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Chemical and Chemotaxonomical Studies of Ferns. XXXVI.[1] Crystallographic Studies of Pterokaurene L_2 and Pteroatisene P_2

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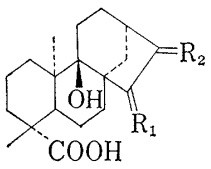
The structures of two isomeric diterpenes, pterokaurene L_2, [I], and pteroatisene P_2, [III], isolated from *Pteris longipes* and *Pteris purpureorachis*, respectively, were elucidated by X-ray crystallographic analysis. The crystal structures were determined by the direct method using the MULTAN program and refined by the block-diagonal least-squares method. The crystal data are: I; tetragonal, space group $P4_322$, $a=12.510(5)$, $b=12.510(5)$, $c=22.923(10)$ Å, V=3587.5 Å^3, $z=8$, Dx=1.239 g cm^{-3}, III; orthorhombic, space group $P2_12_12_1$, $a=14.370(7)$, $b=20.205(10)$, $c=12.808(6)$ Å, $V=3718.8$ Å^3, $z=8$, $Dx=1.227$ g cm^{-3}. The structures of I and III were established to be *ent*-9,15α-dihydroxykaur-16-en-19-oic acid and *ent*-9,15α-dihydroxyatis-16-en-19-oic acid, respectively.

Keywords——X-ray analysis; direct method; *ent*-9,15α-dihydroxykaur-16-en-19-oic acid; *ent*-9,15α-dihydroxyatis-16-en-19-oic acid; *Pteris longipes*; *Pteris purpureorachis*; Pteridaceae

In the previous papers, we reported the structures of five new kaurane-type diterpenes, pterokaurene L_1, L_2, L_3, L_4 and L_5, isolated from *Pteris longipes* Don (Pteridaceae),[2] and also the structures of three new atisane-type diterpenes, pteroatisene P_1 and P_2 and pteroatisenoside P_1, isolated from *Pteris purpureorachis* COPEL. (=*P. tokioi* Masam.).[3] Among them, the structures of two isomeric compounds, pterokaurene L_2 and pteroatisene P_2, were elucidated by X-ray crystallographic analysis . This paper describes the details of these crystallographic studies.

X-Ray Crystallographic Analysis of Pterokaurene L_2

The crystals were grown in a mixed solution of chloroform and acetone as colorless transparent tetragonal dipyramids. A sample with an approximate size of 0.4×0.5×0.5 mm was taken for X-ray diffraction work. The lattice parameters and intensities were measured on a Philips PW 1100 four-circle diffractometer with CuKα radiation monochromated by a graphite plate. The crystal data are: pterokaurene L_2, $C_{20}H_{30}O_4$, MW=334.5, mp 240—



I : $R_1=$  , $R_2=CH_2$

II : $R_1=O$, $R_2=$ 

Fig. 1

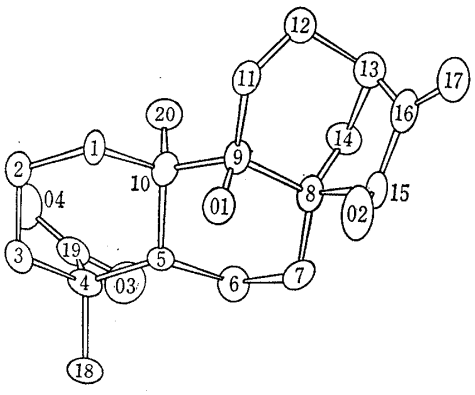


Fig. 2. Perspective Drawing of the Molecular Structure of Pterokaurene L_2

241°, $[\alpha]_D^{20}=-78.7°$, tetragonal, space group $P4_322$,[4] $a=12.510$ (5), $b=12.510$ (5), $c=22.923$-(10) Å, V=3587.5Å^3, $z=8$, $Dx=1.239$ g cm^{-3}, μ for CuKα=6.4 cm^{-1}. The intensities of 3618 reflections were measured within the 2θ range of 6—157°, using the θ—2θ scan method. The symmetry equivalent reflections were averaged and the intensities of 1893 independent reflections corresponding to 87% of the number of theoretically possible ones were evaluated. The R value for the equivalent reflections was 0.03. The crystal structure was determined by the direct method using the MULTAN program[5] and refined by the block-diagonal least-squares method. The weight for the reflection was calculated by means of the following relations: $\sqrt{w}=0.1$ for the reflection with $F_0\leq 1$; $\sqrt{w}=13/(12+|F_0|)$ for the one with $F_0>1$. The final R value was 0.103 including anisotropic thermal parameters. Contributions of

