz), 4.08 (1H, dd, *J*= 10.7, 2.0 Hz), 4.11 (1H, dd, *J*= 8.3, 4.9 Hz), 4.22 (1H, dd, *J*= 12.5, 5.1 Hz), 4.99 (1H, t, *J*= 9.8 Hz), 5.07 (1H, d, *J*= 4.2 Hz), 5.16 (1H, t, *J*= 9.8 Hz), 5.43 (1H, br s), 6.27 (1H, br s), 7.22 (1H, br s), 7.36 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) 13.6 q, 16.2 q, 20.7 q, 20.8 q, 20.9 q, 22.0 q, 22.8 t, 23.4 t, 26.7 t, 27.7 t, 28.6 q, 36.4 s, 36.8 t, 38.4 s, 49.9 d, 53.8 d, 62.2 t, 68.1 d, 68.3 d, 70.7 d, 73.6 d, 85.4 d, 95.4 d, 111.0 d, 122.2 d, 125.0 s, 135.0 s, 138.8 d, 142.8 d, 169.7 s, 170.7 s, 171.1 s; HRMS (FAB) *m/z* 613.3043 (found), calcd for $C_{32}H_{46}O_{10}Na$ 613.2989, and **39p**: Tr 13.8 min; $[\alpha]_D^{25}$ -7.8° (*c* 3.37, $CHCl_3$); ^1H NMR (400 MHz in $CDCl_3$) 0.76 (3H, s), 0.85 (3H, s), 0.95 (3H, s), 0.73 (3H, s), 2.03 (3H, s), 2.06 (3H, s), 2.08 (3H, s), 3.24 (1H, dd, *J*= 12.0, 4.2 Hz), 3.53 (1H, dd, *J*= 8.8, 5.6 Hz), 3.64 (1H, ddd, *J*= 9.8, 8.1, 2.9 Hz), 4.10 (1H, dd, *J*= 12.2, 2.7 Hz), 4.24 (1H, dd, *J*= 12.2, 5.3 Hz), 4.39 (1H, d, *J*= 7.8 Hz), 5.02 (1H, t, *J*= 9.5 Hz), 5.13 (1H, t, *J*= 9.5 Hz), 5.42 (1H, br), 6.27 (1H, br s), 7.22 (1H, br s), 7.36 (1H, br s); ^{13}C NMR ($CDCl_3$) 13.5 q, 15.9 q, 20.7 q, 20.8 q, 20.8 q, 22.0 q, 23.4 t, 23.5 t, 26.8 t, 27.7 t, 27.9 q, 36.3 s, 36.9 t, 38.0 s, 50.1 d, 53.8 d, 62.3 t, 68.9 d, 71.6 d, 72.1 d, 74.4 d, 85.8 d, 100.4 d, 111.0 d, 122.4 d, 125.1 s, 134.9 s, 138.8 d, 142.7 d, 169.7 s, 170.7 s, 170.7 s; HRMS (FAB) *m/z* 613.3004 (found), calcd for $C_{32}H_{46}O_{10}Na$ 613.2989. The ratio of these four isomeric glycosides **37p**, **38p**, **39p**, and **40p** was established by HPLC analysis to be 28:23:25:24, respectively.

(+)-$\Delta^{7,8}$-Baiyunyl 2-*O*-trimethylsilyl-3,4,6-tri-*O*-acethyl-β-D-glucopyranoside (37s). By the same operation described above, **37p** (64.4 mg, 0.109 mmol) was converted to **37s** (65.1 mg, 91% yield): ^1H NMR (400 MHz, $CDCl_3$) 0.12 (9H, s), 0.75 (3H, s), 0.90 (3H, s), 0.98 (3H, s), 1.73 (3H, s), 2.00 (3H, s),

2.04 (3H, s), 2.07 (3H, s), 3.09 (1H, dd, J= 12.0, 3.7 Hz), 3.63-3.68 (2H, m), 4.07 (1H, dd, J= 12.0, 2.4 Hz), 4.27 (1H, dd, J= 12.2, 5.4 Hz), 4.39 (1H, d, J= 9.8 Hz), 4.94 (1H, t, J= 9.8 Hz), 5.07 (1H, t, J= 9.5 Hz), 5.41 (1H, br s), 6.26 (1H, br s), 7.21 (1H, br s), 7.34 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) 0.6 q, 13.6 q, 16.0 q, 20.7 q, 20.8 q, 21.2 q, 22.1 q, 23.3 t, 26.2 t, 26.9 t, 27.7 q, 27.8 t, 36.2 s, 37.5 t, 39.0 s, 50.2 d, 54.0 d, 62.4 t, 69.3 d, 71.2 d, 73.0 d, 75.8 d, 90.1 d, 105.6 d, 111.0 d, 122.3 d, 125.2 s, 134.9 s, 138.8 d, 142.7 d, 169.8 s, 170.3 s, 170.7 s.

