Chemical and Chemotaxonomical Studies of Ferns. LXXXIV.[1] A Novel 2-Tetralol-Type Xyloside from *Asplenium wilfordii*

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A novel 2-tetralol-type xyloside, named asplenoside, was isolated from the fronds of *Asplenium wilfordii*. The structure was determined as (6*R*)-5,6,7,8-tetrahydro-6-*β*-D-xylopyranosyloxy-2-naphthalenecarboxylic acid by chemical and spectral means. Application of the glycosylation shift rule in ^{13}C-NMR spectroscopy to the determination of the absolute configuration is described.

Keywords *Asplenium wilfordii*; asplenoside; glycosylation shift; 2-tetralol; Aspleniaceae; *β*-D-xyloside

Asplenium is a cosmopolitan genus in Aspleniaceae and contains about 700 species.[2] Chemical studies on this genus have revealed the presence of many flavonoids, xanthones, triterpenes, non-protein amino acids, sugar esters and naphthoquinones.[3] However, any characteristic compound of the genus has not yet been isolated.

As part of our continuing chemotaxonomical studies of ferns, the constituents of *Asplenium wilfordii* METT. were investigated, and a novel glycoside was isolated.

In this paper, we describe the structure elucidation of this compound and application of the glycosylation shift rule in ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopy to the determination of its absolute configuration.

A new compound **1**, named asplenoside was isolated by multiple column chromatography of a methanol extract of the air-dried fronds of *Asplenium wilfordii* METT.

Asplenoside (**1**), colorless needles, mp 159—160 °C, $[\alpha]_D$ −9.8° (c=1.0, MeOH), was formulated as $C_{16}H_{20}O_7$ from the elemental analysis and signal count in the ^{13}C-NMR spectrum (C_{16}). The infrared (IR) spectrum of **1** showed the presence of an aromatic carboxyl (1690 cm^{-1}), a benzene ring (1600, 1520 cm^{-1}), and many hydroxyl groups (3470, 3390, 1120, 1080, 1060, 1035 cm^{-1}). The ^{13}C-NMR spectrum of **1** (in C_5D_5N) gave more detailed information, showing the presence of a carboxyl (δ 174.0), a trisubstituted benzene ring [δ 146.8 (C), 144.9 (C), 134.1 (C), 120.0 (CH), 116.9 (CH), 116.4 (CH)] and five oxygenated sp^3 carbons assignable to those of a *β*-D-xylopyranosyloxy moiety [δ 105.2 (C-1′), 74.8 (C-2′), 78.1 (C-3′), 70.9 (C-4′), 66.7 (C-5′)][4]; this left three methylene signals at δ 42.4, 37.6 and 31.0 and an oxygenated methine signal at δ 76.8 to be assigned. Considering the molecular formula and the degree of unsaturation, the carbons for the last four signals were judged to form a tetraline skeleton with the benzene ring. Thus, the structure of **1** was limited to tetralines bearing a carboxyl and a *β*-D-xylopyranosyloxy groups. In the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** (in C_5D_5N), three aromatic proton signals showed the typical coupling pattern of 1,2,4-trisubstituted benzene ring protons at δ 7.30 (1H, d, J=2 Hz), 7.17 (1H, d, J=8 Hz) and 6.86 (1H, dd, J=8, 2 Hz), indicating the carboxyl group to be attached to the C-2 of a 5,6,7,8-tetrahydronaphthalene. In addition, the oxygenated methine proton, that is, the proton geminal to the *β*-D-xylopyranosyloxy group showed a quintet pattern with 6 Hz of coupling constant at δ 4.73. This means the methine has two adjacent methylene groups. Thus, the position of the methine was limited to the C-6 or C-7 of 5,6,7,8-tetrahydro-2-naphthalenecarboxylic acid. In the differential nuclear Overhauser effect (NOE) experiment, irradiation of the meta-coupled aromatic proton at δ 7.30 (H-1) gave a NOE enhancement of methylene protons at δ 3.14 (1H, ddd, J=15, 7, 6 Hz) and 3.05 (1H, ddd, J=15, 7, 6 Hz) which are not adjacent to the methine proton, judging from the chemical shifts and the coupling patterns. Therefore, the structure of **1** was deduced to be 5,6,7,8-tetrahydro-6-*β*-D-xylopyranosyloxy-2-naphthalenecarboxylic acid.

