Simple Synthesis of β-D-Glycopyranosides Using β-Glycosidase from Almonds

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Enzymatic glycosidation of twenty-one kinds of alcohols (*n*-hepanol, *n*-octanol, 2-phenylethanol, 3-phenylpropanol, 4-phenylbutanol, 5-phenylpentanol, 6-phenylhexanol, furfury alcohol, 2-pyridinemethanol, isobutanol, isopentanol, *p*-methoxycinnamylalcohol) including secondary alcohols (isopropanol, cyclohexanol, 1-phenylethanol) and 1,ω-alkanediols (1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol), salicyl alcohol and 4-nitrophenyl β-D-glucopyranoside (5) using β-glucosidase from almonds stereoselectively gave the corresponding β-D-glucopyranosides in moderate yield.

Key words β-glucosidase; β-glucosidation; 4-nitrophenyl β-D-glucopyranoside

There are many β-D-glucopyranosides possessing a primary alcohol moiety as an aglycone part in nature. The development of stereoselective methods for the synthesis of glycosidic linkages presents a considerable challenge to synthetic chemists.[1,2] Although well-developed chemical synthesis of the glycosidic structure is increasingly being established, several steps of selective protection, activation and coupling using a metal catalyst are necessary in their process. This problem in chemical synthesis has promoted the development of enzymatic approaches. Lipase-catalyzed synthesis of acyl sugar has been reported,[3] whereas much less is known about glycosidase-catalyzed synthesis of alkyl glycosides.[4] Glycosidases are responsible for the catalytic hydrolysis of the glycosidic linkage and are increasingly being used in carbohydrate synthesis. For example, β-glucosidase catalyzes the stereospecific hydrolytic cleavage of the β-glucosidic bond in substrate (**1**) to give glucose (**2**) (Chart 1, path a). Meanwhile, the reaction of β-D-glucopyranoside (**1**) and a nucleophile such as an alcohol is reported to afford a new glucopyranoside (**3**) exclusively with the β-configuration (Chart 1, path b).[5]

In the latter case, serine congeners were used as an acceptor alcohol. The success of the glycosidic bond formation requires the reactive intermediate (enzyme bound glycosyl cation) to be trapped faster by the glycosyl acceptor than by water. We are interested in this transglycosylation reaction, since alcohols as the glucosyl acceptor are better bound at the active site than water. There are two approaches to optimizing the product yield from a given glycosidase in enzymatic glycoside synthesis, *i.e.*, the use of either a high donor or high acceptor concentration.[6] High concentrations of both are usually impractical due to solubility limitation. High donor concentrations are only practical if the donor is cheap, such as glucose. High acceptor concentrations are practical if the acceptor is cheap or can be recovered from the reaction mixture. For the purpose of the synthesis of naturally occurring β-D-glucopyranosides, it is desirable to use an equal portion of both the glycosyl donor and the acceptor alcohol from a synthetic point of view. We reported that screening experiments in respect of the enzymes, glycosyl donors in phosphate buffer solution in order to find the best reaction conditions of β-glucosidation of primary alcohols were carried out.[7]

The effective enzyme and glycosyl donor, respectively, for the synthesis of benzyl β-D-glucopyranoside (**4**) as a model transglycosylation appeared to be β-glucosidase (EC 3.2.1.21) from almonds and 4-nitrophenyl β-D-glucopyranoside (**5**).[7,8] The β-glucosidase (EC 3.2.1.21) from almonds was purchased from Sigma Chemical Co. (G-0395, 2.5—3.4 U/mg), and 4-nitrophenyl β-D-glucopyranoside (**5**) as a glycosyl donor was chosen from either several kinds of phenyl β-D-glucopyranoside congeners or cellobiose.[7] In continuation of our studies on the enzymatic β-glucosidation of alcohols, we now report the enzymatic β-glucosidation of twenty-one kinds of alcohols, including primary alcohols,

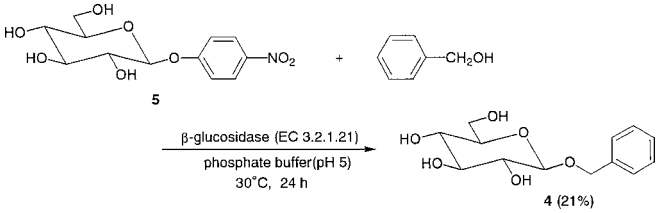

Chart 2

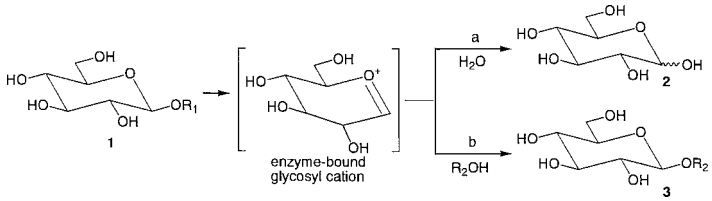

Chart 1

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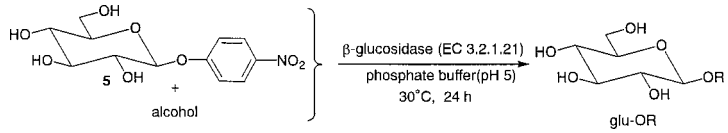
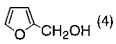
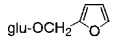
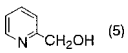
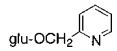
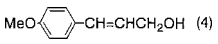
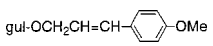
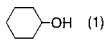
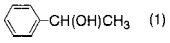
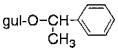
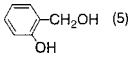
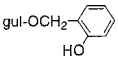
Table 1. Preparative Scale-Synthesis of β-Glucopyranoside Using Twenty-One Kinds of Alcohols



