The Structures of Four Diarylheptanoid Glycosides from the Female Flowers of *Alnus serrulatoides*

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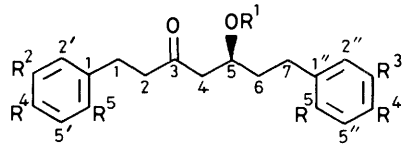
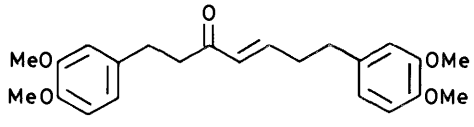
Four diarylheptanoid monoglycosides (**2a**), (**2b**), (**3**), and (**4**), in addition to the hydroxy ketone (**1**), were isolated from the female flowers of *Alnus serrulatoides*. On the basis of the physicochemical and the *X*-ray crystallographic analyses, these were characterized as (5*S*)-1,7-bis(3,4-dihydroxyphenyl)-5-hydroxyheptan-3-one (**1**), (5*S*)-1-(4-hydroxyphenyl)-7-(3,4-dihydroxyphenyl)-5-(β-D-xylopyranosyloxy)heptan-3-one (**2a**), (5*S*)-1-(3,4-dihydroxyphenyl)-7-(4-hydroxyphenyl)-5-(β-D-xylopyranosyloxy)heptan-3-one (**2b**), (5*S*)-1,7-bis(3,4-dihydroxyphenyl)-5-(β-D-xylopyranosyloxy)-heptan-3-one (**3**), and (5*S*)-1,7-bis(3,4-dihydroxyphenyl)-5-(β-D-glucopyranosyloxy)heptan-3-one (**4**), respectively. Of these compounds, the glycosides (**2a**), (**2b**), and (**4**) are new.

In our previous studies we elucidated the structures of five novel C_{31}-dammarane-type triterpenoids [1–4] from the male flowers of *Alnus serrulatoides* Call. (Japanese name: Kawara-hannoki) and also those of four novel C_{31}-secodammarane-type triterpenoid saponins [5] from the female flowers of the plant. In a continuation of the structural elucidation of the chemical constituents, we have recently isolated four diarylheptanoid monoglycosides (**2a**), (**2b**), (**3**), and (**4**), in addition to the hydroxy ketone (**1**), from the female flowers. The glycosides (**2a**), (**2b**), and (**4**) are new. The u.v., i.r., ^{1}H n.m.r. spectra, and electron-impact (e.i.-) and/or field-desorption mass spectra (f.d.-m.s.) and the chemical behaviour of the tetramethyl ether (**5**) and the aglycone (**6**), which were derived from the glycoside (**3**), were coincident with those of the previously reported oregonin tetramethyl ether [6] and hirsutanonol,[7] respectively.† Since the absolute configurations of neither oregonin nor hirsutanonol had been assigned, we elucidated the absolute configuration of the glycoside (**3**) and reported the result in the form of the preliminary communication.[8] During the course of this study, the optical rotations of the tetramethyl ether (**7**) and its dibromo derivative (**8**), which were derived from the glycoside (**3**), were found to be dependent on the solvents used for measurement of the rotations. We here report the evidence leading to our assignments of structure and absolute configuration for compound (**1**) and the glycosides (**2a**), (**2b**), (**3**), and (**4**) and, in addition, our results which show that diarylheptanoid optical rotations are solvent dependent.



(**1**)/(**6**) $R^1 = R^5 = H$, $R^2 = R^3 = R^4 = OH$
(**2a**) R^1 = β-D-xyl, $R^2 = R^5 = H$, $R^3 = R^4 = OH$
(**2b**) R^1 = β-D-xyl, $R^2 = R^4 = OH$, $R^3 = R^5 = H$
(**3**) R^1 = β-D-xyl, $R^2 = R^3 = R^4 = OH$, $R^5 = H$
(**4**) R^1 = β-D-glc, $R^2 = R^3 = R^4 = OH$, $R^5 = H$
(**5**) R^1 = β-D-xyl, $R^2 = R^3 = R^4 = OMe$, $R^5 = H$
(**7**)/(**12**) $R^1 = R^5 = H$, $R^2 = R^3 = R^4 = OMe$
(**8**) $R^1 = H$, $R^2 = R^3 = R^4 = OMe$, $R^5 = Br$
(**9a**) R^1 = β-D-xyl, $R^2 = R^5 = H$, $R^3 = R^4 = OMe$
(**9b**) R^1 = β-D-xyl, $R^2 = R^4 = OMe$, $R^3 = R^5 = H$
(**10a**) $R^1 = R^2 = R^5 = H$, $R^3 = R^4 = OMe$
(**10b**) $R^1 = R^3 = R^5 = H$, $R^2 = R^4 = OMe$
(**11**) R^1 = β-D-glc, $R^2 = R^3 = R^4 = OMe$, $R^5 = H$
(**13**) R^1 = Ac, $R^2 = R^3 = R^4 = OMe$, $R^5 = H$
(**15**) R^1 = Ac, $R^2 = R^3 = R^4 = OMe$, $R^5 = Br$



(**14**)

Results and Discussion

Structural Elucidation.—An acetone extract of the female flowers was subjected to centrifugal chromatography on a silica-gel plate to give the hydroxy ketone (**1**) and the diarylheptanoid glycosides (**2**)—(**4**). These compounds are numbered in order of increasing polarity on a thin-layer chromatogram. The glycoside (**2**) was, however, found to be a mixture [(**2a**) and (**2b**)], since it formed two trimethyl ethers, (**9a**) and (**9b**), separable by preparative h.p.l.c.

Glycoside (**3**).—The glycoside (**3**) was identified as 1,7-bis(3,4-dihydroxyphenyl)-5-(β-D-xylopyranosyloxy)heptan-3-one on the basis of the physical and spectral data obtained for it and its tetramethyl ether (**5**) (see Tables 1—6). The absolute configuration of this glycoside (**3**) was elucidated as follows.

On comparison of the ^{13}C n.m.r. chemical shifts of the glycoside (**3**) with those of the aglycone (**6**), it was found that the glycosylation shift (−3.4 p.p.m.) at C-4 was larger than that (−2.7 p.p.m.) at C-6 (Table 4). By application of the glycosylation shift rule [9] to these shifts, the configuration at C-5 of the glycoside (**3**) was assigned as *S*. This was confirmed by an *X*-ray crystallographic analysis of the dibromo tetramethyl ether derivative (**8**), which was derived from the aglycone (**7**). The structure was solved using the heavy-atom method. Least-squares refinement converged to *R* 0.060 over 1 933 reflections. When the anomalous dispersion [10] of the bromine and oxygen atoms was included in the calculation without further refinement, values of *R* 0.054 and 0.074 were obtained for two enantiomers. Hamilton's test showed that this difference is significant.[11] This result shows that the absolute configuration of compound (**8**) is *S* (see ORTEP [12] in Figure 1). Futhermore,

† Attempts to obtain authentic samples of oregonin and hirsutanonol and their derivatives,[6,7] copies of their spectra, and details of their optical rotations have been unsuccessful. Direct comparisons have, therefore, not been possible.