Xylosylation of 37s with 12 (Preparation of 30p and 31p). According to the same procedure described for the xylosylation of **8s**, **37s** (43.2 mg, 0.066 mmol) was treated with **12** (31 mg, 0.0726 mmol) and trimethylsilyl triflate (1.5 mg, 0.0066 mmol) in toluene (1 ml), and a crude disaccharide (20.3 mg, 31% yield) was obtained along with **37p** (29.5 mg, 76% yield, **30p**:**31p** = 59:41). The disaccharide was subjected to HPLC with Develosil ODS-5 (4.6 × 250 mm) column using a mixture of acetone and water (5:1) in a flow rate of 1.5 ml/min to give **30p** as a colorless solid: Tr 10.2 min; $[\alpha]_D^{20}$ +30.7° (c 0.36, $CHCl_3$); IR ($CHCl_3$) 3010, 2950, 2870, 1755, 1500, 1455, 1365, 1220, 1170, 1070, 1025, 995, 870, 695, 595 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) 0.76 (3H, s), 0.87 (3H, s), 0.95 (3H, s), 1.74 (3H, s), 1.96 (3H, s), 2.00 (3H, s), 2.06 (3H, s), 3.07 (1H, dd, J= 10.3, 2.7 Hz), 3.10 (1H, dd, J= 11.2, 10.0 Hz), 3.27 (1H, t, J= 8.5 Hz), 3.47-3.55 (2H, m), 3.70 (1H, ddd, J= 9.8, 4.2, 2.4 Hz), 3.85 (1H, dd, J= 9.3, 7.8 Hz), 3.89 (1H, dd, J= 11.5, 5.4 Hz), 4.12 (1H, dd, J= 12.2, 2.4 Hz), 4.23 (1H, dd, J= 12.2, 4.9 Hz), 4.45 (1H, d, J= 7.8 Hz), 4.47 (1H, d, J= 7.8 Hz), 4.58 (1H, d, J= 11.2 Hz), 4.60 (1H, d, J= 10.0 Hz), 4.70 (1H, d, J= 11.5 Hz), 4.77 (1H, d, J= 11.2 Hz), 4.78 (1H, d, J= 11.0 Hz), 4.82 (1H, d, J= 10.7 Hz), 4.96 (1H, t, J= 9.5 Hz), 5.24 (1H, t, J= 9.5 Hz), 5.43 (1H, br s), 6.27 (1H, br s), 7.21-7.34 (17H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 13.6 q, 15.5 q, 20.7 q, 20.8 q, 20.8 q, 22.1 q, 23.3 t, 26.2 t, 26.9 t, 27.4 q, 27.8 t, 36.2 s, 37.3 t, 39.2 s, 50.0 d, 54.0 d, 62.4 t, 63.7 t, 69.1 d, 71.2 d, 73.3 t, 75.1 t, 75.2 d, 75.7 d, 75.7 t, 78.3 d, 81.9 d, 84.0 d, 91.2 d, 103.9 d, 104.0 d, 111.1 d, 122.5 d, 125.2 s, 127.5-128.5 (many d), 135.0 s, 138.6 s, 138.6 s, 138.8 s, 138.8 d, 142.8 d, 169.8 s, 170.2 s, 170.7 s, and **31p** as a colorless solid: Tr, 9.6 min; $[\alpha]_D^{20}$ +41.8° (c 0.34, $CHCl_3$); IR ($CHCl_3$) 2950, 1760, 1495, 1455, 1365, 1220, 1165, 1070, 1030, 695, 595 cm^{-1}; ^{1}H NMR (400 MHz in $CDCl_3$) 0.73 (3H, s), 0.83 (3H, s), 0.91 (3H, s), 1.72 (3H, s), 1.99 (3H, s), 2.01 (3H, s), 2.08 (3H, s), 3.12 (1H, dd, J= 11.7, 3.7 Hz), 3.41 (1H, dd, J= 9.8, 3.2 Hz), 3.49-3.62 (3H, m), 3.68 (1H, ddd, J= 10.6, 5.5, 3.2 Hz), 3.76 (1H, t, J= 7.8 Hz), 3.78 (1H, t, J= 9.0 Hz), 4.10 (1H, dd, J= 12.2, 2.7 Hz), 4.26 (1H, dd, J = 12.2, 5.4 Hz), 4.57 (1H, d, J= 12.0 Hz), 4.57 (1H, d, J= 7.3 Hz), 4.67 (1H, d, J= 12.0 Hz), 4.69 (1H, d, J= 11.7 Hz), 4.75 (1H, d, J= 12.0 Hz), 4.79 (1H, d, J= 11.0 Hz), 4.82 (1H, d, J= 11.0 Hz), 4.98 (1H, t, J= 10.0 Hz), 5.24 (1H, t, J= 9.5 Hz), 5.24 (1H, d, J= 3.2 Hz), 5.38 (1H, br s), 6.27 (1H, br s), 7.24-7.35 (17H, m); ^{13}C NMR (100 MHz in $CDCl_3$) 13.6 q, 16.0 q, 20.7 q, 20.7 q, 20.9 q, 22.1 q, 23.3 t, 26.1 t, 26.9 t, 27.8 t, 28.0 q, 36.2 s, 37.5 t, 38.8 s, 50.0 d, 54.1 d, 60.6 t, 62.4 t, 69.4 d, 71.2 d, 73.4 t, 73.6 t, 73.9 d, 75.0 d, 75.6 t, 78.0 d, 79.5 d, 80.8 d, 89.4 d, 96.6 d, 104,1 d, 111.0 d, 122.3 d, 125.2 s, 127.6-128.4 (many d), 134.9 s, 138.4 s, 138.7 s, 138.7 s, 138.7 d, 142.8 d, 169.8 s, 170.2 s, 170.6 s.

