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An X-Ray Crystallographic Study on the Absolute Configuration of Dihydroyashabushiketol and the Solvent-dependence of Its Optical Rotation

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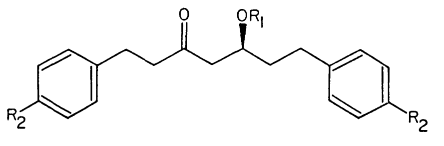
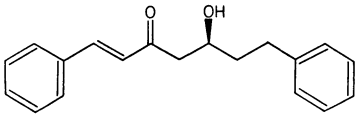
The absolute configuration of dihydroyashabushiketol was established to be *S* on the basis of the X-ray crystallographic analysis of the 4′,4″-dibromo derivative. In addition, it was found that the sense of the optical rotations of dihydroyashabushiketol and its dibromo derivative is determined by the interaction of their C-5 hydroxyl group with the solvent used for the measurements.

The absolute configurations of both dihydroyashabushiketol (**1**) and yashabushiketol (**2**) isolated from the male flowers of *Alnus sieboldiana* are reported to be *S*[1)] on the basis of the benzoate rule[2)] and Horeau's asymmetric synthesis.[3)] However, the benzoate rule is not adapted to such a type of compounds in which the carbinyl carbon is flanked by two methylenes.[4)] In the case of **1**, in addition, the optical yield of α-phenylbutyric acid was too low (only 1.5 %[1)]) to determine the absolute configuration. These suspicious points necessitated the establishment of the absolute configuration of **1**[†] by use of an unambiguous method. Then, the absolute configuration was reexamined by the X-ray crystallographic analysis of the 4′,4″-dibromo derivative (**3**) prepared from **1**, and the absolute configuration proposed previously for **1** was validated. During the course of this reexamination, it was found that the sense of the optical rotation of **1** and **3** is determined by the interaction of their C-5 hydroxyl group with the solvent used for measurements of the optical rotation. We now wish to report these results.



1 $R_1=R_2=H$
3 $R_1=H$, $R_2=Br$
4 $R_1=Ac$, $R_2=H$
5 $R_1=Ac$, $R_2=Br$



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Experimental

General. The ^{1}H NMR spectra were taken on a Hitachi R-22 spectrometer using TMS as an internal standard. The ^{13}C NMR spectra were obtained on a Hitachi R-42 FT NMR (22.6 MHz) spectrometer ($\delta_{TMS}=0$). The Mass spectra were recorded by direct inlet at 70 eV ionization. The optical rotation was measured on a Yanaco Automatic Digital Polarimeter OR-50D spectrometer. The ORD curves were taken on a JASCO ORD/UV-5 spectropolarimeter at 25 °C by use of a 10 mm cell in path-length. The UV spectra were obtained on a Shimadzu UV-240 spectrometer. Analytical TLC and preparative TLC were carried out on 0.25 and 0.75 mm thick silica gel plates (Merck 60, GF_{254}), respectively.

The physical and spectral data of compounds **1** and **3**—**5** are summarized in Tables 1—4.

*Isolation and Identification of Dihydroyashabushiketol (**1**).* The benzene extract of the male flowers (13 kg) of *Alnus sieboldiana* MATSUM., which were collected on the mountain in the suburbs of Hiroshima City in February, was worked up in a similar manner as described in the literature[1)] to give compound (**1**) (1.35 g). This compound (**1**) was