Table 1. Physical, electronic absorption spectral, and i.r. spectral data for compounds (**1**), (**3**), (**5**)—(**8**), (**9a**), (**9b**), and (**11**)—(**15**)

Compound	M.p. (°C)	$[\alpha]_D^{25}$/° (*c*, solvent)	$\lambda_{max.}$ (log ε)/nm[a]	$\nu_{max.}$ (neat)/cm^{-1}
(**1**)	Oil	−1.5 ±1.0 (0.20, MeOH)	221 (4.07), 283 (3.75)	3 370 (OH), 1 700 (C=O), 1 603, 1 518 (aromatic ring)
(**3**)	Oil	−19.6 ±0.1 (13.0, MeOH)	222 (4.07), 283 (3.75)	3 360 (OH), 1 702 (C=O) 1 608, 1 510 (aromatic ring)
(**5**)	Oil	−20.2 ±0.7 (0.59, MeOH) −17.8 ±0.7 (0.59, $CHCl_3$)	228 (4.07), 280 (3.69)	3 440 (OH). 1 710 (C=O) 1 608, 1 593, 1 512 (aromatic ring)
(**6**)	Oil	−1.7 ±0.3 (0.78, MeOH)	220 (4.00), 283 (3.67)	3 345 (OH), 1 700 (C=O) 1 603, 1 517 (aromatic ring)
(**7**)	89.0—89.5[d]	−2.3 ±0.1 (1.85, MeOH) +12.0 ±0.1 (1.85, $CHCl_3$)	229 (4.13), 280 (3.70)	3 540 (OH), 1 710 (C=O) 1 608, 1 592, 1 512 (aromatic ring)[b]
(**8**)	93.0[e]	−1.3 ±0.2 (0.92, MeOH) +6.3 ±0.2 (0.92, $CHCl_3$)	230 (4.32), 286 (3.89)	3 515 (OH), 1 703 (C=O) 1 605, 1 575, 1 508 (aromatic ring)[c]
(**9a**)	Oil	−16.9 ±3.1 (0.65, MeOH) −9.2 ±3.1 (0.65, $CHCl_3$)	225 (4.24), 287 (3.70), 284 (3.65)	3 400 (OH), 1 705 (C=O) 1 610, 1 590, 1 509 (aromatic ring)
(**9b**)	Oil	−14.4 ±2.2 (0.90, MeOH) −12.2 ±2.2 (0.90, $CHCl_3$)	225 (4.26), 278 (3.71), 284 (3.66)	3 400 (OH), 1 706 (C=O) 1 611, 1 590, 1 510 (aromatic ring)
(**11**)	Oil	−10.0 ±3.3 (0.60, MeOH) −8.3 ±3.3 (0.60, $CHCl_3$)	228 (4.14), 280 (3.73)	3 403 (OH), 1 702 (C=O) 1 603, 1 591, 1 506 (aromatic ring)
(**12**)	89.0—89.5[d]	−3.5 ±0.8 (0.52, MeOH) +6.5 ±0.5 (0.52, $CHCl_3$)		3 470 (OH), 1 709 (C=O) 1 605, 1 598, 1 515 (aromatic ring)[c]
(**13**)	Oil	+2.9 ±0.5 (0.38, MeOH) +3.5 ±0.5 (0.38, $CHCl_3$)	229 (4.25), 280 (3.80)	1 738 ($OCOCH_3$), 1 715 (C=C) 1 608, 1 592, 1 515 (aromatic ring)
(**14**)	Oil		227 (4.24), 279 (3.73)	1 667 (conjugated C=O), 1 628 (C=O), 1 611, 1 594, 1 513 (aromatic ring)[b]
(**15**)	Oil	+3.5 ±0.7 (0.57, MeOH) +3.1 ±0.7 (0.57, $CHCl_3$)	231 (4.25), 287 (3.79)	1 735 ($OCOCH_3$), 1 715 (C=O) 1 603, 1 573, 1 505 (aromatic ring)

[a] Taken in EtOH. [b] Taken in $CHCl_3$. [c] Taken in a Nujol mull. [d] Crystallized from EtOAc–hexane mixture. [e] Crystallized from benzene–hexane mixture.

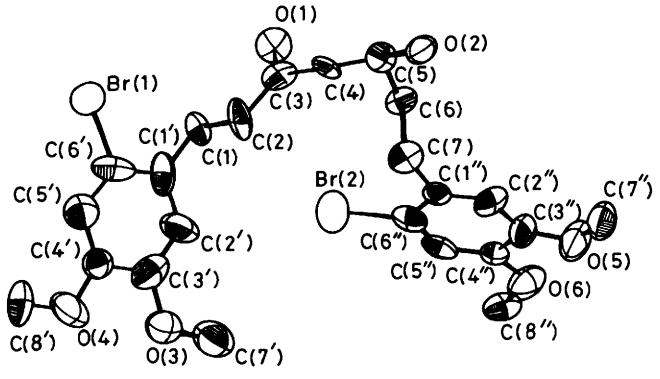


Figure 1. ORTEP drawing of the molecular structure for dibromo tetramethyl ether (**8**) with crystallographic numbering scheme

the observed and calculated Bijvoet inequalities[13] for the *S* configuration were in good agreement with each other, as shown in Table 7. Thus, the absolute configuration of the glycoside (**3**) was necessarily concluded to be *S* and its structure was defined as (5*S*)-1,7-bis(3,4-dihydroxyphenyl)-5-(β-D-xylopyranosyloxy)heptan-3-one.

In addition, the molecular arrangement and the hydrogen bond networks of the dibromo derivative (**8**) were found to be as shown in Figure 2. As given in Table 8, the heptane chain possesses torsion angles of +139°, −58°, and −59° at C(2)–C(3)–C(4)–C(5), C(3)–C(4)–C(5)–C(6), and C(4)–C(5)–C(6)–C(7), respectively and is not planar. These torsion angles may result from intermolecular hydrogen bonding between the hydrogen atom of the 5-hydroxy group and the oxygen atom of the 4″-methoxy group of the adjacent molecule. In this way, the molecules build up, along the *b* axis, an infinite chain which is coupled, in turn, to the next chain by van der Waals force between the hydrophobic groups.