Further confirmation was given by several chemical reactions as follows. On acid hydrolysis with 3% HCl, **1** gave D-xylose and many degraded compounds originating from the genuine aglycone. Also acid methanolysis of the methyl ester (**2**) which was formed from **1** by reaction with CH_2N_2 gave a methyl ester (**3**) of the genuine aglycone. Dehydration of **3** with thionyl chloride in pyridine, followed by dehydrogenation with 2,3-dichloro-5,6-dicyanobenzoquinone yielded methyl 2-naphthalenecarboxylate (**4**) which was identified by direct comparison with an authentic sample.

Finally, the absolute configuration at C-6 was determined by the glycosylation shift rule in ^{13}C-NMR spectroscopy.

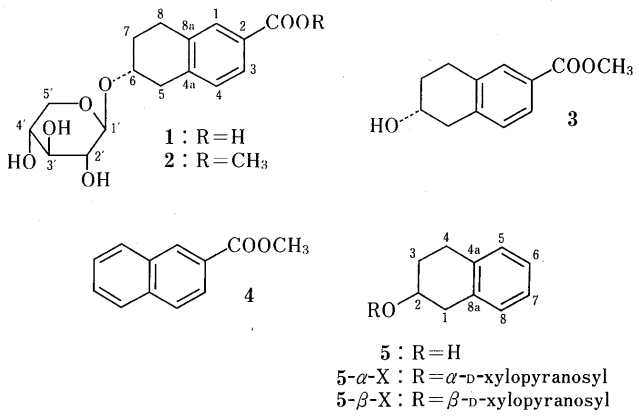

Fig. 1

TABLE I. ^{13}C-NMR Data in C_5D_5N Solution

C[a]	1	2	3	Δ_{2-3}	C[a]	5	(*R*)-5-β-X	Δ_{X-5}	(*S*)-5-β-X	Δ_{X-5}	(*R*)-5-α-X	Δ_{X-5}	(*S*)-5-α-X	Δ_{X-5}
1	120.0	119.9	119.9		5	135.0	135.2		135.0		135.0		135.1	
2	134.1	134.0	134.0		6	128.9	128.9		128.9		128.9		128.9	
3	116.9	117.0	116.9		7	126.0	126.1		126.1		126.2		126.1	
4	116.4	116.5	116.5		8	126.0	126.1		126.1		126.2		126.1	
5	42.4	41.8	43.4	−1.6	1	39.3	37.1	−2.2	35.9	−3.4	35.5	−3.8	36.8	−2.5
6	76.8	76.7	67.6	+9.1	2	66.4	73.3	+6.9	74.6	+8.2	73.4	+7.0	72.3	+5.9
7	37.6	37.7	40.3	−2.6	3	32.5	28.0	−4.5	30.4	−2.1	30.3	−2.2	27.9	−4.6
8	31.0	31.1	32.1		4	27.6	26.7		27.3		27.7		27.0	
4a	146.8	147.1	147.1		8a	129.8	129.8		129.8		129.8		129.7	
8a	144.9	145.1	145.1		4a	136.6	136.5		136.6		136.3		136.5	
1′	105.2	105.5			1′		103.6		104.5		99.4		98.7	
2′	74.8	75.0			2′		74.9		75.0		73.8		73.7	
3′	78.1	78.4			3′		78.5		78.5		75.5		75.5	
4′	70.9	71.0			4′		71.2		71.2		71.8		71.9	
5′	66.7	67.0			5′		67.3		67.3		63.8		63.7	
COO–	174.0	171.8	172.6											
CH_3		51.3	51.2											

a) Though the numbering system is different for asplenoside and 2-tetralol (see Fig. 1), the values of the corresponding carbons are shown in the same lines.

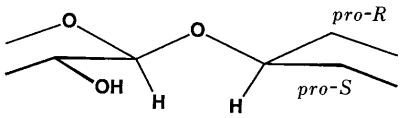

Fig. 2

Tanaka and co-workers[5] and also Tori and co-workers[6] have examined D-glucosylation shifts of secondary alcohols having two β-methylene groups and found that signals of *pro-S*-carbon or its equivalent are always more shielded (by −3.6——4.4) than those of the *pro-R*-carbon or its equivalent (by −1.8——2.7 ppm) on D-glucosylation. They showed that these D-glucosylation shifts mainly depend on the chirality of the aglycone alcohols and seem to be independent of their axial–equatorial cofiguration. In these D-glucopyranosides, rotation around the glucosidic bond is rather restricted and a conformation where an anomeric proton and a *sec*-carbinyl proton are *syn* to each other (see Fig. 2) is predominant.[7] This causes unequal D-glucosylation shifts of the β-methylene groups.