Table I. Final Atomic Parameters ($\times 10^4$)
Temperature factors are of the form: $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C 1	6679(5)	8525(5)	7050(3)	45(4)	54(4)	17(1)	−10(3)	−11(2)	13(2)
C 2	5482(5)	8406(6)	6946(3)	47(4)	75(5)	21(1)	−6(4)	−7(2)	9(2)
C 3	4887(5)	8396(5)	7538(3)	49(3)	59(4)	23(1)	7(4)	3(2)	6(2)
C 4	5276(5)	7536(5)	7978(3)	50(4)	51(4)	19(1)	3(3)	7(2)	3(2)
C 5	6517(5)	7653(5)	8057(2)	60(4)	43(3)	11(1)	4(3)	1(2)	2(1)
C 6	7038(6)	6897(5)	8505(3)	67(4)	66(5)	16(1)	14(4)	4(2)	17(2)
C 7	8154(6)	7302(6)	8660(2)	81(5)	78(5)	10(1)	19(4)	−3(2)	1(2)
C 8	8882(5)	7350(4)	8129(2)	58(4)	40(3)	13(1)	6(3)	−7(2)	−2(1)
C 9	8359(4)	8017(4)	7617(2)	44(3)	36(3)	13(1)	−5(3)	−5(1)	2(1)
C 10	7163(4)	7663(4)	7470(2)	40(3)	38(3)	11(1)	−7(3)	−2(2)	2(1)
C 11	9110(5)	8065(5)	7084(2)	46(4)	63(4)	14(1)	−10(3)	−5(2)	7(2)
C 12	9768(6)	7037(6)	6948(3)	56(4)	90(5)	16(1)	3(4)	−1(2)	−1(2)
C 13	10235(5)	6531(5)	7514(3)	57(4)	61(4)	19(1)	6(4)	0(2)	−3(2)
C 14	9292(6)	6258(5)	7915(3)	61(4)	44(4)	20(1)	6(4)	−1(2)	1(2)
C 15	10006(6)	7821(6)	8316(3)	64(4)	71(4)	19(1)	7(5)	−17(2)	−12(2)
C 16	10803(6)	7397(7)	7872(3)	58(4)	83(6)	21(1)	−2(4)	−12(2)	4(2)
C 17	11810(7)	7724(10)	7805(5)	61(6)	160(12)	39(2)	−31(7)	−15(3)	−2(5)
C 18	4738(7)	7756(7)	8583(3)	87(6)	94(6)	17(1)	21(5)	18(2)	0(2)
C 19	4898(5)	6425(5)	7771(3)	52(4)	52(4)	20(1)	−3(4)	9(2)	4(2)
C 20	7104(5)	6575(5)	7142(3)	55(4)	53(4)	16(1)	−11(4)	0(2)	−9(2)
O 1	8241(4)	9098(3)	7855(2)	66(3)	37(3)	20(1)	−2(2)	−7(1)	−3(1)
O 2	10034(7)	8949(4)	8367(3)	121(6)	66(4)	54(2)	8(5)	−47(3)	−29(3)
O 3	5104(5)	5646(4)	8154(2)	94(4)	64(3)	22(1)	−11(4)	3(2)	10(2)
O 4	4467(4)	6241(4)	7306(2)	68(4)	58(3)	32(1)	−3(3)	−15(2)	3(2)