Glycoside (**2a**).—The f.d.-m.s. of the trimethyl ether (**9a**) of the glycoside (**2a**) exhibited the M^+ and $[M - 150]^+$ ion peaks at *m/z* 504 and 354, respectively. These peaks indicated the presence of a pentose moiety. This pentose moiety was found to be D-xylopyranose, the C-1′ position of which, on the evidence of the ^{13}C n.m.r. chemical shifts and the coupling constant of the anomeric proton, binds to the 5-position of the aglycone (**10a**) *via* a β-glycosidic linkage. On the other hand, appearance of signals at δ_H 3.77 and 3.86 (3 H and 6 H, each s) in the ^1H n.m.r. spectrum of compound (**9a**) indicated the presence of three methoxy groups in the aglycone moiety. On the basis of comparison of the ^{13}C n.m.r. chemical shifts of compound (**9a**) with those of compound (**5**) and appearance of the e.i.-m.s. ion peaks at *m/z* 191.1028 $\{[(MeO)_2C_6H_3CH_2CH_2CH{=}CH]^+\}$, 177.0917 $([MeOC_6H_4CH_2CH_2COCH_2]^+)$, 164.0837 $([MeOC_6H_4CH_2CH_2COH]^+)$, and 163.0734 $([MeOC_6H_4CH_2CH_2CO]^+)$, it was found that compound (**9a**) is 1-(4-methoxyphenyl)-7-(3,4-dimethoxyphenyl)-5-(β-D-xylopyranosyloxy)heptan-3-one.

The absolute configuration of this compound (**9a**) was shown to be *S* by considering the glycosylation shifts between compound (**9a**) (Table 4) and an aglycone (**10**), which was obtained from compound (**9**) by hydrolysis with Takadiastase.[14] Consequently, the glycoside (**2a**) was defined as (5*S*)-1-(4-hydroxyphenyl)-7-(3,4-dihydroxyphenyl)-5-(β-D-xylopyranosyloxy)heptan-3-one.

Glycoside (**2b**).—The trimethyl ether (**9b**) of the glycoside (**2b**) gave the M^+ and $[M - 150]^+$ ion peaks at *m/z* 504 and 354, respectively, in the f.d.-m.s. On the basis of the ^{13}C n.m.r. chemical shifts, the e.i.-m.s. ion peaks at *m/z* 193.0889 $\{[(MeO)_2C_6H_3CH_2CH_2CO]^+\}$ and 147.0780 $([MeOC_6H_4CH_2CH{=}CH]^+)$, and the coupling constant of the anomeric proton, it was shown that compound (**9b**) is the 5-*O*-β-D-xylopyranoside of 1-(3,4-dimethoxyphenyl)-7-(4-methoxy-

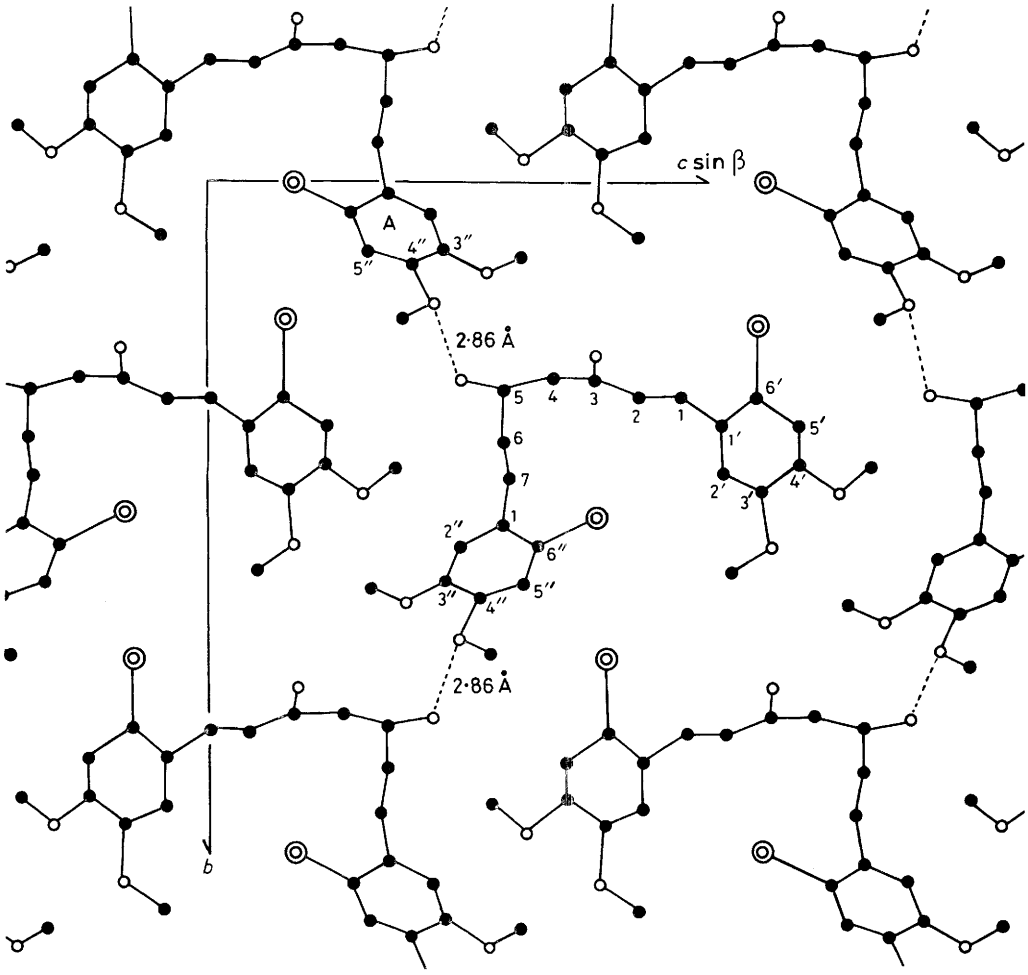


Figure 2. The projection of dibromo tetramethyl ether (**8**) along the *a* axis. The atoms indicated with ●, ○, and ◎ denote carbon, oxygen, and bromine atoms, respectively. The hydrogen bondings are shown by a broken line. The transformations of the atomic co-ordinates are (A) *x*, *y*, *z*; (B) $1 - x$, $1/2 + y$, $1 - z$

phenyl)-5-hydroxyheptan-3-one (**10b**). The absolute configuration of compound (**9b**) was elucidated as *S* in the same way as for compound (**9a**). The glycoside (**2b**) was thus established as (5*S*)-1-(3,4-dihydroxyphenyl)-7-(4-hydroxyphenyl)-5-(β-D-xylopyranosyloxy)heptan-3-one.