As D-xylopyranosides have the same partial structure around the glycosidic bond as D-glucopyranosides, the same results were expected on D-xylosylation. To examine this deduction, the β-D-xylopyranosides of cholestan-3α-ol and cholestan-3β-ol were prepared and ^{13}C-NMR spectra were recorded in C_5D_5N solution. D-Xylosylation shifts on the β-methylene groups were −4.2 ppm (C-2, *pro-S*) and −1.9 ppm (C-4, *pro-R*) for cholestan-3α-ol, and −2.3 ppm (C-2, *pro-R*) and −4.3 ppm (C-4, *pro-S*) for cholestan-3β-ol. These results were the same as those for D-glucosylation.[5,6] Therefore, β-D-xylopyranosides, (*R*)-**5**-β-X and (*S*)-**5**-β-X, of (*R*)-2-tetralol [(*R*)-**5**] and (*S*)-2-tetralol [(*S*)-**5**] were prepared as model compounds for asplenoside. As shown in Table I, β-D-xylosylation shifts of −2.2 ppm (C-1) and −4.5 ppm (C-3) for (*R*)-2-tetralol and −3.4 ppm (C-1) and −2.1 ppm (C-3) for (*S*)-2-tetralol were observed. The table also shows the data of the corresponding α-D-xylopyranosides, (*R*)-**5**-α-X and (*S*)-**5**-α-X, which were obtained as by-products. In the case of the asplenoside methyl ester (**2**), C-5 and C-7 signals showed β-D-xylosylation shifts of −1.6 ppm and −2.6 ppm, respectively, corresponding to those for (*R*)-2-tetralol (Table I). Thus, the structure of asplenoside (**1**) was established as (6*R*)-5,6,7,8-tetrahydro-6-β-D-xylopyranosyloxy-2-naphthalenecarboxylic acid.

Recently, Speranza and co-workers determined the absolute configuration of the *O*-glucosylated 1-methyl-3-hydroxytetralin derivatives, feroxins A and B, in a similar manner to that described here.[8] Application of ^{13}C-NMR spectroscopy to the determination of the absolute configuration of glycosylated carbinol is effective in some cases.

Experimental

The instruments, materials and experimental conditions were the same as described in Part LXXXI[9] of this series.

Isolation Procedure The air-dried fronds (540 g) of *Asplenium wilfordii*, collected in July at Aya, Miyazaki Prefecture, were extracted twice with 2 l MeOH under reflux for 6 h. The combined extracts followed by 8 l MeOH were passed over activated charcoal (60 g) packed in a column of 5 cm diameter. The resulting solution was concentrated to a syrup under reduced pressure. The syrup was chromatographed on silica gel (eluent, $CHCl_3$–MeOH) and then Sephadex LH-20 (eluent, 80% MeOH) to yield 290 mg of compound **1**.

Compound 1 (Asplenoside) Colorless needles, mp 159—160 °C, $[\alpha]_D$ −9.8° (c=1.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 223 (3.60), 285 (3.35). IR ν_{max}^{KBr} cm^{-1}: 3470, 3390, 2900, 2870, 1690, 1600, 1520, 1280, 1220, 1120, 1080, 1060, 1035, 985. ^{1}H-NMR (400 MHz, C_5D_5N) δ: 7.30 (1H, d, J=2 Hz, H-1), 7.17 (1H, d, J=8 Hz, H-4), 6.86 (1H, dd, J=8, 2 Hz, H-3), 4.98 (1H, d, J=9 Hz, H-1′), 4.73 (1H, quintet, J=6 Hz, H-6), 4.28 (1H, dd, J=9, 5 Hz, H-5′), 4.20 (1H, td, J=9, 5 Hz, H-4′), 4.14 (1H, t, J=9 Hz, H-3′), 4.04 (1H, t, J=9 Hz, H-2′), 3.65 (1H, t, J=9 Hz, H-5′), 3.33 (1H, dd, J=15, 6 Hz, H-5), 3.14 (1H, ddd, J=15, 7, 6 Hz, H-8), 3.05 (1H, ddd, J=15, 7, 6 Hz, H-8), 2.95 (1H, dd, J=15, 6 Hz, H-5), 2.30 (2H, m, H_2-7). *Anal.* Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.10; H, 6.35.