Table 1. Physical data of **1**, **3**, **4**, and **5**

Compd	Mp θ_m/°C	$[\alpha]_D^{25}$/°(Solvent)	Molecular formula	Found(Calcd)(%) C	H	Br
1	72.5—73.0	-2.7 ± 0.6(*c* 0.67, MeOH)	$C_{19}H_{22}O_2$	80.64	7.94	
		$+14.0\pm0.6$(*c* 0.67, $CHCl_3$)		(80.81)	(7.85)	
3	96.0—96.5	-3.6 ± 0.7(*c* 0.30, MeOH)	$C_{19}H_{20}O_2Br_2$	51.88	4.51	36.18
		$+10.2\pm0.7$(*c* 0.30, $CHCl_3$)		(51.84)	(4.58)	(36.31)
4	Viscous oil	$+4.1\pm0.3$(*c* 1.22, MeOH)				
		$+3.6\pm0.3$(*c* 1.22, $CHCl_3$)				
5	Viscous oil	$+3.1\pm0.9$(*c* 2.25, MeOH)				
		$+2.7\pm0.9$(*c* 2.25, $CHCl_3$)				

[†] Although the preparative TLC of the benzene extract of the male flowers was meticulously carried out in the same manner as previously described,[1)] even a trace of yashabushiketol (**2**) was not found in the benzene extract.

TABLE 2. UV, IR, AND Mass SPECTRAL DATA OF **1**, **3**, **4**, AND **5**

Compd	UV(EtOH) λ_{max}/nm (log ε)	IR ν_{max}/cm^{-1} a) OH	IR ν_{max}/cm^{-1} a) C=O	IR $\nu_{max}/cm^{-1}(CCl_4)$ intramolecular hydrogen bonded OH	Mass m/z(fragment ion and/or rel int.)
1	261(2.85), 264(2.80) 268(2.80), 287(2.64)	3410 and 3360	1708	3556(0.0006 M) b)	282(M^+, 0.8), 264($M-H_2O$, 18), 159(18), 148(23), 133(22), 105(61), 91(100), 77(18), 43(25)
3	255(2.78), 262(2.87) 269(2.94), 277(2.85)	3355 and 3275	1711	3566(0.001 M) b)	442, 440, 438(M^+, 2, 4, 2), 424, 422, 420(M^+-H_2O, 24, 50, 24), 213(58), 211(56), 197(10), 195(13), 171(100), 169(100); 212.9770 and 210.9741 (C_9H_8OBr), 196.9749 and 194.9773 (C_9H_8Br)
4	260(2.95), 264(2.89) 268(2.88), 284(2.69)		1740 and 1719		324(M^+, 0.2), 264(M−AcOH, 21), 159(24), 133(18), 117(10), 105(40), 91(100), 77(15), 43(43)
5	255(2.84), 262(2.88) 269(2.93), 277(2.82)		1738 and 1718		424, 422, 420(M−AcOH, 11, 22, 11), 213(15), 211(19), 171(64), 169(61), 43(100)

a) IR spectra of **1** and **3** were taken in Nujol and those of **4** and **5** in the neat film. b) 1 M=1 mol dm^{-3}.

TABLE 3. ^{1}H NMR SPECTRAL DATA OF **1**, **3**, **4**, AND **5**(δ_H, CCl_4)$^{a)}$

Compd	C_6-H_2	C_1-, C_2-, C_4-, C_7-H_2	C_5-H	Arom. H	OH	OAc
1	1.41—1.81 m	2.35—2.88 m	3.94 quin	7.11 m	2.95 brs	
3	1.43—1.71 m	2.35—2.87 m	3.87 quin	6.90—7.36AA′BB′	3.02 brs	
4	1.68—1.92 m	2.26—2.90 m	5.12 quin	7.12 m		1.88 s
5	1.66—2.05 m	2.28—2.87 m	5.08 quin	6.94—7.40AA′BB′		1.91 s

a) s: singlet, brs: broad singlet, m: multiplet, quin: quintet (J=6 Hz), AA′BB′: J=8 and/or 2 Hz.