Table II. Bond Lengths in Å Unit

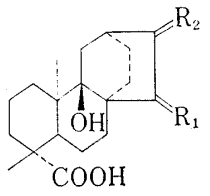
Atom 1	Atom 2	Length (STD)	Atom 1	Atom 2	Length (STD)
C 1	-C 2	1.523(9)	C 9	-C 10	1.595(7)
C 1	-C 10	1.567(8)	C 9	-C 11	1.543(8)
C 2	-C 3	1.549(10)	C 9	-O 1	1.465(7)
C 3	-C 4	1.551(9)	C 10	-C 20	1.556(8)
C 4	-C 5	1.570(9)	C 11	-C 12	1.558(10)
C 4	-C 18	1.568(9)	C 12	-C 13	1.557(10)
C 4	-C 19	1.543(9)	C 13	-C 14	1.534(9)
C 5	-C 6	1.542(9)	C 13	-C 16	1.534(10)
C 5	-C 10	1.571(7)	C 15	-C 16	1.521(10)
C 6	-C 7	1.527(10)	C 15	-O 2	1.416(9)
C 7	-C 8	1.522(8)	C 16	-C 17	1.333(12)
C 8	-C 9	1.582(7)	C 19	-O 3	1.336(8)
C 8	-C 14	1.539(9)	C 19	-O 4	1.217(8)
C 8	-C 15	1.585(10)			

TABLE III. Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle (STD)	Atom 1	Atom 2	Atom 3	Angle (STD)
C 2	-C 1	-C 10	114.2(5)	C 8	-C 9	-O 1	104.6(4)
C 3	-C 2	-C 1	109.6(5)	C 11	-C 9	-O 1	108.7(4)
C 4	-C 3	-C 2	115.1(5)	C 20	-C 10	-C 1	106.6(4)
C 5	-C 4	-C 3	108.7(5)	C 20	-C 10	-C 5	112.5(4)
C 5	-C 4	-C 18	107.8(5)	C 20	-C 10	-C 9	112.9(4)
C 5	-C 4	-C 19	114.9(5)	C 1	-C 10	-C 5	109.4(4)
C 3	-C 4	-C 18	108.6(5)	C 1	-C 10	-C 9	107.6(4)
C 3	-C 4	-C 19	109.3(5)	C 5	-C 10	-C 9	107.7(4)
C 18	-C 4	-C 19	107.3(5)	C 12	-C 11	-C 9	116.6(5)
C 6	-C 5	-C 4	116.0(5)	C 13	-C 12	-C 11	111.6(5)
C 6	-C 5	-C 10	111.0(5)	C 14	-C 13	-C 12	107.5(5)
C 4	-C 5	-C 10	114.3(5)	C 14	-C 13	C 16	101.1(5)
C 7	-C 6	-C 5	109.7(5)	C 12	-C 13	-C 16	109.4(6)
C 8	-C 7	-C 6	112.0(5)	C 16	-C 15	-C 8	105.7(5)
C 9	-C 8	-C 7	111.5(5)	C 16	-C 15	-O 2	112.8(6)
C 9	-C 8	-C 14	111.7(5)	C 8	-C 15	-O 2	114.5(6)
C 9	-C 8	-C 15	111.8(5)	C 17	-C 16	-C 13	126.4(8)
C 7	-C 8	-C 14	114.8(5)	C 17	-C 16	-C 15	126.0(8)
C 7	-C 8	-C 15	109.2(5)	C 13	-C 16	-C 15	107.5(6)
C 14	-C 8	-C 15	96.9(5)	O 3	-C 19	-C 4	113.4(5)
C 10	-C 9	-C 8	113.5(4)	O 3	-C 19	-O 4	121.6(6)
C 10	-C 9	-C 11	114.5(4)	C 4	-C 19	-O 4	125.1(6)
C 10	-C 9	-O 1	103.9(4)	C 8	-C 14	-C 13	104.5(5)
C 8	-C 9	-C 11	110.8(4)				

hydrogen atoms were not taken into account. The chemical structure was confirmed to be as shown in Fig. 1, I. The absolute configuration was determined based on the circular dichroism spectrum of II, derived from pterokaurene L_2, $[\theta]^{20}_{325}$ −317° (MeOH).[2] Fig. 2 shows a perspective drawing of the molecular structure of pterokaurene L_2.

The final atomic parameters are listed in Table I, and the bond lengths and angles are given in Tables II and III, respectively. The values are normal for compounds of this type. Some significant lengthening of the bond lengths was observed for bonds involving one or two fully substituted tertiary carbon atoms. When both atoms are tertiary carbon, such as C9—C10 (1.595Å) and C8—C9 (1.582Å), the lengthening is quite remarkable. The carboxyl group forms a pair of hydrogen bonds [03-H……04 (at x, 1-y, 3/2-z) = 2.705Å] with that of the neighboring molecule related by a diad axis. Thus, the two molecules form a dimer, as is often seen in aliphatic carboxylic acids. The following three hydrogen bonds also link the molecules in the crystal: 01 at x,y,z……01 at x,2-y,3/2-z, 2.784(6)A; 02 at x,y,z……02 at 2-y, 2-x, 7/4-z, 2.512Å; 03 at x,y,z……03 at 1-y, 1-x, 7/4-z, 3.038 (7)Å.