Acid Hydrolysis of 1 Compound **1** (15 mg) was hydrolyzed with 3% HCl (10 ml) under reflux for 2 h. The reaction mixture was extracted with ethyl acetate. TLC of the ethyl acetate layer indicated the presence of several compounds derived from the genuine aglycone. The water layer was concentrated and the residue was chromatographed on silica gel using 30% MeOH in $CHCl_3$ as an eluent to yield 4 mg of D-xylose, $[\alpha]_D$ +20° (c=0.2, H_2O). Its trimethylsilyl ether was identical to an authentic sample on GLC.

Methyl Ester of 1 A solution of **1** (140 mg) in MeOH (10 ml) was treated with ethereal CH_2N_2 at room temperature for 2 h. After removal of the solvent and excess reagent by evaporation, the residue was chromatographed on Sephadex LH-20 using MeOH as an eluent to yield the methyl ester of **1** (**2**, 120 mg).

Compound 2 A colorless amorphous powder. UV λ_{max}^{MeOH} nm (log ε): 221

(3.12), 283 (3.00). IR ν_{max}^{KBr} cm^{-1}: 3380, 2910, 1716, 1597, 1521, 1433, 1354, 1275, 1199, 1157, 1111, 1063, 1030, 900. ^{1}H-NMR (100 MHz, C_5D_5N) δ: 7.22 (1H, d, J=2 Hz, H-1), 7.14 (1H, d, J=8 Hz, H-4), 6.78 (1H, dd, J=8, 2 Hz, H-3), 4.83 (1H, d, J=8 Hz, H-1'), 4.49 (1H, quintet, J=6 Hz, H-6), 4.32—3.61 (5H), 3.60 (3H, s, CH_3O), 3.18—2.58 (4H), 2.11 (2H). *Anal.* Calcd for $C_{17}H_{22}O_7$: C, 60.35; H, 6.55. Found: C, 60.27; H, 6.60.

Acid Methanolysys of 2 A solution of compound **2** (100 mg) in MeOH (20 ml) containing 2% H_2SO_4 was heated under reflux for 3 h. the mixture was poured into ice-water, and extracted with ethyl acetate, then the extract was washed with water, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed on Sephadex LH-20 using MeOH as an eluent to yield compound **3** (43 mg).

Compound 3 A colorless amorphous powder, $[\alpha]_D$ +17° (c=1.5, MeOH). UV λ_{max}^{MeOH} nm (log ε): 283 (3.54), 325 (2.46). IR ν_{max}^{KBr} cm^{-1}: 3535, 3300, 2920, 1724, 1515, 1433, 1270, 1222, 1194. ^{1}H-NMR (100 MHz, C_5D_5N) δ: 7.25 (1H, d, J=2 Hz, H-1), 7.17 (1H, d, J=8 Hz, H-4), 6.81 (1H, dd, J=8, 2 Hz, H-3), 4.47 (1H, quintet, J=6 Hz, H-6), 3.58 (3H, s, CH_3O), 3.18—2.67 (4H), 2.05 (2H). EI-MS m/z: 206 $[M]^+$, 191, 149, 123, 91, 77.

Conversion of 3 into Methyl 2-Naphthoate (4) Thionyl chloride (95 mg) was added to a solution of **3** (30 mg) in pyridine and the mixture was allowed to stand at room temperature for 6 h, then poured into ice-water. The products were extracted with ether, washed with 5% HCl solution, 5% Na_2CO_3 solution and water, then dried over anhydrous Na_2SO_4 and concentrated. The residue was dissolved in benzene (10 ml) and 2,3-dichloro-5,6-dicyanobenzoquinone (60 mg) was added. The mixture was stirred under reflux for 5 h. The benzene solution was diluted with ether, washed with water, dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel to yield methyl 2-naphthoate (**4**, 5 mg).