TABLE 4. ^{13}C NMR SPECTRAL DATA OF **1**, **3**, **4**, AND **5**(δ_C, $CDCl_3$)

i) 5-Hydroxy(or acetoxy)-3-heptanone moiety

Compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	$-OCO\underline{C}H_3$	$-O\underline{C}OCH_3$
1	29.4	44.9	210.7	49.4	66.8	38.1	31.7		
3	28.6	44.5	209.8	49.2	66.4	37.8	30.9		
4	29.5	44.7	206.4	47.2	70.0	35.7	31.6	20.9	170.2
5	28.8	44.5	206.0	47.2	69.7	35.5	31.0	21.0	170.3

ii) Diphenyl moiety

Compd	C-1′	C-1″	C-2′	C-2″	C-3′	C-3″	C-4′	C-4″	C-5′	C-5″	C-6′	C-6″
1	140.7	141.8	128.4	128.4	128.4	128.4	126.1	125.8	128.4	128.4	128.4	128.4
3	139.5	140.6	130.1	130.1	131.4	131.4	119.8	119.4	131.4	131.4	130.1	130.1
4	140.9	141.2	128.4	128.4	128.4	128.4	126.1	126.1	128.4	128.4	128.4	128.4
5	139.8	140.0	130.1	130.1	131.5	131.5	119.9	119.9	131.5	131.5	130.1	130.1

confirmed to be identical with dihydroyashabushiketol[1)] by direct comparison of the ^{1}H NMR spectra taken in $CDCl_3$ and the Mass spectra,[5)] and then characterized as 1,7-diphenyl-5-hydroxy-3-heptanone on the basis of the elemental analysis and the UV, IR, ^{1}H and ^{13}C NMR, and Mass spectral data. Acetylation of **1** (96 mg) with a mixture of acetic anhydride (2 cm^3) and dry pyridine (2 cm^3) gave its acetate (**4**) (108 mg).

*Bromination of **1**.* Following the method for the iodination of veratrole described in the literature,[6)] the bromination of **1** (129 mg) was carried out by use of bromine (183 mg) in place of iodine under the conditions similar to those described. The resulting mixture was subjected to preparative TLC with EtOAc–hexane (3:7 v/v) to give a dibromo derivative (**3**) (48 mg), which was characterized as 1,7-bis(4-bromophenyl)-5-hydroxy-3-heptanone on the basis of the elemental analysis and the spectral data. Acetylation of **3** (48 mg) in the same way as in the case of **1** gave its acetate (**5**) (50 mg).

X-Ray Crystallographic Analysis. The single-crystals of **3** for the X-ray analysis were obtained by crystallization from $MeOH$–H_2O. The single-crystal used was about 0.2 mm × 0.5 mm × 0.7 mm in size. Cell dimensions were determined by least-squares calculations from 2θ values of 16 reflections measured on a Syntex R-3 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Crystal data: orthorhombic, space group $P2_12_12_1$, four molecules per unit cell with dimensions a=5.012(3), b=

Table 5. Bijvoet inequalities of **3**

h	k	l	$\langle\lvert F_c\rvert\rangle$	$\langle\lvert F_o\rvert\rangle$	$\Delta\lvert F_o\rvert^{a)}$	$\Delta\lvert F_c\rvert^{b)}$	$\lvert S\rvert^{c)}$
1	1	4	133.1	132.6	3.82	8.12	6
1	1	3	169.3	169.8	4.38	6.69	5
1	3	9	47.2	45.8	7.54	6.61	5
1	1	5	113.9	114.2	−6.54	−6.54	5
2	1	1	71.6	67.0	−4.15	−6.05	4
1	2	11	54.2	52.5	−7.49	−5.57	4
1	6	4	36.4	37.5	−4.78	−5.56	4
1	1	1	118.2	124.2	−6.50	−5.47	4
1	1	6	134.3	134.3	4.30	5.22	4
2	3	4	75.4	75.9	4.35	4.67	3
1	1	16	34.2	31.8	6.03	4.58	3
1	2	1	54.6	59.2	3.55	4.53	3
2	5	8	12.9	16.4	4.72	4.50	3
1	4	6	25.5	22.6	−7.14	−4.46	3
1	5	15	20.7	25.0	3.39	4.45	3
2	3	11	40.0	40.1	3.67	4.42	3
1	2	10	42.1	41.7	−6.06	−4.27	3
1	6	12	17.6	17.5	−6.62	−4.27	3
1	3	6	84.7	91.2	−5.59	−4.24	3
2	5	2	27.3	28.0	−4.31	−4.18	3
1	3	8	40.1	37.5	4.89	4.13	3