III : R_1 =  , $R_2 = CH_2$

IV : $R_1 = O$, R_2 = 

Fig. 3

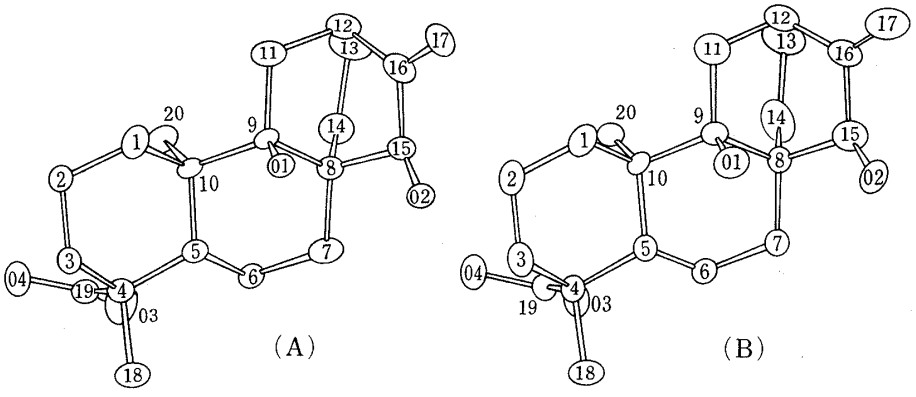


Fig. 4. Perspective Drawing of the Molecular Structure of Pteroatisene P_2 A and B Molecules