Entry	ROH (eq)	β-Glucosidase/buffer (U/ml)	glu-OR (yield; %)	
1	$CH_3(CH_2)_6OH$ (1)	1.0	glu-$O(CH_2)_6CH_3$	**6** (11)
2	$CH_3(CH_2)_7OH$ (1)	0.5	glu-$O(CH_2)_7CH_3$	**7** (2)
3	$Ph(CH_2)_2OH$ (1)	15	glu-$O(CH_2)_2Ph$	**8** (22)
4	$Ph(CH_2)_3OH$ (1)	8.0	glu-$O(CH_2)_3Ph$	**9** (18)
5	$Ph(CH_2)_4OH$ (1)	0.5	glu-$O(CH_2)_4Ph$	**10** (13)
6	$Ph(CH_2)_5OH$ (0.5)	0.4	glu-$O(CH_2)_5Ph$	**11** (11)
7	$Ph(CH_2)_6OH$ (0.5)	0.2	glu-$O(CH_2)_6Ph$	**12** (5)
8	 (4)	10		**13** (31)
9	 (5)	4.0		**14** (24)
10	$(CH_3)_2CHCH_2OH$ (10)	4.1	glu-$OCH_2CH(CH_3)_2$	**15** (34)
11	$(CH_3)_2CH(CH_2)_2OH$ (1)	10	glu-$O(CH_2)_2CH(CH_3)_2$	**16** (16)
12	 (4)	12		**17** (11)
13	$(CH_3)_2CHOH$ (10)	4.2	glu-$OCH(CH_3)_2$	**18** (20)
14	 (1)	15		**19** (4)
15	 (1)	10		**20** (12)
16	$HO(CH_2)_5OH$ (1)	4	glu-$O(CH_2)_5OH$	**21** (26)
17	$HO(CH_2)_6OH$ (1)	2	glu-$O(CH_2)_6OH$	**22** (28)
18	$HO(CH_2)_7OH$ (1)	9	glu-$O(CH_2)_7OH$	**23** (24)
19	$HO(CH_2)_8OH$ (1)	16	glu-$O(CH_2)_8OH$	**24** (25)
20	$HO(CH_2)_9OH$ (1)	2	glu-$O(CH_2)_9OH$	**25** (16)
21	 (5)	4		**26** (31)

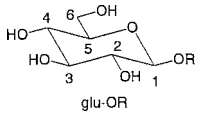
secondary alcohols and 1,ω-alkanediol.

Results

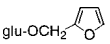
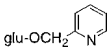
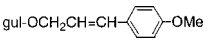
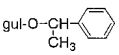
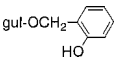
Addition of the glycosyl donor **5** to a solution of the acceptor substrate dissolved in phosphate buffer (pH 5) containing β-glucosidase was carried out over a period of 16—32 h. The reaction can be easily monitored by reverse phase HPLC and terminated when the formation of the desired product is at a maximum. The results are summarized in Table 1.

The structures of all products were determined by either direct comparison with the corresponding β-glucopyranosides or analysis of ^{1}H- and ^{13}C-NMR data. Identification of the β-configuration of the anomeric center was easily achieved *via* analysis of the C–H/C–H coupling constant (d, J=7.8 Hz), as shown in Table 2. The physical data of the synthetic β-D-glucosides (**6**; mp 74—75 °C, $[\alpha]_D$ −32.0° (c=0.51, MeOH), **7**; $[\alpha]_D$ −39.8° (c=0.58, H_2O), **8**; $[\alpha]_D$ −35.3° (c=0.5, MeOH), **16**; mp 86—87 °C, $[\alpha]_D$ −37.3° (c=0.5, H_2O), **17**; mp 132—134 °C, $[\alpha]_D$ −53.3° (c=0.34, MeOH), **18**; mp 126—127 °C, $[\alpha]_D$ −35.5° (c=0.5, H_2O), **26**; mp 67—69 °C, $[\alpha]_D$ −45.3° (c=0.36, MeOH)) were identical with those of the reported β-D-glucosides (*n*-heptyl-β-glucopyranoside **6**[9]; mp 74—77 °C, $[\alpha]_D$ −34.2° (H_2O), *n*-octyl-β-glucopyranoside **7**; $[\alpha]_D$ −34.2° (H_2O),[9] ^{13}C-NMR,[10] 2-phenylethyl-β-glucopyranoside **8**[11]; $[\alpha]_D$ −36.5° (MeOH), and ^{13}C-NMR, isopentyl-β-glucopyranoside **16**[12]; mp 86—88 °C, $[\alpha]_D$ −33.0° (c=0.7, MeOH), ^{13}C-NMR, 4-methoxycinnamyl-β-glucopyranoside **17**[13]; mp 139—141 °C, $[\alpha]_D$ −48.6° (c=1.0, MeOH), ^{13}C-NMR, isopropyl-β-glucopyranoside **18**; mp 129—131 °C,[12] mp 128—129 °C,[14] $[\alpha]_D$ −35.6° (c=1.1, MeOH),[12] $[\alpha]_D$ −36.3° (c=1.1, H_2O),[14] ^{13}C-NMR,[12] 2-hydroxybenzyl-β-glucopyranoside **26**[11]; mp 66—68 °C, $[\alpha]_D$ −41.0° (c=0.2, MeOH), ^{13}C-NMR), respectively. Chemical yield of β-D-glucopyranosides varied from 2 to 34% depending on the alcohols used. The primary hydroxyl group is more reactive than the secondary one (entries 13—15). In spite of the moderate chemical yield, β-D-glucopyranoside was the only product in all cases. Prolonged reaction times (>24 h) generally resulted in decreased yields of the β-D-glucopyranoside, presumably due to competing hydrolysis of the product by β-glucosidase. In the case of transglucosylation of an alcohol with 2-nitrophenylglucopyranoside or 4-nitrophenyl-β-glucopyranoside

Table 2. NMR Data of Sugar Part of β-D-Glucopyranosides



^{13}C-NMR (in Pyridine-d_5)
^{1}H-NMR (in DMSO-d_6)