a) $\Delta\lvert F_o\rvert = \lvert F_o(hkl)\rvert - \lvert F_o(\bar{h}\bar{k}\bar{l})\rvert$. b) $\Delta\lvert F_c\rvert = \lvert F_c(hkl)\rvert - \lvert F_c(\bar{h}\bar{k}\bar{l})\rvert$. c) $\lvert S\rvert = \lvert\,\lvert F_c(hkl)\rvert - \lvert F_c(\bar{h}\bar{k}\bar{l})\rvert\,\rvert/\sigma(F_o)$.

12.315(6), c=30.480(15) Å; U=1881(2) Å; D_c=1.55 g cm^{-3}; D_m=1.54 g cm^{-3}; μ(Mo $K\alpha$)=45.7 cm^{-1}. A total of 2130 reflections with the Friedel pair of (h,k,l) and $(\bar{h},\bar{k},\bar{l})$ were collected by use of the ω-scan technique in the range $2\theta \leq 50.0°$. 1286 reflections having $F_o > 2\sigma(F_o)$ were used for the structure determination. The structure was solved by the conventional heavy-atom method. The bromine atom positions were obtained from a 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 $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ with w=1.0 for all the reflections. Final refinements were done by use of the anomalous dispersion effect[7] of bromine and oxygen atoms and the index $R=[\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum\lvert F_o\rvert^2]^{1/2}$ was 0.094 for the S configuration and 0.105 for the R configuration, respectively. Bijvoet pairs[8] of 1286 reflections were considered for the S configuration and 20 pairs having the largest $\lvert\,\lvert F_c(hkl)\rvert - \lvert F_c(\bar{h}\bar{k}\bar{l})\rvert\,\rvert/\sigma(F_o)$ values are given in Table 5.

The complete $F_o - F_c$ data and the tables of anisotropic thermal parameters for **3** are deposited as Document No. 8346, at the Chemical Society of Japan.

Results and Discussion

The absolute configuration of dihydroyashabushiketol (**1**) was examined by the X-ray crystallographic analysis of the dibromo derivative (**3**). The absolute configuration of **3** was established by the X-ray anomalous-scattering technique.[7] Comparison of the R factors[9] for two enantiomeric configurations indicated that the absolute configuration of **3** is S. Final atomic

Table 6. Final atomic coordinates of **3**, with standard deviations in parentheses

Atom	10^4x	10^4y	10^4z	B_{eq}/Å$^{2\ a)}$
Br(1)	4247(7)	−1237(3)	2957(1)	9.1
Br(2)	11614(9)	8902(3)	−1247(1)	11.1
O(1)	14998(28)	2001(12)	1048(6)	6.0
O(2)	12933(29)	2653(10)	165(5)	4.7
C(1)	12506(38)	908(18)	1726(8)	6.2
C(2)	11040(37)	1812(20)	1448(8)	5.5
C(3)	12814(24)	2326(14)	1143(7)	4.7
C(4)	11990(32)	3314(17)	868(7)	4.3
C(5)	13323(29)	3549(13)	486(5)	3.4
C(6)	12475(37)	4537(14)	195(7)	3.2
C(7)	13898(67)	4774(20)	−150(9)	8.8
C(1')	10439(44)	354(21)	2008(8)	6.3
C(2')	9864(51)	751(20)	2344(9)	6.2
C(3')	7892(65)	493(19)	2716(9)	7.4
C(4')	6868(59)	−457(21)	2610(8)	7.0
C(5')	7201(46)	−1036(18)	2265(8)	6.5
C(6')	9054(56)	−690(17)	1903(10)	7.9
C(1'')	13323(46)	5765(22)	−436(8)	6.3
C(2'')	11475(71)	5747(20)	−711(10)	9.2
C(3'')	10765(63)	6717(22)	−944(10)	9.0
C(4'')	12353(75)	7650(19)	−860(8)	7.0
C(5'')	14174(67)	7589(24)	−578(12)	8.6
C(6'')	14783(53)	6685(22)	−356(12)	8.1

a) $B_{eq}=8\pi^2(U_1+U_2+U_3)/3$, where U_1, U_2, and U_3 are the principal components by U matrix.