TABLE IV. Final Atomic Parameters ($\times 10^4$)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C 1	369(3)	380(3)	2163(4)	27(2)	27(1)	61(3)	2(1)	6(2)	−10(2)
C 2	652(4)	1093(3)	2447(5)	38(3)	26(1)	73(4)	−1(2)	11(3)	−9(2)
C 3	1284(4)	1381(3)	1616(5)	38(2)	22(1)	71(4)	4(1)	3(3)	0(2)
C 4	2181(3)	965(3)	1413(3)	28(2)	24(1)	42(2)	0(1)	3(2)	2(1)
C 5	1891(3)	224(2)	1192(3)	22(2)	21(1)	40(2)	0(1)	0(2)	2(1)
C 6	2721(3)	−241(2)	976(4)	24(2)	22(1)	59(3)	1(1)	10(2)	−1(2)
C 7	2345(3)	−881(3)	451(4)	27(2)	25(1)	59(3)	−3(1)	16(2)	−1(2)
C 8	1600(4)	−1245(2)	1103(4)	33(2)	20(1)	56(3)	3(1)	9(2)	4(2)
C 9	837(3)	−758(3)	1509(4)	29(2)	23(1)	38(2)	2(1)	4(2)	2(1)
C 10	1225(3)	−88(2)	2001(3)	22(2)	23(1)	37(2)	0(1)	3(2)	−1(1)
C 11	186(4)	−1132(3)	2269(4)	39(2)	25(1)	52(3)	−6(1)	10(2)	1(2)
C 12	297(5)	−1888(3)	2158(5)	53(3)	25(1)	58(3)	−2(2)	8(3)	13(2)
C 13	1293(5)	−2060(4)	2602(6)	60(4)	34(2)	87(5)	−3(2)	−8(4)	25(3)
C 14	2039(4)	−1643(3)	2031(5)	44(3)	29(1)	76(4)	6(2)	−4(3)	16(2)
C 15	1147(4)	−1794(3)	442(4)	47(3)	20(1)	57(3)	−4(2)	9(3)	1(2)
C 16	284(4)	−2056(2)	1013(5)	39(2)	17(1)	70(3)	2(1)	7(3)	7(2)
C 17	−420(5)	−2369(3)	548(6)	52(3)	18(1)	88(5)	−1(1)	1(3)	−2(2)
C 18	2669(4)	1257(3)	441(4)	48(3)	29(1)	50(3)	−5(2)	7(3)	8(2)
C 19	2903(3)	1048(3)	2286(4)	31(2)	24(1)	52(3)	−4(1)	1(2)	2(2)
C 20	1697(4)	−177(3)	3077(4)	40(2)	32(1)	34(2)	−2(2)	−3(2)	3(2)
OH1	325(2)	−580(2)	568(3)	32(2)	25(1)	46(2)	1(1)	−4(1)	3(1)
OH2	911(3)	−1596(2)	−625(3)	58(2)	28(1)	49(2)	−9(1)	8(2)	−4(1)
O 3	3605(3)	715(2)	2343(4)	36(2)	37(1)	82(3)	2(1)	−8(2)	−11(2)
OH4	2755(3)	1529(2)	2941(3)	62(2)	28(1)	59(2)	3(1)	−21(2)	−8(1)
C 1′	4708(3)	4733(3)	4493(4)	28(2)	27(1)	66(3)	5(1)	−13(2)	7(2)
C 2′	4580(4)	3996(3)	4782(5)	35(2)	26(1)	80(4)	7(2)	−9(3)	11(2)
C 3′	3979(4)	3641(3)	3982(5)	36(2)	21(1)	74(4)	7(1)	0(3)	1(2)
C 4′	3005(3)	3959(2)	3820(3)	29(2)	20(1)	45(2)	2(1)	0(2)	−2(1)
C 5′	3135(3)	4720(2)	3582(3)	22(2)	17(1)	42(2)	0(1)	2(2)	2(1)
C 6′	2231(3)	5111(2)	3403(4)	25(2)	20(1)	58(3)	−1(1)	−12(2)	4(1)
C 7′	2444(3)	5782(3)	2913(4)	32(2)	21(1)	56(3)	−3(1)	−7(2)	9(2)
C 8′	3099(3)	6207(2)	3579(4)	35(2)	19(1)	47(3)	3(1)	0(2)	4(1)
C 9′	3987(3)	5797(2)	3898(4)	29(2)	18(1)	42(2)	0(1)	−1(2)	1(1)
C 10′	3762(3)	5091(2)	4378(3)	24(2)	16(1)	39(2)	1(1)	−7(2)	2(1)
C 11′	4609(4)	6218(3)	4635(4)	49(3)	25(1)	60(3)	−10(2)	−3(3)	−1(2)
C 12′	4290(6)	6930(3)	4665(5)	89(5)	24(1)	62(4)	−13(2)	−10(4)	−2(2)
C 13′	3298(8)	6949(4)	5182(6)	107(6)	33(2)	78(5)	1(3)	10(5)	−19(3)
C 14′	2606(5)	6499(3)	4551(4)	63(3)	25(1)	59(3)	9(2)	20(3)	−2(2)
C 15′	3423(5)	6834(3)	2967(4)	58(3)	21(1)	51(3)	−5(2)	−1(3)	3(2)
C 16′	4223(6)	7180(3)	3551(5)	101(5)	24(1)	68(4)	−20(2)	−27(4)	4(2)
C 17′	4743(10)	7613(5)	3127(8)	174(11)	58(4)	101(7)	−69(6)	−53(8)	32(4)
C 18′	2558(5)	3614(3)	2869(4)	51(3)	24(1)	54(3)	−3(2)	−3(3)	−8(2)
C 19′	2327(4)	3836(2)	4740(4)	40(2)	16(1)	53(3)	0(1)	2(2)	2(1)
C 20′	3313(4)	5120(2)	5483(4)	43(2)	22(1)	41(2)	−4(1)	−3(2)	2(1)
OH1′	4455(2)	5704(2)	2915(3)	28(1)	27(1)	49(2)	−2(1)	6(1)	1(1)
OH2′	3667(3)	6728(2)	1895(3)	60(2)	30(1)	42(2)	−6(1)	−3(2)	8(1)
O 3′	1570(3)	4091(2)	4811(3)	32(2)	27(1)	72(3)	2(1)	11(2)	9(1)
OH4′	2605(3)	3389(2)	5426(3)	56(2)	28(1)	54(2)	7(1)	8(2)	9(1)
OW1	14(8)	581(5)	−1138(9)	253(13)	54(3)	209(12)	0(5)	−101(11)	13(4)