Glycoside (**4**).—Methylation of the glycoside (**4**) with CH_2N_2 gave a tetramethyl ether (**11**) whose f.d.-m.s. exhibited peaks due to the ions $[M + H]^+$ and $[M - 180]^+$ at *m/z* 565 and 384, respectively. The structural elucidation of the tetramethyl ether (**11**) was made by use of the physical and spectral data, given in Tables 1—5, in the same manner as for other compounds. From these data, the glycoside (**4**) was characterized as (5*S*)-1,7-bis(3,4-dihydroxyphenyl)-5-(β-D-glucopyranosyloxy)heptan-3-one.

Solvent-dependence of the Optical Rotation.—During the course of the structural elucidation, it was observed that when the solvent was changed from MeOH to $CHCl_3$, the optical rotation of compounds (**7**) and (**8**) changed from laevorotatory to dextrorotatory; this was not, however, the case for their corresponding acetates (**13**) and (**15**) which were dextrorotatory in both solvents. A similar solvent-dependence of the optical rotation was also observed for dihydroyashabushiketol and its acetate.[15] These phenomena indicate that the intermolecular hydrogen bonding between the solvent and the 5-hydroxy group in these diarylheptanoids participates in the inversion of optical rotation. A detailed investigation of these phenomena is now in progress.

Experimental

The ^1H and ^{13}C n.m.r. spectra were obtained at 90 and 22.6 MHz, respectively, with $SiMe_4$ as internal standard. The e.i.-m.s. were recorded on a Hitachi RMU-6L mass spectrometer at 70 eV. The f.d.-m.s. were taken on a JEOL JMS-D 300 mass spectrometer equipped with a silicone emitter; the emitter current was 0—20 mA. The optical rotation was obtained on a Yanaco OR-50D Automatic Digital polarimeter. The u.v. spectra were taken on a Shimadzu UV-240 spectrometer. Analytical t.l.c. and preparative t.l.c. (p.l.c.) were carried out on Merck 60 GF_{254} silica-gel plates with 0.25 and 0.75 mm layers of the adsorbent, respectively. Compounds were visualized as coloured spots by spraying with vanillin–H_2SO_4 (1:134, w/w) and then by heating on a hot-plate.

The physical and spectral data for compounds (**1**), (**3**), (**5**)—(**8**), (**9a**), (**9b**), and (**11**)—(**15**) are summarized in Tables 1—6, except for the ^1H n.m.r. data of compound (**14**).

Extraction and Isolation.—Female flowers (444 g) of *Alnus serrulatoides* Call., which grows naturally on the river side in the suburbs of Hiroshima City, were collected in April (*ca.* 1 month after the flowering of the male flowers). The flowers were minced mechanically and then immersed in acetone at room

Table 2. Mass spectral data for compounds (**1**), (**3**), (**5**)—(**8**), (**9a**), (**9b**), and (**11**)—(**15**)

Compound	F.d.-m.s. *m/z* (abundance %)	E.i.-m.s. *m/z* (abundance %)
(**1**)		346 (2, M^+), 328 (8, $[M - H_2O]^+$), 180 (5), 165 (4), 123 (100), 43 (45)
(**3**)	501 (7, $[M + Na]^+$), 351 (29, $[M + Na - 150]^+$), 328 (100, $[M - 150]^+$), 164 (10, $[M - 150]^{2+}$)	328.1267 (4, $C_{19}H_{20}O_5$ requires 328.1308, $[M - 150]^+$), 180.0788 (1, $C_{10}H_{12}O_3$ requires 180.0786), 165.0530 (2, $C_9H_9O_3$ requires 165.0550), 123.0448 (24, $C_7H_7O_2$ requires 123.0446), 43.0186 (100, C_2H_3O requires 43.0184)
(**5**)	534 (29, M^+), 384 (100, $[M - 150]^+$), 192 (15, $[M - 150]^{2+}$)	384 (58, $[M - 150]^+$), 219 (10), 193 (4), 191 (5), 177 (16), 176 (8), 165 (15), 164 (11), 151 (100), 121 (40)
(**6**)		346 (0.5, M^+), 328 (2, $[M - H_2O]^+$), 180 (7), 165 (3), 123 (20), 43 (100)
(**7**)		402 (1, M^+), 384 (7, $[M - H_2O]^+$), 208 (5), 177 (7), 165 (10), 164 (8), 151 (100), 107 (11)
(**8**)		562, 560, 558 (1, 1.5, 1, M^+), 544, 542, 540 (2, 3, 2, $[M - H_2O]^+$), 463, 461 (4, 4, $[M - Br - H_2O]^+$), 382 (3, $[M - 2Br - H_2O]^+$), 231, 229 (98, 100)
(**9a**)	504 (100, M^+), 354 (70, $[M - 150]^+$), 252 (10, M^{2+}), 177 (3, $[M - 150]^{2+}$)	354.1775 (19, $[M - 150]^+$, $C_{22}H_{26}O_4$ requires 354.1829), 191.1028 (2, $C_{12}H_{15}O_2$ requires 191.1071), 177.0917 (6, $C_{11}H_{13}O_2$ requires 177.0915), 164.0837 (3, $C_{10}H_{12}O_2$ requires 164.0836), 163.0734 (1, $C_{10}H_{11}O_2$ requires 163.0758), 151.0779 (100, $C_9H_{11}O_2$ requires 151.0759), 121.0666 (33, C_8H_9O requires 121.0653)
(**9b**)	504 (86, M^+), 354 (100, $[M - 150]^+$), 252 (4, M^{2+}), 177 (7, $[M - 150]^{2+}$)	354.1798 (23, $[M - 150]^+$, $C_{22}H_{26}O_4$ requires 354.1829), 193.0889 (1, $C_{11}H_{13}O_3$ requires 193.0864), 151.0761 (28, $C_9H_{11}O_2$ requires 151.0758), 147.0780 (2, $C_{10}H_{11}O$ requires 147.0808), 121.0650 (100, C_8H_9O requires 121.0652)
(**11**)	565 (50, $[M + H]^+$), 384 (100, $[M - 180]^+$)	384 (16, $[M - 180]^+$), 219 (2), 193 (2), 191 (2), 177 (5), 176 (2), 165 (6), 164 (3), 151 (100)
(**12**)		402 (14, M^+), 384 (5, $[M - H_2O]^+$), 208 (18), 177 (6), 165 (14), 164 (6), 151 (100), 107 (9)
(**13**)		444 (3, M^+), 384 (7, $[M - AcOH]^+$), 219 (1), 151 (35), 43 (100)
(**14**)		384 (3, M^+), 208 (69), 165 (42), 151 (100), 43 (61)
(**15**)		604, 602, 600 (0.3, 0.5, 0.3, M^+), 544, 542, 540 (2, 4, 2, $[M - AcOH]^+$), 463, 461 (4, 4), 382 (2), 231, 229 (44, 45), 43 (100)

temperature for 2 months. Removal of the solvent from the acetone solution gave a brown, viscous oil (76.0 g). This oil was divided into five parts and each part was subjected to centrifugal chromatography on a silica gel disc, 5 mm in thickness and 30 cm in diameter, with $CHCl_3$–MeOH–H_2O (85:14:1, v/v) as eluant. This gave four fractions each of which was further purified by repeated centrifugal chromatography under the same conditions as described above to give compound (**1**) (190 mg), the glycoside (**2**) (230 mg), the glycoside (**3**) (14.9 g), and the glycoside (**4**) (48 mg); these gave spots with R_F values of 0.45, 0.38, 0.30, and 0.25, respectively, on analytical t.l.c. with $CHCl_3$–MeOH–H_2O (30:9:1 v/v) as developer.