Table 7. Interatomic distances of **3**, with standard deviations in parentheses

Interatomic distance	l/Å	Interatomic distance	l/Å
C(1)-C(2)	1.58(3)	C(2′)-C(3′)	1.54(4)
C(1)-C(1′)	1.51(3)	C(3′)-C(4′)	1.32(4)
C(2)-C(3)	1.43(3)	C(4′)-C(5′)	1.28(3)
C(3)-O(1)	1.20(2)	C(4′)-Br(1)	1.94(3)
C(3)-C(4)	1.54(3)	C(5′)-C(6′)	1.51(4)
C(4)-C(5)	1.38(3)	C(1″)-C(2″)	1.25(4)
C(5)-O(2)	1.49(2)	C(1″)-C(6″)	1.37(4)
C(5)-C(6)	1.56(2)	C(2″)-C(3″)	1.43(4)
C(6)-C(7)	1.31(4)	C(3″)-C(4″)	1.42(4)
C(7)-C(1″)	1.53(4)	C(4″)-C(5″)	1.25(5)
C(1′)-C(2′)	1.17(4)	C(4″)-Br(2)	1.98(3)
C(1′)-C(6′)	1.50(3)	C(5″)-C(6″)	1.34(4)

Table 8. Bond angles of **3**, with standard deviations in parentheses

Bond angle	ϕ/°	Bond angle	ϕ/°
C(1′)-C(1)-C(2)	108(2)	C(3′)-C(4′)-Br(1)	125(2)
C(1)-C(2)-C(3)	112(2)	Br(1)-C(4)-C(5′)	105(2)
C(2)-C(3)-O(1)	125(2)	C(3′)-C(4′)-C(5′)	130(3)
C(2)-C(3)-C(4)	122(2)	C(4′)-C(5′)-C(6′)	122(2)
O(1)-C(3)-C(4)	112(2)	C(5′)-C(6′)-C(1′)	112(2)
C(3)-C(4)-C(5)	120(2)	C(7)-C(1″)-C(2″)	121(3)
C(4)-C(5)-O(2)	110(1)	C(7)-C(1″)-C(6″)	117(2)
C(4)-C(5)-C(6)	121(2)	C(2″)-C(1″)-C(6″)	122(3)
O(2)-C(5)-C(6)	100(1)	C(1″)-C(2″)-C(3″)	120(3)
C(5)-C(6)-C(7)	119(2)	C(2″)-C(3″)-C(4″)	117(3)
C(6)-C(7)-C(1″)	122(2)	C(3″)-C(4″)-Br(2)	115(2)
C(1)-C(1′)-C(2′)	119(2)	Br(2)-C(4″)-C(5″)	126(2)
C(1)-C(1′)-C(6″)	126(2)	C(3″)-C(4″)-C(5″)	119(3)
C(2′)-C(1′)-C(6′)	116(2)	C(4″)-C(5″)-C(6″)	124(3)
C(1′)-C(2′)-C(3′)	136(3)	C(1″)-C(6″)-C(5″)	118(3)
C(2′)-C(3′)-C(4′)	105(2)		

coordinates, bond lengths, and bond angles are given in Tables 6—8. The observed and calculated Bijvoet inequalities[8)] for the *S* configuration were in good agreement with each other, as shown in Table 5. Thus, the absolute configuration of **3** was determined to be *S*, as shown in the ORTEP drawing of Fig. 1, and that of dihydroyashabushiketol (**1**) was necessarily