β-D-Glucopyranosides		^{13}C-NMR (δ)						^{1}H-NMR (δ)
		Glc-1	Glc-2	Glc-3[a]	Glc-4	Glc-5[a]	Glc-6	Glc-1
glu-O$(CH_2)_6CH_3$	**6**	104.6	75.2	78.4	71.7	78.5	62.9	4.09 (d, J=7.8 Hz)
glu-O$(CH_2)_7CH_3$[b]	**7**	104.4	75.1	77.9	71.7	78.1	62.8	4.09 (d, J=7.8 Hz)
glu-O$(CH_2)_2$Ph[c]	**8**	103.1	73.9	76.6	71.6	76.8	61.6	4.32 (d, J=8.3 Hz)[d]
glu-O$(CH_2)_3$Ph	**9**	102.4	75.2	78.4	71.7	78.5	62.8	4.11 (d, J=7.8 Hz)
glu-O$(CH_2)_4$Ph	**10**	104.6	75.2	78.5	71.7	78.6	62.9	4.09 (d, J=7.8 Hz)
glu-O$(CH_2)_5$Ph	**11**	104.4	75.0	78.2	71.6	78.4	62.8	4.09 (d, J=7.8 Hz)
glu-O$(CH_2)_6$Ph	**12**	104.5	75.1	78.3	71.6	78.4	62.7	4.09 (d, J=7.8 Hz)
	**13**	103.6	75.1	78.5	71.7	78.7	62.8	4.21 (d, J=7.8 Hz)
	**14**	104.4	75.3	78.5	71.5 (or 71.9)	78.6	62.7	4.35 (d, J=7.8 Hz)
glu-O$CH_2CH(CH_3)_2$	**15**	104.6	75.0	78.2	71.6	78.4	62.7	4.09 (d, J=7.8 Hz)
glu-O$(CH_2)_2CH(CH_3)_2$	**16**	104.4	74.9	78.2	71.6	78.4	62.7	4.09 (d, J=7.8 Hz)
	**17**	103.8	75.2	78.5	71.7	78.5	62.8	4.97 (d, J=7.3 Hz)[e]
glu-O$CH(CH_3)_2$	**18**	102.4	75.1	78.2	71.6	78.4	62.8	4.16 (d, J=7.8 Hz)
	**19**	102.6	75.3	78.5	71.8	78.7	63.0	4.21 (d, J=7.8 Hz)
	**20**	101.5	75.4	78.4	71.8	78.5	62.9	3.93 (d, J=6.8 Hz)
glu-O$(CH_2)_5$OH	**21**	104.4	75.0	78.2	71.5	78.3	62.7	4.09 (d, J=7.7 Hz)
glu-O$(CH_2)_6$OH[c]	**22**	103.0	74.0	76.7	71.4 (or 70.5)	76.7	62.6 (or 61.6)	4.09 (d, J=7.8 Hz)
glu-O$(CH_2)_7$OH	**23**	104.4	75.0	78.2	71.5	78.2	62.7	4.09 (d, J=8.0 Hz)
glu-O$(CH_2)_8$OH[c]	**24**	103.0	74.0	76.7	71.5 (or 70.5)	76.7	62.7 (or 61.6)	4.09 (d, J=7.9 Hz)
glu-O$(CH_2)_9$OH	**25**	104.4	75.0	78.2	71.5	78.3	62.7	4.09 (d, J=7.7 Hz)
	**26**	103.7	74.7	78.0	71.1	78.0	62.1	4.26 (d, J=7.8 Hz)

a) Assignments may be interchanged. *b*) ^{13}C-NMR data were taken in MeOH-d_4. *c*) ^{13}C-NMR data were taken in D_2O–acetone. *d*) ^{1}H-NMR data were taken in D_2O–acetone. *e*) ^{1}H-NMR data were taken in pyridine-d_5.

in the presence of β-glucosidase in phosphate buffer, chemical yield of the β-D-glucopyranoside is reported to be low and less than 27%.[5] In order to avoid the cleavage of the glycosidic bond of the produced β-D-glucopyranoside, transglucosylation of 5-phenyl-1-pentanol with 4-nitrophenyl-β-D-glucopyranoside using lipid-coated β-glucosidase in dry isopropyl ether is reported to give the corresponding β-glucoside in 23% yield.[15] In the case of using 1-phenyl ethanol as a sugar acceptor, a diastereomeric mixture of β-D-glucopyranoside (**20**) possessing a 42% diastereomeric excess (d.e.) was obtained in 12% yield (entry 15). When five kinds of 1,ω-alkanediols were applied in the present enzymatic glycosylation, monoglycosylation products (**21**—**25**) were obtained in moderate yield in spite of possessing long methylene side chains (entries 16—20). When salicyl alcohol was applied in the enzymatic glycosylation reaction, an aliphatic hydroxyl group was only active for glycosylation, and a phenolic hydroxyl group was unchanged and intact. The presence of an *ortho*-hydroxyl group seems to have a positive effect on the enzyme-catalyzed glycosylation by the β-glucosidase.[16]

Discussion

The enzymatic formation of a glycosidic bond is thought to be mechanistically similar to the acid-catalyzed formation of glycosides.[17] The active site of β-glucosidase was constructed with two carboxylic acid parts which play the important role of catalyzing the hydrolysis of glycosidic linkages. One is the carboxylate ion, which acts as a general base, and the other is carboxylic acid which acts as a general acid. When the substrate is brought close to the active site of the enzyme, the oxocarbenium ion with an α-configuration at the anomeric carbon, as shown in Chart 3, was formed. This oxonium ion or the enzyme-bound glycosyl cation was stabilized by an ion-pair intermediate or covalent bonding, and can be captured by an alcohol to yield a glycoside. Nucleophilic alcohol presumably attacks at the anomeric carbon from the β-side to exclusively afford β-D-glucopyranoside.

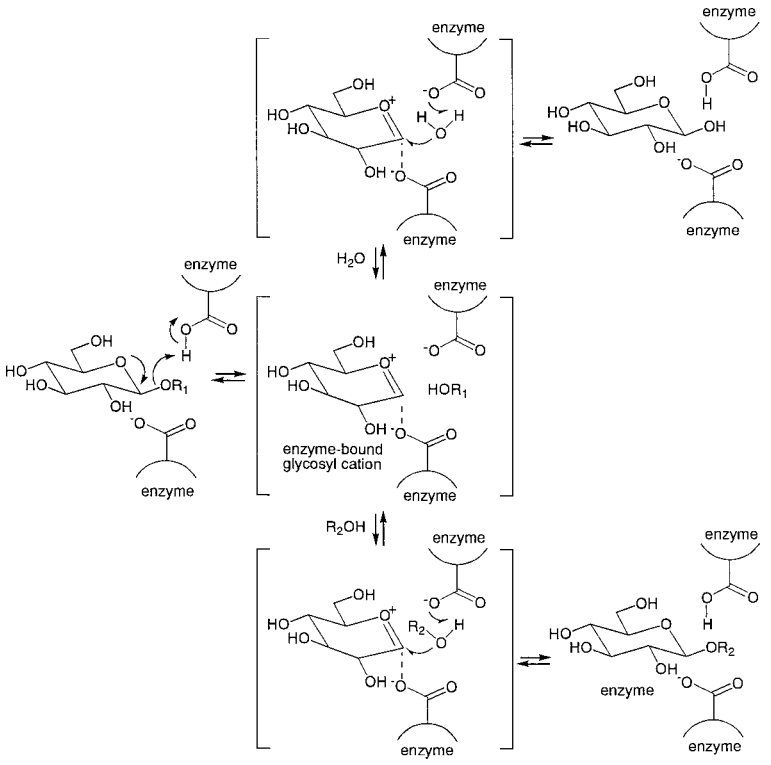


Chart 3

Conclusion

Enzymatic glycosidation of twenty-one kinds of alcohols (*n*-hepanol, *n*-octanol, 2-phenylethanol, 3-phenylpropanol, 4-phenylbutanol, 5-phenylpentanol, 6-phenylhexanol, furfury alcohol, 2-pyridinemethanol, isobutanol, isopentanol, 4-methoxycinnamylalcohol, including secondary alcohols isopropanol, cyclohexanol, 1-phenylethanol) and 1,ω-alkanediols (1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol), salicyl alcohol and 4-nitrophenyl β-D-glucopyranoside (**5**) using β-glucosidase from almonds stereoselectively gave the corresponding β-D-glucopyranosides (**6**—**26**) in moderate yield, respectively.