Hydrolysis of the Glycoside (**3**) *with Taka-diastase.*—Taka-diastase (Sankyo Co. Ltd.,[14] 1.5 g) dissolved in water (20 cm^3) was added to a solution of the glycoside (**3**) (760 mg) in water (20 cm^3), followed by addition of toluene (1 cm^3) and incubation for 2 days at 33 °C. The reaction mixture was extracted with Bu^nOH. Removal of the solvent and purification by p.l.c. gave 1,7-bis(3,4-dihydroxyphenyl)-5-hydroxyheptan-3-one (**6**) (156 mg). The aqueous liquor from the above reaction was lyophilized and then acetylated with acetic anhydride–pyridine to give tetra-*O*-acetylxylopyranose; this was identified by co-t.l.c. and co-g.l.c. (2%OV-17, 150 °C) with an authentic sample.

Methylation of the Glycoside (**3**) *with* CH_2N_2.—The glycoside (**3**) (585 mg) dissolved in MeOH was methylated with CH_2N_2 at 0 °C after which the excess of CH_2N_2 was quenched with a few drops of acetic acid. After addition of a few drops of toluene the mixture was evaporated; p.l.c. of the residue gave the tetramethyl ether (**5**) (191 mg).

Hydrolysis of Compound (**5**) *with* H_2SO_4.—Compound (**5**) (23 mg) was refluxed with 2% H_2SO_4 (3 cm^3) for 1 h, followed by extraction with $CHCl_3$. The $CHCl_3$ extract was subjected to p.l.c. with EtOAc–hexane (1:1, v/v) to give two bands at R_F 0.3 and 0.7, which, on extraction with $CHCl_3$, gave an alcohol derivative (**7**) (2 mg) and a dehydrated product (**14**) (6 mg) [$\delta_H(CDCl_3)$ 2.44—2.83 (8 H, m, $CH_2 \times 4$), 6.10 (1 H, d, *J* 16 Hz, COC*H*=CH), and 6.63—7.00 (7 H, m, ArH and COCH=C*H*), respectively. Compounds (**7**) and (**14**) were confirmed as being identical with the tetramethyl ether derivatives of hirsutanonol and hirsutenone, respectively, by comparison of their spectral data with those described in refs. 6 and 7. The aqueous liquor, from the above experiment, after neutralization with Dowex-WGR, was treated in the same way as the glycoside (**3**) to confirm the presence of xylose.

Hydrolysis of Compound (**5**) *with Taka-diastase.*—After water (20 cm^3) had been added to the methanolic solution (1 cm^3) of the tetramethyl ether (**5**) (64 mg), MeOH was evaporated off to leave a suspension. This suspension was treated with Taka-diastase under conditions similar to those employed for the glycoside (**1**) to afford its aglycone (**7**) (18 mg) and xylose. Acetylation of compound (**7**) (103 mg) with acetic anhydride–pyridine gave its acetate (**13**) (92 mg).

Bromination of Compound (**7**) *with* Br_2.—Following the method described in the literature,[16] the bromination of compound (**7**) (172 mg) was carried out by use of bromine (170 mg) dissolved in $CHCl_3$ (5 cm^3) with stirring for 1 h at 0 °C under a N_2 atmosphere. The resulting mixture was subjected to p.l.c. with EtOAc–hexane (3:2, v/v) to give a dibromo derivative (**8**) (139 mg) (Found: C, 49.1; H, 5.05; Br, 28.5. $C_{23}H_{28}Br_2O_6$ requires C, 49.30; H, 5.04; Br, 28.52%). Acetylation of the dibromo derivative (**8**) (72 mg) in a similar

Table 3. ^{1}H n.m.r. chemical shifts (δ_H, $CDCl_3$) of compounds (**1**), (**3**), (**5**)—(**8**), (**9a**), (**9b**), (**11**)—(**13**), and (**15**)[a]

Compound	6-H	1-, 2-, 4-, 7-H	5-H	Aromatic H	OH[e]	OMe	OAc	Anomeric H
(**1**)[b]	1.54—1.78 (2 H, m)	2.32—2.79 (8 H, m)	4.05 (1 H, quin, *J* 6)	6.47—6.78 (6 H, m)	7.56 (4 H, brs)			
(**3**)[c]	1.70—2.23 (2 H, m)	2.43—3.08 (8 H, m)	*d*	6.58—7.15 (6 H, m)				4.63 (1 H, d, *J* 7)
(**5**)[c]	1.77—2.20 (2 H, m)	2.43—3.02 (8 H, m)	*d*	6.70—6.93 (6 H, m)		3.72 (12 H, s)		4.67 (1 H, d, *J* 7)
(**6**)[b]	1.44—1.86 (2 H, m)	2.48—2.74 (8 H, m)	4.07 (1 H, quin, *J* 6)	6.45—6.84 (6 H, m)	7.65 (4 H, brs)			
(**7**)	1.55—1.92 (2 H, m)	2.39—2.99 (8 H, m)	4.03 (1 H, m)	6.52—6.71 (6 H, m)	3.24 (1 H, brs)	3.72, 3.74 3,76, 3.79 (each 3 H, s)		
(**8**)	1.59—1.83 (2 H, m)	2.54—3.01 (8 H, m)	4.08 (1 H, m)	6.75, 6.77 (each 1 H, s), 6.99 (2 H, s)	3.07 (1 H, brs)	3.84 (12 H, s)		
(**9a**)	1.70—1.98 (2 H, m)	2.52—2.91 (8 H, m)	*d*	6.64—7.14 (7 H, m)		3.77, 3.86 (3 H, and 6 H, each s)		4.28 (1 H, d, *J* 7) 4.81 (1 H, d, *J* 7)[c]
(**9b**)	1.73—2.00 (2 H, m)	2.43—2.91 (8 H, m)	*d*	6.72—7.13 (7 H, m)		3.77, 3.85 3.86 (each s)		4.27 (1 H, d, *J* 7) 4.72 (1 H, d, *J* 7)[c]
(**11**)	1.60—1.96 (2 H, m)	2.31—2.90 (8 H, m)	*d*	6.51—6.82 (6 H, m)		3.80 (12 H, s)		4.81 (1 H, d, *J* 7)[c]
(**12**)	1.56—1.93 (2 H, m)	2.49—2.84 (8 H, m)	4.02 (1 H, m)	6.63—6.84 (6 H, m)	2.90 (1 H, brs)	3.83, 3.85 (each 6 H, s)		
(**13**)	1.68—2.04 (2 H, m)	2.39—2.91 (8 H, m)	5.26 (1 H, quin, *J* 6)	6.59—6.82 (6 H, m)		3.79, 3.80 3.82 (6 H, 3 H, 3 H, each s)	1.97 (3 H, s)	
(**15**)	1.74—2.04 (2 H, m)	2.44—3.02 (8 H, m)	5.29 (1 H, quin, *J* 6)	6.73, 6.77 (each 1 H, s) 6,99 (2 H, s)		3.84 (12 H, s)	2.01 (3 H, s)	