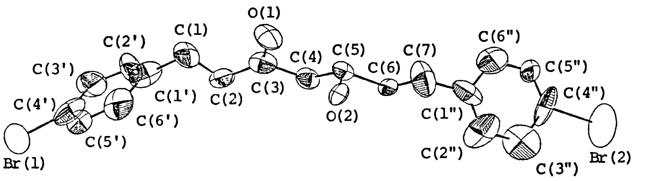

Fig. 1. ORTEP drawing[10)] of the molecular structure of the 4′,4″-dibromo derivative (**3**).

TABLE 9. TORSION ANGLES OF **3**

Torsion angle	$\phi/°$
C(2′)-C(1′)-C(1)-C(2)	+84.0
C(1′)-C(1)-C(2)-C(3)	−175.4
C(1)-C(2)-C(3)-C(4)	−173.2
C(1)-C(2)-C(3)-O(1)	+12.6
C(2)-C(3)-C(4)-C(5)	−157.7
O(1)-C(3)-C(4)-C(5)	+17.1
C(3)-C(4)-C(5)-C(6)	+178.6
C(3)-C(4)-C(5)-O(2)	+63.5
C(4)-C(5)-C(6)-C(7)	+175.6
O(2)-C(5)-C(6)-C(7)	−64.3
C(5)-C(6)-C(7)-C(1″)	−176.1
C(6)-C(7)-C(1″)-C(2″)	−78.7

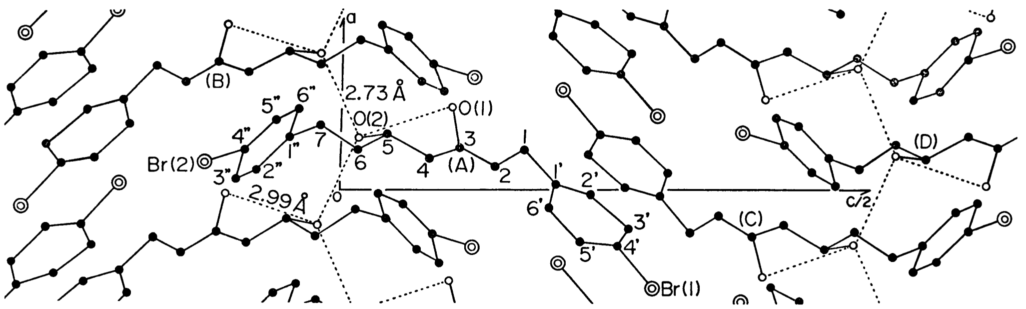

Fig. 2. Projection of the 4′,4″-dibromo derivative (**3**) along the b axis. The atoms indicated with ●, ○, and ◎ denote carbon, oxygen, and bromine atoms respectively. The hydrogen bondings are shown by a broken line. The transformations of the atomic coordinates are (A) *x*, *y*, *z*; (B) 1/2+*x*, 1/2−*y*, −*z*; (C) −*x*, 1/2+*y*, 1/2−*z*; (D) 1/2−*x*, −*y*, 1/2+*z*.