Experimental

^{1}H- and ^{13}C-NMR spectra were recorded by a JEOL EX 400 spectrometer (Tokyo, Japan). Spectra were taken with 5—10% (w/v) solution in DMSO-d_6, D_2O and pyridine-d_5 with Me_4Si as an internal reference. Melting points were determined on a Yanaco MP-3S micro melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-370 digital polarimeter. The FAB mass spectra were obtained with a JEOL JMS-AX 500 spectrometer (matrix; glycerol). IR spectra were recorded on a JASCO FT/IR-300 spectrometer. The HPLC system was composed of a detector (Shodex RI SE-61), pump (Shodex DS-3), integrator (Sic chromatocorder 12), column oven (Shodex OVEN AO-50) and column (Shodex KS-801, solvent: H_2O, temperature; 80 °C, flow rate; 1 ml/min). All evaporations were performed under reduced pressure. For column chromatography, silica gel (Kieselgel 60) was employed.

***n*-Heptyl β-D-Glucopyranoside (6)** A mixture of **5** (0.5 g, 1.66 mmol), *n*-heptanol (191 mg, 1.64 mmol) and β-glucosidase 5 mg (17 unit) in phosphate buffer (pH 5, 17 ml) was incubated for 20 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (20 g, $CHCl_3$/MeOH=30 : 1) to afford **6** (50 mg, 11%) as colorless crystals. **6**: mp 74—75 °C; $[\alpha]_D^{26}$ −32.0° (c=0.51, MeOH); IR (KBr): 3378, 2930, 2864, 1079, 1037 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 0.86 (3H, t, J=6.8 Hz), 3.66 (1H, dq, J=1.8, 5.9 Hz), 3.75 (1H, q, J=6.8 Hz), 4.09 (1H, d, J=7.8 Hz), 4.87 (2H, dd, J=4.6, 12.4 Hz), 4.92 (1H, d, J=5.3 Hz); ^{13}C-NMR (pyridine-d_5): δ: 104.6, 78.5, 78.4, 75.2, 71.7, 69.9, 62.9, 32.1, 30.4, 29.5, 26.5, 22.9, 14.4; HR-MS (FAB-MS) *m/z*: 279.1816; Calcd for $C_{13}H_{27}O_6$ *m/z*: 279.1808 (M+1)$^+$; *Anal.* Found: C, 55.12; H, 9.68. Calcd for $C_{16}H_{24}O_4 \cdot 1/4H_2O$: C, 55.20; H, 9.44%.

***n*-Octyl β-D-Glucopyranoside (7)** A mixture of **5** (2 g, 6.64 mmol), *n*-octanol (862 mg, 6.62 mmol) and β-glucosidase 10 mg (34 unit) in phosphate buffer (pH 5, 68 ml) was incubated for 17 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (80 g, $CHCl_3$/MeOH=30 : 1) to afford **7** (44 mg, 2%) as colorless crystals. **7**: $[\alpha]_D^{27}$ −39.8° (c=0.58, H_2O); IR (KBr): 3412, 2928, 1078, 1036 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 0.86 (3H, t, J=6.8 Hz), 1.50 (2H, dt, J=6.8 Hz), 3.66 (1H, dd, J=4.4, 11.2 Hz), 3.75 (1H, q, J=6.8 Hz), 4.09 (1H, d, J=7.8 Hz), 4.45 (1H, t, J=5.6 Hz), 4.88 (2H, dd, J=4.9, 12.5 Hz), 4.92 (1H, d, J=4.9 Hz); ^{13}C-NMR (MeOH-d_4): δ: 104.4, 78.1, 77.9, 75.1, 71.7, 70.9, 62.8, 33.0, 30.8, 30.6, 30.4, 27.1, 23.7, 14.4; FAB-MS *m/z*: 293 (M+1)$^+$; *Anal.* Found: C, 57.37; H, 9.71. Calcd for $C_{14}H_{28}O_6$: C, 57.51; H, 9.65%.

2-Phenylethyl β-D-Glucopyranoside (8) A mixture of **5** (1 g, 3.32 mmol), 2-phenylethanol (406 mg, 3.33 mmol) and β-glucosidase 150 mg (510 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=30 : 1) to afford **8** (205 mg, 22%) as colorless crystals. **8**: mp 38—40 °C; $[\alpha]_D^{27}$ −35.3° (c=0.5, MeOH); IR (KBr): 3368, 2924, 1083, 1058, 1036 cm^{-1}, ^{1}H-NMR (D_2O, acetone): δ: 2.83 (2H, t, J=6.8 Hz), 3.11 (1H, dd, J=8.3, 9.3 Hz), 3.21—3.30 (2H, m), 3.34 (1H, dd, J=8.8, 9.3 Hz), 3.58 (1H, dd, J=5.9, 12.7 Hz), 3.75—3.81 (2H, m), 4.02 (1H, dt, J=6.8, 10.3 Hz), 4.32 (1H, d, J=8.3 Hz), 7.15—7.27 (5H, m); ^{13}C-NMR (D_2O, acetone): δ: 139.5, 129.9, 129.9, 129.5, 129.5, 127.4, 103.1, 76.8, 76.6, 73.9, 71.6, 70.5, 61.6, 36.1; FAB-MS *m/z*: 285 (M+1)$^+$; *Anal.* Found: C, 59.06; H, 7.28. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.09%.

3-Phenylpropyl β-D-Glucopyranoside (9) A mixture of **5** (1 g, 3.32 mmol), 3-phenylpropanol (464 mg, 3.41 mmol) and β-glucosidase 81 mg (273 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 16 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=30 : 1) to afford **9** (176 mg, 18%) as colorless crystals. **9**: mp 91—92 °C; $[\alpha]_D^{27}$ −26.9° (c=0.33, MeOH); IR (KBr): 3346, 2912, 1116, 1087, 1056, 1035 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 2.65 (2H, t, J=7.6 Hz), 3.67 (1H, dd, J=5.5, 11.5 Hz), 3.78 (1H, dt, J=6.6 Hz), 4.11 (1H, d, J=7.8 Hz), 4.47 (1H, t, J=5.9 Hz), 4.91 (2H, dd, J=4.4, 15.1 Hz), 5.00 (1H, dd, J=4.9 Hz); ^{13}C-NMR (pyridine-d_5): δ: 142.4, 128.8, 128.8, 128.6, 128.6,

126.0, 102.6, 78.5, 78.4, 75.2, 71.7, 69.0, 62.8, 32.6, 32.1; FAB-MS *m/z*: 299 $(M+1)^+$; *Anal.* Found: C, 60.24; H, 7.46. Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43%.