[a] Coupling constants (*J*) are in Hz. [b] Taken in $(CD_3)_2CO$. [c] Taken in C_5D_5N. [d] Overlapped with the proton signals of the sugar moiety. [e] These signals disappeared in D_2O. The proton signals of the hydroxy groups of the sugar moiety are not given here.

way to that employed for compound (**7**) gave its acetate (**15**) (66 mg).

X-*Ray Crystallographic Analysis*.—The crystal used was *ca.* 0.2 mm × 0.85 mm × 0.6 mm in size. Cell dimensions were determined by least-squares calculations from 2θ values of 30 reflections measured on a Syntex R-3 automated four-circle diffractometer with graphite-monochromated Mo-K_α radiation.

Crystal data. $C_{23}H_{28}Br_2O_6$, M = 560.4, Monoclinic, a = 4.720(1), b = 18.806(7), c = 13.651(6) Å, β = 98.65(3)°, U = 1 197.9(7) Å^3, D_m = 1.52 g cm^{-3}, Z = 2, D_c = 1.55 g cm^{-3}, F(000) 568, space group $P2_1$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 36.0 cm^{-1}.

A total of 2 355 reflections ($|F_o| > 0$) which included 1 114 Friedel pairs (*hkl* and $\bar{h}\bar{k}\bar{l}$) were collected by use of the ω scan technique in the range 2θ ≤ 50.0°, and used for the structure determination. The data were corrected for Lorentz and polarization factors, but no absorption corrections were applied. The structure was solved by the conventional heavy-atom method. The position of the bromine atom was obtained from a sharpened Patterson function, and then the positions of oxygen and carbon atoms were determined by difference-Fourier syntheses. A least-squares refinement was carried out by use of anisotropic temperature factors for bromine, carbon, and oxygen atoms and isotropic temperature factors for hydrogen atoms. In the least-squares calculation, the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with w = 1.0 for all the reflections. Refinement finally gave R and R_w values of 0.074 and 0.076, respectively. Then the reflections with $|F_o| < 7$ were removed from the refinement. Two more cycles of least-squares refinement gave R and R_w values of 0.060 and 0.067, respectively, for 1 933 reflections. Finally, structure-factor calculations were performed including anomalous dispersion of bromine and oxygen atoms to obtain an indication of absolute configuration. The R factor was 0.054 (R_w 0.062) for *S* configuration and 0.074 (R_w 0.083) for *R* configuration. One cycle of least-squares refinement for the *S* configuration gave R and R_w values of 0.054 and 0.061, respectively. For 148 Bijvoet pairs[13] with an $|S| = ||F_c(hkl)| - |F_c(\bar{h}\bar{k}\bar{l})||/\sigma(F_o)$ value greater than 3, the signs of $\Delta|F_o|$ were in good agreement with those of $\Delta|F_c|$. Of these pairs, 30 pairs having the largest $|S|$ value are listed in Table 7. Final atomic co-ordinates, interatomic distances, and bond angles are given in Tables 9—11. Although their standard deviations are large, the results of *X*-ray crystallographic analysis is enough for determination of the absolute configuration of compound (**8**). Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. Sup. 23867 (14 pp.).*

Isolation of Compounds (**9a**) *and* (**9b**).—Methylation of the glycoside (**2**) (247 mg) with CH_2N_2 gave a methylated product

* For details of the Supplementary Publication scheme, see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984 Issue 1.

Table 4. ^{13}C N.m.r. chemical shifts (δ_C) for compounds (**3**), (**5**)—(**8**), (**9a**), (**9b**), (**11**), and (**12**), for solutions in C_5D_5N[a]

(i) 5-Hydroxyheptan-3-one moiety

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	OMe
(**3**)	29.2	45.8	209.1	47.8	75.2	37.8	31.0	
(**5**)	29.4	45.6	208.6	48.1	75.0	37.9	31.4	55.9 (4)
(**6**)	29.4	45.8	209.7	51.2	67.3	40.5	31.9	
(**7**)	29.4	45.6	209.6	51.1	67.3	40.2	32.0	55.9 (4)
(**8**)	29.8	43.7	208.6	50.6	67.0	38.2	32.2	55.9 (4)
(**9a**)	29.0	45.8	208.8	48.2	75.2	38.1	31.5	55.1, 55.9 (2)
(**9b**)	29.4	45.7	208.7	48.1	75.2	38.1	31.0	55.9 (2), 55.0
(**11**)	29.2	45.4	208.6	48.0	75.3	37.8	31.2	55.7 (4)
(**12**)	29.5	45.6	209.4	51.2	67.3	40.3	32.0	55.9 (4)

(ii) Diphenyl moiety

Compound	C-1′	C-1″	C-2′	C-2″	C-3′	C-3″	C-4′	C-4″	C-5′	C-5″	C-6′	C-6″
(**3**)	132.8	134.0	116.2[b]	116.2[b]	146.4	146.4	144.6[c]	1.44.5[c]	116.3[b]	116.3[b]	119.7	119.7
(**5**)	(133.6)	(134.6)	112.7[b]	112.7[b]	(149.0)	(149.0)	(147.5)	(147.5)	113.1[b]	113.3[b]	120.7	120.7
(**7**)	133.1	134.6	116.5[b]	116.5[b]	147.0	147.0	145.0	145.0	116.8[b]	116.8[b]	119.7	119.7
(**6**)	(133.7)	(134.7)	112.9[b]	112.9[b]	(149.2)	(149.2)	(147.7)	(147.7)	113.2[b]	113.2[b]	120.9	120.9
(**8**)	132.7	133.8	114.0	114.0	(148.4)	(148.4)	(148.1)	(147.9)	116.4	116.4	114.0	114.0
(**9a**)	(132.6)	(134.4)	129.8	112.9[b]	114.3	(149.0)	158.4	(147.3)	114.3	113.3[b]	129.8	120.9
(**9b**)	(133.6)	(133.5)	112.8[b]	129.7	(148.9)	114.1	(147.5)	158.3	113.2[b]	114.1	120.7	129.7
(**11**)	(133.4)	(134.3)	113.0[b]	113.0[b]	(149.0)	(149.0)	(147.5)	(147.5)	113.1[b]	113.1[b]	120.5	120.5
(**12**)	(133.4)	(134.5)	113.0	113.0	(149.1)	(149.1)	(147.6)	(147.4)	113.0	113.0	120.8	120.8