The primed atoms belong to molecule B and non-primed atoms to molecule A.
The temperature factors are of the form, $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Table V. Bond Lengths in Å Unit

Atom 1	Atom 2	A molecule	B molecule	Atom 1	Atom 2	A molecule	B molecule
C 1	-C 2	1.540(8)	1.546(8)	C 9	-C 10	1.593(7)	1.586(6)
C 1	-C 10	1.566(7)	1.547(6)	C 9	-C 11	1.548(7)	1.554(7)
C 2	-C 3	1.515(8)	1.520(8)	C 9	-OH1	1.457(6)	1.440(6)
C 3	-C 4	1.560(7)	1.554(7)	C 10	-C 20	1.547(6)	1.557(6)
C 4	-C 5	1.579(7)	1.580(6)	C 11	-C 12	1.542(8)	1.510(9)
C 4	-C 18	1.546(7)	1.543(7)	C 12	-C 13	1.579(10)	1.573(14)
C 4	-C 19	1.535(7)	1.548(7)	C 12	-C 16	1.505(8)	1.516(9)
C 5	-C 6	1.543(6)	1.538(6)	C 13	-C 14	1.548(10)	1.570(11)
C 5	-C 10	1.545(6)	1.553(6)	C 15	-C 16	1.535(8)	1.540(10)
C 6	-C 7	1.555(7)	1.525(7)	C 15	-OH2	1.463(7)	1.434(7)
C 7	-C 8	1.544(7)	1.533(7)	C 16	-C 17	1.333(9)	1.271(14)
C 8	-C 9	1.563(7)	1.576(7)	C 19	-O 3	1.215(7)	1.208(6)
C 8	-C 14	1.567(8)	1.549(8)	C 19	-OH4	1.301(7)	1.322(6)
C 8	-C 15	1.540(7)	1.560(7)				

Table VI. Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	A molecule	B molecule
C 2	-C 1	-C 10	112.8(4)	111.6(4)
C 3	-C 2	-C 1	110.6(5)	111.1(5)
C 4	-C 3	-C 2	113.9(5)	114.0(5)
C 5	-C 4	-C 3	108.8(4)	108.7(4)
C 5	-C 4	-C 18	109.6(4)	109.7(4)
C 5	-C 4	-C 19	114.4(4)	112.2(4)
C 3	-C 4	-C 18	107.6(4)	107.1(4)
C 3	-C 4	-C 19	112.2(4)	113.5(4)
C 18	-C 4	-C 19	103.8 4)	105.5(4)
C 6	-C 5	-C 4	113.9(4)	115.4(3)
C 6	-C 5	-C 10	110.5(4)	109.9(3)
C 4	-C 5	-C 10	115.4(4)	114.3(3)
C 7	-C 6	-C 5	108.4(4)	110.3(4)
C 8	-C 7	-C 6	113.7(4)	113.1(4)
C 9	-C 8	-C 7	111.5(4)	110.2(4)
C 9	-C 8	-C 14	110.7(4)	111.2(4)
C 9	-C 8	-C 15	109.9(4)	108.4(4)
C 7	-C 8	-C 14	112.0(4)	112.4(4)
C 7	-C 8	-C 15	109.8(4)	111.0(4)
C 14	-C 8	-C 15	102.6(4)	103.4(4)
C 10	-C 9	-C 8	114.9(4)	114.1(4)
C 10	-C 9	-C 11	112.2(4)	112.0(4)
C 10	-C 9	-OH1	107.1(3)	108.5(3)
C 8	-C 9	-C 11	109.0(4)	109.6(4)
C 8	-C 9	-OH1	103.6(4)	102.7(3)
C 11	-C 9	-OH1	109.5(4)	109.4(4)
C 20	-C 10	-C 1	107.3(4)	107.2(4)
C 20	-C 10	-C 5	112.0(4)	112.0(3)
C 20	-C 10	-C 9	114.0(4)	113.7(4)
C 1	-C 10	-C 5	109.2(4)	110.3(4)
C 1	-C 10	-C 9	106.9(4)	106.2(4)
C 5	-C 10	-C 9	107.3(3)	107.3(3)
C 12	-C 11	-C 9	111.3(4)	111.2(5)
C 13	-C 12	-C 11	106.2(5)	108.0(6)
C 13	-C 12	-C 16	108.2(5)	109.3(6)
C 11	-C 12	-C 16	108.2(5)	108.3(6)
C 14	-C 13	-C 12	109.8(6)	110.0(7)
C 16	-C 15	-C 8	109.1(4)	110.4(5)
C 16	-C 15	-OH2	110.6(4)	110.5(5)