4-Phenylbutyl β-D-Glucopyranoside (10) A mixture of **5** (1 g, 3.32 mmol), 4-phenylbutanol (496 mg, 3.30 mmol) and β-glucosidase 5 mg (17 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 18 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=30 : 1) to afford **10** (139 mg, 13%). **10**: $[\alpha]_D^{29}$ −27.0° (*c*=0.59, MeOH); IR (KBr): 3344, 2936, 2874, 1079, 1028 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 2.58 (2H, t, *J*=7.3 Hz), 3.66 (1H, dq, *J*=1.5, 5.9 Hz), 3.78 (1H, q, *J*=6.6 Hz), 4.09 (1H, d, *J*=7.8 Hz), 4.44 (1H, t, *J*=5.9 Hz), 4.87 (2H, dd, *J*=4.6, 11 Hz), 4.93 (1H, d, *J*=4.9 Hz), 7.14—7.28 (5H, m); ^{13}C-NMR (pyridine-d_5): δ: 142.8, 128.8, 128.8, 128.6, 128.6, 126.0, 104.6, 78.6, 78.5, 75.2, 71.7, 69.6, 62.9, 36.0, 30.0, 28.5; FAB-MS *m/z*: 313 $(M+1)^+$; *Anal.* Found: C, 61.02; H, 7.92. Calcd for: $C_{16}H_{24}O_6$; C, 61.52; H, 7.74%.

5-Phenylpentyl β-D-Glucopyranoside (11) A mixture of **5** (2 g, 6.64 mmol), 5-phenylpentanol (558 mg, 3.40 mmol) and β-glucosidase 8 mg (27 unit) in phosphate buffer (pH 5, 68 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (80 g, $CHCl_3$/MeOH=30 : 1) to afford **11** (236 mg, 11%) as colorless crystals. **11**: mp 65—66 °C; $[\alpha]_D^{28}$ −25.3° (*c*=0.9, MeOH); IR (KBr): 3414, 2934, 1075, 1035 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 2.56 (2H, t, *J*=7.6 Hz), 3.66 (1H, dq, *J*=1.5, 5.9 Hz), 3.75 (1H, q, *J*=6.8 Hz), 4.09 (1H, d, *J*=7.8 Hz), 4.45 (1H, t, *J*=5.9 Hz), 4.88 (2H, dd, *J*=4.9, 12.2 Hz), 4.92 (1H, d, *J*=4.9 Hz), 7.14—7.28 (5H, m); ^{13}C-NMR (pyridine-d_5): δ: 142.8, 128.7, 128.7, 128.6, 128.6, 126.0, 104.4, 78.4, 78.2, 75.0, 71.6, 69.7, 62.8, 36.1, 31.7, 30.1, 26.1; FAB-MS *m/z*: 327 $(M+1)^+$; *Anal.* Found: C, 62.33; H, 8.30. Calcd for $C_{17}H_{26}O_6$: C, 62.56; H, 8.03%.

6-Phenylhexyl β-D-Glucopyranoside (12) A mixture of **5** (2 g, 6.64 mmol), 6-phenylhexanol (594 mg, 3.33 mmol) and β-glucosidase 4 mg (14 unit) in phosphate buffer (pH 5, 68 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (80 g, $CHCl_3$/MeOH=30 : 1) to afford **12** (114 mg, 5%) as colorless crystals. **12**: mp 50—52 °C; $[\alpha]_D^{29}$ −24.4° (*c*=0.44, MeOH); IR (KBr): 3398, 2932, 2860, 1076, 1031 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 2.56 (2H, t, *J*=8 Hz), 3.66 (1H, q, *J*=5.9 Hz), 3.74 (1H, q, *J*=6.6 Hz), 4.09 (1H, d, *J*=7.8 Hz), 4.59 (1H, t, *J*=5.9 Hz), 4.88 (2H, dd, *J*=4.9, 11.7 Hz), 4.92 (1H, d, *J*=5.3 Hz), 7.13—7.28 (5H, m); ^{13}C-NMR (pyridine-d_5): δ: 143.0, 128.7, 128.7, 128.6, 128.6, 126.0, 104.5, 78.4, 78.3, 75.1, 71.6, 69.7, 62.7, 35.9, 31.6, 30.1, 29.2, 26.1; FAB-MS *m/z*: 341 $(M+1)^+$; *Anal.* Found: C, 62.97; H, 8.62. Calcd for $C_{18}H_{28}O_6$: C, 63.51; H, 8.29%.

2-Furfuryl β-D-Glucopyranoside (13) A mixture of **5** (1 g, 3.32 mmol), furfuryl alcohol (1.31 g, 13.4 mmol) and β-glucosidase 100 mg (340 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 27 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=30 : 1) to afford **13** (269 mg, 31%) as colorless crystals. **13**: mp 109—110 °C; $[\alpha]_D^{23}$ −72.0° (*c*=0.51, MeOH); IR (KBr): 3414, 2920, 1071, 1015 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 3.46 (1H, dt, *J*=5.9 Hz), 3.70 (1H, d, *J*=6.3 Hz), 4.21 (1H, d, *J*=7.8 Hz), 4.52 (1H, dd, *J*=3, 12.2 Hz), 4.74 (1H, d, *J*=12.7 Hz), 4.92 (1H, dd, *J*=4.9, 13.8 Hz), 5.05 (1H, d, *J*=5.4 Hz), 6.43 (1H, d, *J*=3 Hz), 6.45 (1H, d, *J*=3 Hz), 7.64 (1H, d, *J*=1 Hz); ^{13}C-NMR (pyridine-d_5): δ: 152.1, 143.2, 110.9, 110.0, 103.6, 78.7, 78.5, 75.1, 71.7, 63.0, 62.8; HR-MS (FAB-MS) *m/z*: 261.0936; Calcd for $C_{11}H_{17}O_7$ *m/z*: 261.0974 $(M+1)^+$; *Anal.* Found: C, 49.62; H, 6.17. Calcd for $C_{11}H_{16}O_7 \cdot 1/3H_2O$: C, 49.62; H, 6.31%.