(iii) Sugar moiety

Compound	C-1	C-2	C-3	C-4	C-5	C-6
(**3**)	103.7	74.4	77.7	70.6	66.6	
(**5**)	103.9	74.7	78.1	70.7	67.0	
(**9a**)	104.2	74.9	78.4	71.0	67.2	
(**9b**)	104.1	74.7	78.2	70.9	67.0	
(**11**)	103.2	74.4	78.0[d]	71.3	77.8[d]	62.6

[a] Values in parentheses were obtained in $CDCl_3$. [b–d] Assignments could be interchangeable although these values are preferred.

Table 5. Observed molecular rotation values, $[M]_D$(obs.), of the glycosiae (**3**) and the tetramethyl ethers (**5**) and (**11**), calculated $[M]_D$(calc.) values for the sugar moieties in the glycosides, and the assigned configuration at C-1 of the sugars

Compound	$[M]_D$(obs.) (°)	$[M]_D$(calc.) (°) (sugar)[a]	Assigned configuration at C-1[b]
Glycoside (**3**)	−93.5		
Xylopyranose in (**3**)		−87.7	β
Tetramethyl ether (**5**)	−107.6		
Xylopyranose in (**5**)		−98.2	β
Tetramethyl ether (**11**)	−56.4		
Glucopyranose in (**11**)		−47.0	β

[a] The $[M]_D$ value for the sugar moiety in the glycoside (**3**) was evaluated from that of compound (**6**) (Table 6), and those for the sugar moieties in the tetramethyl ethers (**5**) and (**11**) from that of the tetramethyl ether (**7**) (Table 6). [b] Configuration at C-1 of the sugars was assigned by the application of Klyne's rule, which appears in *Biochem. J.*, 1950, **47**, xli.

Table 6. Observed $[M]_D$ values of compounds (**6**) and (**7**) and methyl glycosides

Compound	$[M]_D$ (°)	Ref.
(**6**)	−5.8	
(**7**)	−9.4	
Methyl α-D-xylopyranoside	+249	*a*
Methyl β-D-xylopryanoside	−107	*a*
Methyl α-D-glucopyranoside	+305	*b*
Methyl β-D-glucopyranoside	−62	*b*

[a] A. Tada, M. Kobayashi, and J. Shoji, *Chem. Pharm. Bull.*, 1973, **21**, 308. [b] C. S. Hudson, *J. Am. Chem. Soc.*, 1909, **31**, 66; C. S. Hudson, *ibid.*, 1916, **38**, 1566.

Table 7. Bijvoet inequalities for compound (**8**)

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\Delta\lvert F_c\rvert$[a]	$\Delta\lvert F_o\rvert$[b]	$\lvert S\rvert$[c]
0	1	2	65.5	73.9	11.6	12.3	20
0	4	0	94.0	93.6	8.5	9.0	14
1	1	1	71.6	70.1	9.7	8.9	14
0	6	0	28.0	30.4	−9.3	−8.7	14
1	5	−3	46.6	46.5	−7.9	−7.9	13
1	2	−6	49.3	49.6	−7.1	−7.0	11
1	1	3	54.7	49.8	8.3	6.9	11
2	6	−2	54.8	54.8	7.1	6.6	11
1	3	0	39.8	35.8	6.6	6.3	10
0	8	0	39.0	38.7	−6.6	−5.9	9
0	5	2	61.9	62.6	−8.5	−5.8	9
2	7	0	28.0	28.1	−5.9	−5.4	9
1	1	−1	38.1	36.6	6.2	5.4	9
2	1	5	57.3	57.1	7.0	5.4	9
1	7	−2	42.2	42.4	4.5	5.4	9
2	7	−4	29.7	28.9	−5.0	−5.3	9
1	1	0	99.4	97.5	5.5	5.2	8
1	3	5	23.9	25.0	4.6	5.1	8
1	3	−5	96.0	96.9	3.6	5.0	8
1	10	2	47.6	47.3	5.2	5.0	8
1	5	4	69.7	66.1	−5.8	−5.0	8
0	6	2	10.6	12.0	−5.6	−4.7	7
1	2	−3	57.7	58.3	−4.7	−4.6	7
1	2	0	63.1	64.9	3.3	4.6	7
1	2	6	18.3	18.0	−3.3	−4.5	7
1	8	2	47.7	47.4	−5.2	−4.5	7
2	1	1	34.2	31.7	4.6	4.5	7
2	1	−6	29.7	30.2	4.8	4.3	7
0	10	1	18.3	18.8	4.6	4.3	7
1	1	4	55.3	56.2	5.0	4.2	7

[a] $\Delta|F_o| = |F_o(hkl)| - |F_o(\bar{h}\bar{k}\bar{l})|$. [b] $\Delta|F_c| = |F_c(hkl)| - |F_c(\bar{h}\bar{k}\bar{l})|$. [c] $|S| = ||F_c(hkl)| - |F_c(\bar{h}\bar{k}\bar{l})||/\sigma(F_o)$

Table 8. Torsion angles (°) for compound (**8**)

C(7′)–O(3)–C(3′)–C(2′)	+2
C(8′)–O(4)–C(4′)–C(5′)	+3
C(2′)–C(1′)–C(1)–C(2)	−82
C(1′)–C(1)–C(2)–C(3)	+175
C(1)–C(2)–C(3)–C(4)	−173
C(1)–C(2)–C(3)–O(1)	+11
O(1)–C(3)–C(4)–C(5)	−44
C(2)–C(3)–C(4)–C(5)	+139
C(3)–C(4)–C(5)–C(6)	−58
C(3)–C(4)–C(5)–O(2)	+179
O(2)–C(5)–C(6)–C(7)	+69
C(4)–C(5)–C(6)–C(7)	−59
C(5)–C(6)–C(7)–C(1″)	−170
C(6)–C(7)–C(1″)–C(2″)	+87
C(2″)–C(3″)–O(5)–C(7″)	+3
C(5″)–C(4″)–O(6)–C(8″)	−1

Table 9. Final atomic co-ordinates ($\times 10^4$) for compound (**8**), with standard deviations in parentheses