Methyl 2-Naphthoate (4) Colorless needles, mp 78—79 °C. UV λ_{max}^{MeOH} nm (log ε): 254 (3.33), 272 (3.76), 288 (3.69), 304 (2.89), 327 (3.09). IR ν_{max}^{KBr} cm^{-1}: 2945, 1712, 1438, 1298, 1235, 1202, 1131, 1101, 783, 767. ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 8.55 (1H, d, J=2 Hz, H-1), 8.02 (1H, dd, J=8, 2 Hz, H-3), 7.94—7.76 (3H), 7.62—7.36 (2H), 3.95 (3H, s, CH_3O). ^{13}C-NMR (C_5D_5N) δ: 167.0 (C), 135.8 (C), 132.9 (C), 131.3 (C), 129.6 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.0 (CH), 127.1 (CH), 125.6 (CH), 52.1 (CH_3). EI-MS m/z: 186 $[M]^+$, 155, 127, 101, 77. Physical properties and spectral data were identical to those of an authentic sample.

Cholestan-3α-ol β-D-Xylopyranoside A mixture of cholestan-3α-ol (0.5 g), triacetyl-α-D-xylosyl bromide (1 g) and Ag_2O (0.7 g) in $CHCl_3$ (10 ml) was stirred at room temperature for 3 h and filtered. The filtrate was washed with water, dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel using benzene and $CHCl_3$ as eluents to yield cholestan-3α-ol β-D-triacetylxyloside (140 mg), colorless needles, mp 182—183 °C, $[\alpha]_D$ −35° (c=1.0, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 2930, 1750, 1360, 1250, 1230, 1075, 1045. Cholestan-3α-ol β-D-triacetylxyloside (130 mg) was dissolved in MeOH (15 ml) containing 3% KOH and refluxed for 3 h. The reaction mixture was poured into ice-water and the products were extracted with *n*-BuOH. The extract was washed with water and evaporated. The residue was chromatographed on silica gel using $CHCl_3$ and MeOH as eluents to yield cholestan-3α-ol β-D-xylopyranoside (95 mg), a colorless amorphous powder, $[\alpha]_D$ +18° [c=1.0, $CHCl_3$–MeOH (1:1)]. ^{13}C-NMR (C_5D_5N) δ: 32.2 (C-1), 25.7 (C-2), 73.3 (C-3), 35.0 (C-4), 39.7 (C-5), 28.8 (C-6), 32.8 (C-7), 36.4 (C-8), 54.1 (C-9), 36.0 (C-10), 21.0 (C-11), 40.2 (C-12), 42.8 (C-13), 56.6 (C-14), 24.3 (C-15), 28.5 (C-16), 56.5 (C-17), 12.2 (C-18), 11.5 (C-19), 36.0 (C-20), 18.9 (C-21), 35.6 (C-22), 24.2 (C-23), 39.7 (C-24), 28.2 (C-25), 22.6 (C-26), 22.9 (C-27), 103.4 (C-1'), 74.9 (C-2'), 78.4 (C-3'), 71.1 (C-4'), 67.0 (C-5').

Cholestan-3β-ol β-D-Xylopyranoside Under the same reaction conditions as cholestan-3α-ol, cholestan-3β-ol (0.5 g) yielded cholestan-3β-ol β-D-triacetylxyloside (160 mg), colorless needles, mp 168—169 °C, $[\alpha]_D$ +20° (c=1.0, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 2930, 1750, 1375, 1260, 1225, 1075, 1050, 1035. The alkaline methanolysis of cholestan-3β-ol β-D-triacetylxyloside gave cholestan-3β-ol β-D-xylopyranoside, a colorless amorphous powder, $[\alpha]_D$ +10° [c=1.0, $CHCl_3$–MeOH (1:1)]. ^{13}C-NMR (C_5D_5N) δ: 36.5 (C-1), 30.1 (C-2), 77.5 (C-3), 34.9 (C-4), 44.8 (C-5), 29.1 (C-6), 32.3 (C-7), 37.8 (C-8), 54.5 (C-9), 35.7 (C-10), 21.5 (C-11), 40.2 (C-12), 42.8 (C-13), 56.6 (C-14), 24.5 (C-15), 28.5 (C-16), 56.6 (C-17), 12.3 (C-18), 12.3 (C-19), 36.0 (C-20), 19.0 (C-21), 35.6 (C-22), 24.2 (C-23), 39.7 (C-24), 28.3 (C-25), 22.7 (C-26), 22.9 (C-27), 103.0 (C-1'), 75.0 (C-2'), 78.5 (C-3'), 71.2 (C-4'), 67.1 (C-5').