2-Pyridylmethyl β-D-Glucopyranoside (14) A mixture of **5** (1 g, 3.32 mmol), 2-pyridinemethanol (1.82 g, 16.7 mmol) and β-glucosidase 40 mg (136 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 22 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=20 : 1) to afford **14** (216 mg, 24%) as colorless crystals. **14**: mp 114—116 °C; $[\alpha]_D^{26}$ −42.4° (*c*=0.45, MeOH); IR (KBr): 3340, 2928, 1081, 1058, 1040 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 3.52 (1H, quintet, *J*=5.9 Hz), 3.75 (1H, dq, *J*=1.5, 5.9 Hz), 4.35 (1H, d, *J*=7.8 Hz), 4.59 (1H, t, *J*=5.9 Hz), 4.74 (1H, d, *J*=13.7 Hz), 4.96 (2H, dd, *J*=4.5, 8.4 Hz), 5.03 (1H, d, *J*=4.9 Hz), 5.30 (1H, d, *J*=4.4 Hz), 7.34 (1H, dd, *J*=8, 4 Hz), 7.66 (1H, d, *J*=8 Hz), 7.86 (1H, dt, *J*=2, 8 Hz), 8.56 (1H, d, *J*=4 Hz); ^{13}C-NMR (pyridine-d_5): δ: 159.0, 149.2, 136.6, 122.5, 121.8, 104.4, 78.6, 78.5, 75.3, 71.9, 71.5, 62.7; HR-MS (FAB-MS) *m/z*: 272.1119; Calcd. for $C_{12}H_{18}NO_6$ *m/z*: 272.1134 $(M+1)^+$; *Anal.* Found: C, 52.50; H, 6.40; N, 5.01. Calcd for $C_{12}H_{17}NO_6 \cdot 1/4H_2O$: C, 52.26; H, 6.40; N, 5.08%.

Isobutyl β-D-Glucopyranoside (15) A mixture of **5** (0.5 g, 1.66 mmol), isobutanol (1.23 g, 16.6 mmol) and β-glucosidase 20 mg (70 unit) in phosphate buffer (pH 5, 17 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (20 g, $CHCl_3$/MeOH=40 : 1) to afford **15** (133 mg, 34%) as colorless crystals. **15**: mp 111—114 °C; $[\alpha]_D^{27}$ −39.1° (*c*=0.5, H_2O); IR (KBr): 3392, 2912, 1087, 1062, 1038 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 0.87 (3H, d, *J*=6.4 Hz), 0.88 (3H, d, *J*=6.4 Hz), 3.17 (1H, dd, *J*=6.8, 9.3 Hz), 3.54 (1H, dd, *J*=6.8, 9.3 Hz), 3.66 (1H, dd, *J*=5.6, 10.5 Hz), 4.09 (1H, d, *J*=7.8 Hz), 4.89 (1H, dd, *J*=4.6, 12.4 Hz), 4.94 (1H, q, *J*=4.9 Hz); ^{13}C-NMR (pyridine-d_5): δ: 104.6, 78.4, 78.2, 76.4, 75.0, 71.6, 62.7, 29.0, 19.6, 19.6; FAB-MS *m/z*: 237 $(M+1)^+$; *Anal.* Found: C, 50.58; H, 8.59. Calcd for $C_{10}H_{20}O_6$: C, 50.83; H, 8.53%.

Isopentyl β-D-Glucopyranoside (16) A mixture of **5** (1 g, 3.32 mmol), isopentanol (295 mg, 3.35 mmol) and β-glucosidase 100 mg (340 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=20 : 1) to afford **16** (136 mg, 16%) as colorless crystals. **16**: mp 86—87 °C; $[\alpha]_D^{27}$ −37.3° (*c*=0.5, H_2O); IR (KBr): 3425, 2945, 1075, 1030 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 0.87 (6H, d, *J*=6.8 Hz), 1.42 (2H, q, *J*=6.8 Hz), 1.68 (1H, septet, *J*=6.8 Hz), 3.79 (1H, dt, *J*=7.1 Hz), 4.09 (1H, d, *J*=7.8 Hz), 4.46 (1H, t, *J*=5.9 Hz), 4.88 (2H, dd, *J*=4.9, 12.2 Hz), 4.92 (1H, q, *J*=4.9 Hz); ^{13}C-NMR (pyridine-d_5): δ: 104.4, 78.4, 78.2, 74.9, 71.6, 68.2, 62.7, 38.9, 25.2, 22.8, 22.8; FAB-MS *m/z*: 251 $(M+1)^+$; *Anal.* Found: C, 52.40; H, 8.89. Calcd for $C_{11}H_{22}O_6$: C, 52.78; H, 8.86%.

4-Methoxycinnamyl β-D-Glucopyranoside (17) A mixture of **5** (1 g, 3.32 mmol), 4-methoxycinnamylalcohol (1.10 g, 6.71 mmol) and β-glucosidase 120 mg (408 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=20 : 1) to afford **17** (114 mg, 11%) as colorless crystals. **17**: mp 132—134 °C; $[\alpha]_D^{28}$ −53.3° (*c*=0.34, MeOH); IR (KBr): 3350, 2936, 1085, 1019 cm^{-1}, ^{1}H-NMR (pyridine-d_5): δ: 3.68 (3H, s), 3.93—4.00 (1H, m), 4.11 (1H, t, *J*=8 Hz), 4.23—4.30 (2H, m), 4.39 (1H, dd, *J*=5.3, 11.7 Hz), 4.47 (1H, dd, *J*=6.3, 12.7 Hz), 4.58 (1H, dd, *J*=2.0, 11.7 Hz), 4.75 (1H, dd, *J*=5.6, 12.5 Hz), 4.97 (1H, d, *J*=7.3 Hz), 5.73 (4H, br s), 6.37 (1H, dt, *J*=5.8, 15.8 Hz), 6.73 (1H, d, *J*=15.8 Hz), 6.95 (2H, d, *J*=8.3 Hz), 7.38 (2H, d, *J*=8.3 Hz); ^{13}C-NMR (pyridine-d_5): δ: 159.8, 132.0, 130.1, 128.1, 128.1, 124.5, 114.5, 114.5, 103.8, 78.5, 78.5, 75.2, 71.7, 70.0, 62.8, 55.2; HR-MS (FAB-MS) *m/z*: 327.1483; Calcd for $C_{14}H_{21}O_6$ *m/z*: 327.1444 $(M+1)^+$; *Anal.* Found: C, 57.66; H, 6.72. Calcd for $C_{16}H_{22}O_7 \cdot 1/3H_2O$: C, 57.82; H, 6.87%.