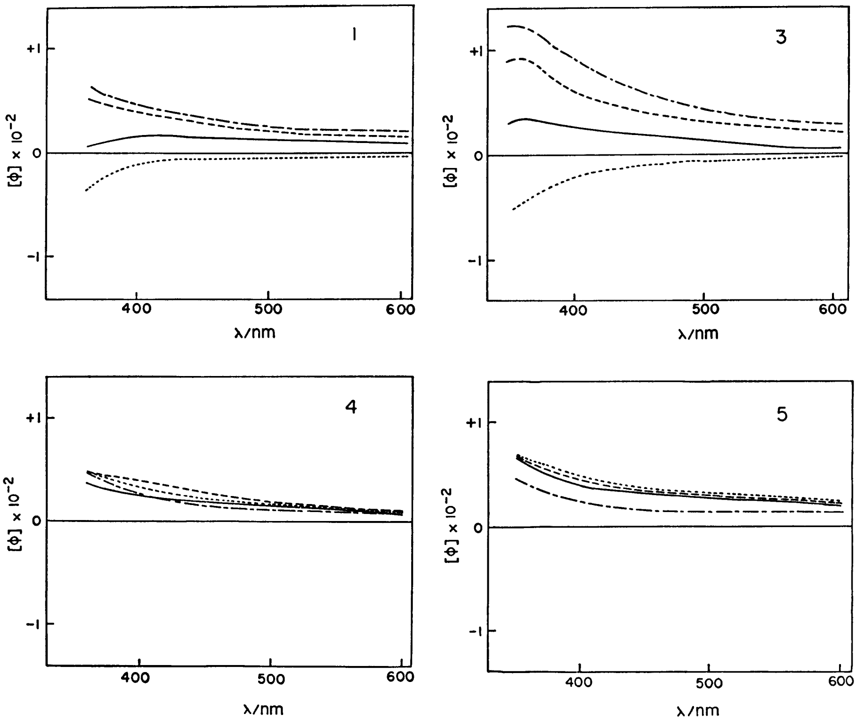

Fig. 3. ORD curves of **1**, **3**, **4**, and **5** in selected solvents at 25 °C: — — — in CCl_4; ---- in $CHCl_3$; —— in dioxane; ······ in MeOH. The measurements were carried out under the following concentrations in each solvent: **1**, *c* 0.85; **3**, *c* 2.20; **4**, *c* 0.97; **5**, *c* 2.60.

concluded to be *S*.

As shown in Table 2, the IR spectrum of **3** taken in a Nujol mull exhibited the bands at 3355 and 3275 cm^{-1} due to the inter- and intramolecular hydrogen bondings, respectively.11) The presence of these bondings was confirmed by the diagnosis of the crystal structure as described below. The molecular arrangement and the hydrogen bond networks of **3** are given in Fig. 2. As shown in Table 9, the heptane chain was almost on the same plane, with the exception of the torsion angle of −157.7° at C2–C3–C4–C5. This torsion angle may result from the intramolecular hydrogen bonding between the carbonyl group at the 3-position and the hydroxyl group at C-5. This hydroxyl group is furthermore linked with the hydroxyl groups at C-5 of the adjacent molecules by intermolecular hydrogen bonds, and the molecules build up an infinite chain along the a axis by intermolecular hydrogen bondings. The chain is coupled with the next chain by the van der Waals force among the hydrophobic groups.

During the course of the study on the absolute configuration, it was observed that when the solvent used for measuring the optical rotation was changed from $CHCl_3$ to MeOH, the optical rotations of **1** and **3** changed from the dextrorotatory sense to the levorotatory one, but this was not the case for the corresponding acetates (**4** and **5**); these acetates were dextrorotatory in both of the solvents. These phenomena were also observed for ORD curves in the wavelength range of 350 to 600 nm, as shown in Fig. 3. The compounds **1** and **3** showed positive ORD curves in CCl_4, $CHCl_3$, and dioxane, while negative ORD curves in MeOH. On the other hand, their corresponding acetates (**4** and **5**) showed positive plain curves in all the solvents used. This indicates that the intermolecular hydrogen bonding between the hydroxyl group at C-5 of **1** and **3** and the functional or polar group of the solvent molecule participates in the inversion in the sense of their optical rotation. A similar solvent-dependence of the optical rotation is also observed for *cis*-verbenol,12) (*S*)-marmesin,13) and (*R*)-1-methylindan.14) However, any causes for the inversion in the sense of the optical rotation have not been solved yet. Detailed investigations on causes involved for the inversion in the sense of the optical rotation of the diarylheptanoids are now in progress, and the results will be reported elsewhere.

The elemental analysis for bromine atom was performed in the Elemental Analytical Center of Kyoto University.

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