Atom	*x*	*y*	*z*
Br(1)	7 027(4)	−2 823(1)	−1 197(1)
Br(1)	1 538(4)	0	1 764(1)
O(1)	2 691(19)	−2 426(5)	1 929(7)
O(2)	7 452(21)	−1 944(5)	4 752(6)
O(3)	7 131(33)	360(6)	−1 428(10)
O(4)	9 448(26)	−384(6)	−2 714(8)
O(5)	3 272(26)	1 346(5)	5 765(8)
O(6)	−675(21)	1 857(5)	4 413(7)
C(1)	4 075(32)	−1 785(8)	191(10)
C(2)	6 056(36)	−1 830(9)	1 159(11)
C(3)	4 947(30)	−2 128(7)	2 016(9)
C(4)	6 720(29)	−2 099(7)	3 005(11)
C(5)	5 500(28)	−1 937(7)	3 867(10)
C(6)	3 944(30)	−1 214(7)	3 817(10)
C(7)	5 731(27)	−551(7)	3 665(11)
C(1′)	5 433(33)	−1 421(9)	−576(10)
C(2′)	5 562(38)	−693(8)	−653(11)
C(3′)	6 982(33)	−366(7)	−1 348(11)
C(4′)	8 239(34)	−757(8)	−2 050(10)
C(5′)	8 238(33)	−1 485(8)	−1 999(11)
C(6′)	6 764(33)	−1 780(8)	−1 257(14)
C(7′)	5 799(62)	792(11)	−735(17)
C(8′)	10 673(41)	−781(10)	−3 436(11)
C(1″)	4 185(25)	101(7)	3 811(10)
C(2″)	4 450(36)	422(8)	4 679(11)
C(3″)	2 965(33)	1 005(7)	4 917(10)
C(4″)	825(30)	1 277(7)	4 144(9)
C(5″)	539(31)	959(8)	3 254(10)
C(6″)	2 219(31)	376(7)	3 046(12)
C(7″)	5 567(50)	1 097(10)	6 538(13)
C(8″)	−2 724(29)	2 154(10)	3 661(11)

(**9**) (117 mg). The methylated product (**9**) (31 mg) was subjected to preparative h.p.l.c. on Radial PAK C_{18} (10 μ) with CH_3CN–H_2O (1:4, v/v) as the mobile phase. The column effluent was monitored at 280 nm to give compound (**9a**) (13 mg) and compound (**9b**) (18 mg). The methylated product (**9**) (86 mg), on hydrolysis with Taka-diastase in the same way as the tetramethyl ether (**5**), afforded xylose and the aglycone (**10**) (34 mg) [$\delta_C(C_5D_5N)$ 209.6 (s, C-3), 67.4 (d, C-5), 51.3 (t, C-4), 45.8 (t, C-2), and 40.5 (t, C-6)].

Identification of Compound (**1**).—Methylation of compound (**1**) with CH_2N_2 gave a tetramethyl ether (**12**). The physical and spectral data of compounds (**1**) and (**12**) were in good agreement with those of compounds (**6**) and (**7**), respectively. Compound

Table 10. Interatomic distances (Å) for compound (**8**), with standard deviations in parentheses

C(1)–C(2)	1.51(2)	C(4′)–C(5′)	1.37(2)
C(1)–C(1′)	1.48(2)	C(5′)–C(6′)	1.43(2)
C(2)–C(3)	1.47(2)	C(6′)–Br(1)	1.97(2)
C(3)–O(1)	1.20(2)	O(3)–C(7′)	1.46(3)
C(3)–C(4)	1.48(2)	O(4)–C(8′)	1.43(2)
C(4)–C(5)	1.42(2)	C(1″)–C(2″)	1.32(2)
C(5)–O(2)	1.41(2)	C(1″)–C(6″)	1.39(2)
C(5)–C(6)	1.55(2)	C(2″)–C(3″)	1.37(2)
C(7)–C(7)	1.54(2)	C(3″)–O(5)	1.31(2)
C(6)–C(1″)	1.46(2)	C(3″)–C(4″)	1.44(2)
C(1′)–C(2′)	1.38(2)	C(4″)–O(6)	1.38(2)
C(1′)–C(6′)	1.38(2)	C(4″)–C(5″)	1.34(2)
C(2′)–C(3′)	1.39(2)	C(5″)–C(6″)	1.41(2)
C(3′)–C(3)	1.38(2)	C(6″)–Br(2)	1.87(2)
C(3′)–C(4′)	1.41(2)	O(5)–C(7″)	1.48(2)
C(4′)–O(4)	1.34(2)	O(6)–C(8″)	1.42(2)

Table 11. Bond angles (°) for compound (**8**), with standard deviations in parentheses

C(1′)–C(1)–C(2)	112(1)	C(3′)–C(4′)–O(4)	117(1)
C(1)–C(2)–C(3)	118(1)	C(4′)–O(4)–C(8′)	117(1)
C(2)–C(3)–O(1)	121(1)	C(4′)–C(5′)–C(6′)	115(1)
C(2)–C(3)–C(4)	120(1)	C(5′)–C(6′)–C(1′)	128(1)
O(1)–C(3)–C(4)	119(1)	C(5′)–C(6′)–Br(1)	112(1)
C(3)–C(4)–C(5)	121(1)	C(7)–C(1″)–C(2″)	122(1)
C(4)–C(5)–O(2)	114(1)	C(7)–C(1″)–C(6″)	120(1)
C(4)–C(5)–C(6)	114(1)	C(2″)–C(1″)–C(6″)	118(1)
O(2)–C(5)–C(6)	107(1)	C(1″)–C(2″)–C(3″)	127(1)
C(5)–C(6)–C(7)	117(1)	C(2″)–C(3″)–C(4″)	116(1)
C(6)–C(7)–C(1″)	112(1)	C(2″)–C(3″)–O(5)	127(1)
C(1)–C(1′)–C(2′)	123(1)	C(3″)–O(5)–C(7″)	117(1)
C(1)–C(1′)–C(6′)	123(1)	C(3″)–C(4″)–C(5″)	118(1)
C(2′)–C(1′)–C(6′)	114(1)	C(3″)–C(4″)–O(6)	115(1)
C(1′)–C(2′)–C(3′)	122(1)	C(4″)–O(6)–C(8″)	116(1)
C(2′)–C(3′)–C(4′)	122(1)	C(4″)–C(5″)–C(6″)	123(1)
C(2′)–C(3′)–O(3)	122(1)	C(5″)–C(6″)–C(1″)	118(1)
C(3′)–O(3)–C(7′)	118(1)	C(5″)–C(6″)–Br(2)	117(1)
C(3′)–C(4′)–C(5′)	119(1)		

(**1**) was thus identified as (5*S*)-1,7-bis(3,4-dihydroxyphenyl)-5-hydroxyheptan-3-one.

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