Isopropyl δ-D-Glucopyranoside (18) A mixture of **5** (1 g, 3.32 mmol), isopropanol (2 g, 33.2 mmol) and β-glucosidase 40 mg (145 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=20 : 1) to afford **18** (147 mg, 20%) as colorless crystals. **18**: mp 126—127 °C; $[\alpha]_D^{27}$ −35.5° (*c*=0.5, H_2O); IR (KBr): 3390, 2950, 1080, 1040, 1030 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 1.10 (3H, d, *J*=6.3 Hz), 1.14 (3H, d, *J*=5.9 Hz), 3.42 (1H, quintet, *J*=5.9 Hz), 3.65 (1H, dq, *J*=1.7, 5.6 Hz), 3.90 (1H, dq, *J*=6.4 Hz), 4.16 (1H, d, *J*=7.8 Hz), 4.43 (1H, t, *J*=5.6 Hz), 4.86 (2H, d, *J*=4.9 Hz), 4.89 (1H, q, *J*=4.9 Hz); ^{13}C-NMR (pyridine-d_5): δ: 102.4, 78.4, 78.2, 75.1, 71.6, 70.9, 62.8, 24.0, 22.1; FAB-MS *m/z*: 223 $(M+1)^+$; *Anal.* Found: C, 48.22; H, 8.17. Calcd for $C_9H_{18}O_6$: C, 48.64; H, 8.16%.

Cyclohexyl β-D-Glucopyranoside (19) A mixture of **5** (2 g, 6.64 mmol), cyclohexanol (0.673 g, 6.72 mmol) and β-glucosidase 300 mg (1020 unit) in phosphate buffer (pH 5, 68 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (80 g, $CHCl_3$/MeOH=30 : 1) to afford **19** (77 mg, 4%) as colorless crystals. **19**: mp 128—130 °C; $[\alpha]_D^{26}$ −46.3° (*c*=0.32, MeOH); IR (KBr): 3378, 2934, 1075, 1025 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 4.21 (1H, d, *J*=7.8 Hz), 4.41 (1H, t, *J*=5.9 Hz), 4.83 (1H, d, *J*=4.9 Hz), 4.86 (2H, dd, *J*=4.4, 9.3 Hz); ^{13}C-NMR (pyridine-d_5): δ: 102.6, 78.7, 78.5, 76.6, 75.3, 71.8, 63.0, 34.3, 32.4, 26.2, 24.5, 24.3; HR-MS (FAB-MS) *m/z*: 263.1523; Calcd for $C_{12}H_{23}O_6$ *m/z*: 263.1495 $(M+1)^+$; *Anal.* Found: C, 53.82; H, 8.50. Calcd for $C_{12}H_{22}O_6 \cdot 1/3H_2O$: C, 53.72; H,8.51%.

Diastereomeric Mixture of 1-Phenylethyl β-D-Glucopyranoside (20) A mixture of **5** (1 g, 3.32 mmol), 1-phenylethanol (405 mg, 3.32 mmol) and β-glucosidase 100 mg (340 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 32 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on sil-

ica gel (40 g, $CHCl_3$/MeOH=30 : 1) to afford a diasteromeric mixture of **20** (112 mg, 12%, 42% d.e.). **20**: mp 36—38 °C; $[\alpha]_D^{25}$ −81.9° (c=0.34, MeOH); IR (KBr): 3398, 2926, 1069, 1029 cm^{-1}, ^{1}H-NMR (DMSO-d_6): major: δ: 1.37 (3H, d, J=6.8 Hz), 3.68 (1H, dq, J=1.9, 5.9 Hz), 3.93 (1H, d, J=6.8 Hz), 4.50 (1H, t, J=5.9 Hz); minor: δ: 1.39 (3H, d, J=6.8 Hz), δ 1.37 (major): δ: 1.39 (minor)=2.46 : 1 (42% de); ^{13}C-NMR (pyridine-d_5): major: δ 143.9, 128.7, 128.7, 127.6, 127.6, 127.1, 101.5, 78.5, 78.4, 75.4, 74.8, 71.8, 62.9, 25.1; HR-MS (FAB-MS) m/z: 285.1345; Calcd for $C_{14}H_{21}O_6$ m/z: 285.1338 $(M+1)^+$; *Anal.* Found: C, 57.32; H, 7.22. Calcd for $C_{14}H_{20}O_6 \cdot 1/2H_2O$: C, 57.29; H, 7.30%.

5-Hydroxypentyl β-D-Glucopyranoside (21) A mixture of **5** (1 g, 3.32 mmol), 1,5-pentanediol (349 mg, 3.35 mmol) and β-glucosidase 40 mg (136 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=15 : 1) to afford **21** (230 mg, 26%) as colorless crystals. **21**: mp 97—99 °C; $[\alpha]_D^{24}$ −28.5° (c=0.54, MeOH); IR (KBr): 3374, 2934, 2864, 1079, 1024 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 3.65 (1H, dq, J=1.5, 5.8 Hz), 3.75 (1H, q, J=6.8 Hz), 4.09 (1H, d, J=7.7 Hz), 4.34 (1H, t, J=5.1 Hz), 4.46 (1H, t, J=5.9 Hz), 4.87 (2H, dd, J=4.6, 11.6 Hz), 4.92 (1H, d, J=4.9 Hz); ^{13}C-NMR (pyridine-d_5): δ: 104.4, 78.3, 78.2, 75.0, 71.5, 69.8, 62.7, 61.9, 33.3, 30.1, 23.0; HR-MS (FAB-MS) m/z: 267.1459; Calcd for $C_{11}H_{23}O_7$ m/z: 267.1444 $(M+1)^+$.

6-Hydroxyhexyl β-D-Glucopyranoside (22) A mixture of **5** (1 g, 3.32 mmol), 1,6-hexanediol (404 mg, 3.42 mmol) and β-glucosidase 20 mg (68 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=15 : 1) to afford **22** (264 mg, 28%) as colorless crystals. **22**: mp 109—111 °C; $[\alpha]_D^{28}$ −32.5° (c=0.46, MeOH); IR (KBr): 3374, 2934, 2864, 1079, 1024 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 3.66 (1H, dq, J=1.6, 5.9 Hz), 3.75 (1H, q, J=6.8 Hz), 4.09 (1H, d, J=7.8 Hz), 4.33 (1H, t, J=4.6 Hz), 4.45 (1H, t, J=5.9 Hz), 4.88 (2H, dd, J=4.9, 11.7 Hz), 4.92 (1H, d, J=4.9 Hz); ^{13}C-NMR (D_2O, acetone): δ: 103.0, 76.7, 76.7, 74.0, 71.4, 70.5, 62.6, 61.6, 32.0, 29.5, 25.7, 25.6; FAB-MS m/z: 281 $(M+1)^+$; *Anal.* Found: C, 51.04; H, 9.01. Calcd for $C_{12}H_{24}O_7$: C, 51.42; H, 8.63%.