Disaccharide 30. According to the same procedure for the deprotection of **1p**, **30p** (7.1 mg, 0.0071 mmol) was converted to **30** (2.6 mg, 61% yield): $[\alpha]_D^{20}$ +4.4° (c 0.12, CH_3OH) ^{1}H NMR (400 MHz in C_5D_5N) 0.74 (3H, s), 1.19 (3H, s), 1.32 (3H, s), 1.75 (3H, s), 3.36 (1H, dd, J= 11.2, 3.9 Hz), 3.72 (1H, t, J= 11.2 Hz), 3.73 (1H, m), 3.91 (1H, m), 4.12-4.27 (4H, m), 4.33 (1H, t, J= 8.8 Hz), 4.37-4.42 (2H, m), 4.56 (1H, dd, J= 11.7, 1.7 Hz), 4.93 (1H, d, J= 7.6 Hz), 5.31 (1H, d, J= 7.1 Hz), 5.42 (1H, br s), 6.51 (1H, br s), 7.63 (br s); ^{13}C NMR (100 MHz in C_5D_5N) 13.7, 16.0, 22.2, 23.7, 26.9, 27.3, 27.8, 28.1, 36.4, 37.4, 39.4, 50.2,

54.4, 62.7, 67.6, 71.1, 71.5, 76.6, 78.0, 78.3, 78.5, 84.0, 89.3, 105,8, 107.0, 111.7, 124.0, 126.0, 136.0, 139.5, 143.4; MS (FAB) *m/z* 619 (M^++ Na).

Disaccharide 31. According to the same procedure for the deprotection of **1p**, **31p** (5.5 mg, 0.0055 mmol) was converted to **31** (1.8 mg, 55% yield): $[\alpha]_D^{20}$ +34.4° (*c* 0.09, CH_3OH); ^1H NMR (400 MHz in C_5D_5N) 0.70 (3H, s), 1.13 (3H, s), 1.34 (3H, s), 1.74 (3H, s), 3.51 (1H, dd, *J* = 12.1, 3.8 Hz), 4.83-4.90 (2H, m), 4.13-4.27 (4H, m), 4.31 (1H, t, *J* = 8.7 Hz), 4.38 (1H, dd, *J* = 12.3, 5.9 Hz), 4.56 (1H, dd, *J* = 11.3, 3.2 Hz), 4.65 (1H, t, *J* = 9.1 Hz), 4.95 (1H, d, *J* = 7.6 Hz), 5.41 (1H, br s), 6.17 (1H, d, *J* = 3.3 Hz), 7.51 (1H, br s), 7.09 (1H, br s), 7.64 (1H, br s); ^{13}C NMR (100 MHz in C_5D_5N) 13.6 q, 16.5 q, 22.1 q, 23.6 t, 26.8 t, 27.2 t, 27.5 t, 28.3 q, 36.3 s, 37.5 t, 39.1 s, 50.1 d, 54.3 d, 62.8 t, 64.0 t, 71.7 d, 72.2 d, 74.0 d, 75.4 d, 77.0 d, 78.1 d, 78.8 d, 88.1 d, 99.3 d, 105.6 d, 111.7 d, 126.0 s, 139.4 d, 143.3 d.

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Acknowledgment: We are grateful to Professor O. Tanaka of Hiroshima University for generous gift of natural baiyunoside, phlomisosides I and II for identification, and Grant-in-Aid from the Ministry of Education, Science and Culture, Japanese Government for financial support.