(*R*)- and (*S*)-2-Tetralol 2-Tetralone (3 g) was diluted with MeOH (15 ml) and cooled to 0 °C. After addition of $NaBH_4$ (0.8 g), the mixture was stirred at 0 °C for 30 min. After neutralization with Amberlite IRA-120 and evaporation, the products were chromatographed on silica gel using $CHCl_3$ and MeOH as eluents to yield racemic 2-tetralol (2.7 g). Resolution of the enantiomers was carried out on a Chiralcel OJ column using a mixture of *n*-hexane and isopropanol (100:1) as an eluent to yield (*R*)-2-tetralol [(*R*)-**5**, 1.2 g], $[\alpha]_D$ +56° (c=0.16, EtOH) and (*S*)-2-tetralol [(*S*)-**5**, 1.1 g], $[\alpha]_D$ −52° (c=0.14, EtOH).[10] IR ν_{max}^{neat} cm^{-1}: 3000, 1500, 1490, 1050. EI-MS m/z: 148 $[M]^+$, 130.

(*R*)-2-Tetralol β-D-Triacetylxyloside (*R*)-2-Tetralol (220 mg) was dissolved in CH_2Cl_2 (6 ml) and stirred at −44 °C for 10 min with particles of a molecular sieve (4A 1/16, 100 mg). After addition of $Hg(CN)_2$ (42 mg) and stirring for 20 min, a chilled CH_2Cl_2 solution of triacetyl-α-D-xylosyl bromide (450 mg) was added and the reaction mixture was maintained below 0 °C and stirred for 20 h. After filtration and evaporation, the residue was chromatographed on silica gel using a mixture of *n*-hexane, $CHCl_3$ and EtOAc (3:2:2) as an eluent to yield (*R*)-2-tetralol β-D-triacetylxyloside (127 mg) together with (*R*)-2-tetralol α-D-triacetylxyloside (256 mg). ^{13}C-NMR (C_5D_5N) δ: β-anomer, 36.7 (C-1), 69.6 (C-2), 28.1 (C-3), 26.7 (C-4), 134.7 (C-5), 128.8 (C-6), 126.2 (C-7), 126.2 (C-8), 129.9 (C-8a), 136.0 (C-4a), 99.9 (C-1'), 72.4 (C-2'), 74.5 (C-3'), 71.8 (C-4'), 62.5 (C-5'). α-anomer, 34.3 (C-1), 70.2 (C-2), 29.6 (C-3), 26.9 (C-4), 134.1 (C-5), 128.9 (C-6), 126.3 (C-7), 126.1 (C-8), 129.7 (C-8a), 136.2 (C-4a), 94.1 (C-1'), 71.7 (C-2'), 72.8 (C-3'), 69.9 (C-4'), 59.0 (C-5'). MS of both α- and β-anomers, m/z: 406 $[M]^+$, 131 (aglycone).

(*S*)-2-Tetralol β-D-Triacetylxyloside Under the same reaction conditions as (*R*)-2-tetralol, (*S*)-2-tetralol gave (*S*)-2-tetralol β-D-triacetylxyloside (110 mg) and its α-anomer (250 mg). ^{13}C-NMR (C_5D_5N) δ: β-anomer, 34.3 (C-1), 69.7 (C-2), 29.3 (C-3), 26.2 (C-4), 134.1 (C-5), 129.0 (C-6), 126.2 (C-7), 126.1 (C-8), 129.8 (C-8a), 136.4 (C-4a), 99.5 (C-1'), 72.5 (C-2'), 73.3 (C-3'), 71.7 (C-4'), 62.7 (C-5'), α-anomer, 36.4 (C-1), 70.2 (C-2), 28.0 (C-3), 27.1 (C-4), 134.6 (C-5), 128.9 (C-6), 126.3 (C-7), 126.3 (C-8), 129.7 (C-8a), 136.0 (C-4a), 94.5 (C-1'), 71.7 (C-2'), 73.5 (C-3'), 69.9 (C-4'), 59.0 (C-5'). MS of both α- and β-anomers, m/z: 406 $[M]^+$, 131 (aglycone).

Deacetylation of 2-Tetralol D-Triacetylxylosides Each sample of 2-tetralol D-triacetylxylosides (60 mg) was dissolved in MeOH (4 ml) and diluted with water (6 ml). After addition of Et_3N (0.15 ml), the mixture was stirred at room temperature for 20 min. After evaporation, the residue was purified by silica gel column chromatography using $CHCl_3$ and MeOH as eluent to yield the corresponding 2-tetralol D-xylosides (35—42 mg). MS of each product, m/z 280 $[M]^+$, 131 (aglycone).

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