7-Hydroxyheptyl β-D-Glucopyranoside (23) A mixture of **5** (1 g, 3.32 mmol), 1,7-heptanediol (450 mg, 3.40 mmol) and β-glucosidase 122 mg (306 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 20 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=15 : 1) to afford **23** (236 mg, 24%) as colorless crystals. **23**: mp 119—121 °C; $[\alpha]_D^{24}$ −25.6° (c=0.53, MeOH); IR (KBr): 3374, 2934, 2864, 1079, 1024 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 1.40 (2H, t, J=6.6 Hz), 1.51 (2H, t, J=7 Hz), 3.65 (1H, dq, J=1.5, 5.8 Hz), 3.75 (1H, q, J=6.8 Hz), 4.09 (1H, d, J=8 Hz), 4.32 (1H, t, J=5.1 Hz), 4.45 (1H, t, J=5.9 Hz), 4.86 (1H, d, J=4.6 Hz), 4.90 (2H, dd, J=4.8, 12.3 Hz); ^{13}C-NMR (pyridine-d_5): δ: 104.4, 78.2, 78.2, 75.0, 71.5, 69.7, 62.7, 62.0, 33.5, 30.2, 29.6, 26.4, 26.4; HR-MS (FAB-MS) m/z: 295.1765; Calcd for $C_{13}H_{27}O_7$ m/z: 295.1757 $(M+1)^+$.

8-Hydroxyoctyl β-D-Glucopyranoside (24) A mixture of **5** (1 g, 3.32 mmol), 1,8-octanediol (485 mg, 3.32 mmol) and β-glucosidase 218 mg (544 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=15 : 1) to afford **24** (253 mg, 25%) as colorless crystals. **24**: mp 126—128 °C; $[\alpha]_D^{29}$ −28.4 (c=0.43, MeOH); IR (KBr): 3419, 3236, 2925, 1371, 1030 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 3.64 (1H, dq, J=1.5, 5.9 Hz), 3.75 (1H, dt, J=6.6 Hz), 4.09 (1H, d, J=7.9 Hz), 4.32 (1H, t, J=5.1 Hz), 4.45 (1H, t, J=5.8 Hz), 4.87 (2H, dd, J=4.6, 11.5 Hz), 4.91 (1H, d, J=4.9 Hz); ^{13}C-NMR (D_2O, acetone): δ: 103.0, 76.7, 76.7, 74.0, 71.5, 70.5, 62.7, 61.6, 32.1, 29.6, 29.3, 29.3, 25.8, 25.8; FAB-MS m/z: 309 $(M+1)^+$; *Anal.* Found: C, 54.34; H, 9.24. Calcd for $C_{14}H_{28}O_7$: C, 54.53; H, 9.15%.

9-Hydroxynonanyl β-D-Glucopyranoside (25) A mixture of **5** (1 g, 3.32 mmol), 1,9-nonanediool (533 mg, 3.33 mmol) and β-glucosidase 27 mg (68 unit) in phosphate buffer (pH 5, 34 ml) was incubated for 19 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (40 g, $CHCl_3$/MeOH=15 : 1) to afford **25** (168 mg, 16%) as colorless crystals. **25**: mp 133—135 °C; $[\alpha]_D^{24}$ −25.3° (c=0.50, MeOH); IR (KBr): 3374, 2934, 2864, 1079, 1024 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 1.40 (2H, t, J=6.5 Hz), 1.51 (2H, t, J=7 Hz), 3.65 (1H, dq, J=1.5, 5.9 Hz), 3.74 (1H, q, J=6.8 Hz), 4.09 (1H, d, J=7.7 Hz), 4.31 (1H, t, J=5.2 Hz), 4.45 (1H, t, J=5.9 Hz), 4.87 (2H, dd, J=4.8, 11.4 Hz), 4.91 (1H, d, J=4.9 Hz); ^{13}C-NMR (pyridine-d_5): δ: 104.4, 78.3, 78.2, 75.0, 71.5, 69.8, 62.7, 62.1, 33.6, 30.3, 29.9, 29.8, 29.7, 26.5, 26.4; HR-MS (FAB-MS) m/z: 323.2070; Calcd for $C_{15}H_{31}O_7$ m/z: 323.2070 $(M+1)^+$.

2-Hydroxybenzyl β-D-Glucopyranoside (26) (Isosalicin) A mixture of **5** (0.6 g, 1.99 mmol), salicyl alcohol (1.235 g, 9.95 mmol) and β-glucosidase 24 mg (80 unit) in phosphate buffer (pH 5, 20 ml) was incubated for 24 h at 30 °C. After the reaction mixture was boiled for 5 min and evaporated under reduced pressure, the residue was chromatographed on silica gel (24 g, $CHCl_3$/MeOH=20 : 1) to afford **26** (175 mg, 31%) as colorless crystals. **26**: mp 67—69 °C; $[\alpha]_D^{23}$ −45.3° (c=0.36, MeOH); IR (KBr): 3418, 3256, 2900, 1102, 1077, 1042, 1019 cm^{-1}, ^{1}H-NMR (DMSO-d_6): δ: 3.47 (1H, quintet, J=5.9 Hz), 3.70 (1H, dq, J=1.5, 5.9 Hz), 4.26 (1H, d, J=7.8 Hz), 4.52 (1H, t, J=5.9 Hz), 4.56 (1H, d, J=13.2 Hz), 4.80 (1H, d, J=13.2 Hz), 4.91 (1H, dd, J=4.9, 5.6 Hz), 5.07 (1H, d, J=4.9 Hz), 6.75—6.80 (2H, m), 7.09 (1H, dt, J=7.8, 8.3 Hz), 7.38 (1H, d, J=7.8 Hz), 9.38 (1H, s); ^{13}C-NMR (pyridine-d_5): δ: 155.7, 129.1, 128.3, 125.1, 118.9, 115.2, 103.7, 78.0, 78.0, 74.7, 71.1, 66.7, 62.1; HR-MS (FAB-MS) m/z: 287.1131; Calcd for $C_{13}H_{19}O_7$ m/z: 287.1130 $(M+1)^+$; *Anal.* Found: C, 51.12; H, 6.71. Calcd for $C_{13}H_{18}O_7 \cdot H_2O$: C, 51.53; H, 6.62%.

Acknowledgements The authors are grateful to Dr. Junichi Kitajima, Showa College of Pharmaceutical Sciences, Japan, for generously giving the spectral data of **16**, **18**, and to Dr. Takao Konoshima, Kyoto Pharmaceutical University, Japan, for generously donating the spectral data of **17**.

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