Atom 1	Atom 2	Atom 3	A molecule	B molecule
C 8	-C 15	-OH2	114.5(4)	115.7(4)
C 17	-C 16	-C 12	123.5(5)	126.5(8)
C 17	-C 16	-C 15	124.3(5)	122.9(8)
C 12	-C 16	-C 15	112.1(5)	110.6(6)
O 3	-C 19	-C 4	123.0(5)	123.8(4)
O 3	-C 19	-OH4	120.7(5)	120.9(5)
C 4	-C 19	-OH4	116.2(4)	115.2(4)
C 8	-C 14	-C 13	111.0(5)	110.2(5)

X-Ray Crystallographic Analysis of Pteroatisene P_2

The crystals of pteroatisene P_2 for the present X-ray study were grown from methanol solution as colorless thick plates flattened on (010). A crystal with approximate dimensions of $0.3\times0.4\times0.6$ mm was used for the diffraction experiment. Intensities and lattice parameters were measured on a Philips PW 1100 diffractometer using graphite-monochromated CuKα radiation. The crystal data are: pteroatisene P_2–hemihydrate, $C_{20}H_{30}O_4\cdot1/2\ H_2O$, FW=343.5, orthorhombic, space group $P2_12_12_1$, a=14.370(7), b=20.205(10), c=12.808(6)Å, V=3718.8Å^3, z=8, Dx=1.227 gcm^{-3}. The intensities of 4212 reflections out of 4463 theoretically possible ones were measured within a 2θ range of 6—156° as above the 2σ (I) level. The θ—2θ scan method was employed and the scans were repeated twice when the total counts during the first scan were less than 5000. The crystal structure was determined by the direct method using the MULTAN program[5] and refined by the least-squares method as described in a preceding section. The final R value was 0.096 including anisotropic thermal parameters for 49 heavier atoms. No hydrogen atom contributions were taken into account. The final atomic parameters are listed in Table IV. The two crystallographically independent molecules A and B have essentially the same structure. The chemical structure was confirmed to be as shown in Fig. 3, [III]. The absolute configuration was determined based on the circular dichroism spectrum of [IV] derived from pteroatisene P_2, $[\theta]^{20}_{290}$ +2660° (MeOH).[3] Fig. 4 shows a perspective drawing of the molecular structure of pteroatisene P_2 A and B molecules.

The bond lengths and angles for the two independent molecules are given in Tables V and VI, respectively. These values are consistent with those expected from the chemical structure. The differences in bond lengths and angles between the A and B molecules were: the mean value of the differences in the bond lengths was 0.015Å with the maximum difference of 0.062Å in C(16)–C(17) ,and the mean value of the differences in the bond angles was 0.8° with the maximum difference of 3.0° in C(17)–C(16)–C(12). The mean differences are within the 2σ values of the estimated standard deviations of 0.008Å in bond lengths and 0.44° in bond angles.

References and Notes

1) Part XXXV: T. Murakami, T. Kimura, H. Wada, N. Tanaka, Y. Saiki, and C.-M. Chen, *Chem. Pharm. Bull.*, **29**, 866 (1981).
2) T. Murakami, H. Iida, N. Tanaka, Y. Saiki, C.-M. Chen, and Y. Iitaka, *Chem. Pharm. Bull.*, **29**, 657 (1981).
3) N. Tanaka, T. Murakami, Y. Saiki, C.-M. Chen, and Y. Iitaka, *Chem. Pharm. Bull.*, **29**, 663 (1981).
4) The space group $P4_322$ was assigned by assuming that the absolute configuration of the molecule was as described later.
5) P. Main, M.M. Woolfson, L. Lessinger, G. Germain, and J.P. Declercq, (1974), MULTAN 74, A System of Computer Programs for the Automatic Solution of Crystal Structure from X-ray Diffraction Data, Univs. of York, England and Louvain-la-Neuve, Belgium.