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A Structure Analysis of a Bromoacetate of Hydroxypiperenone by the X-Ray Diffraction Method

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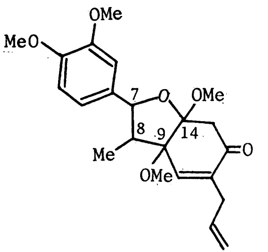
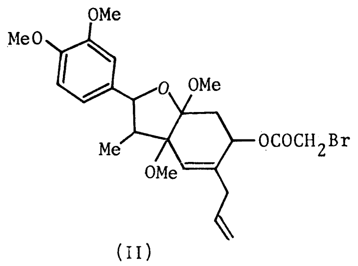
The structure of a bromoacetate of hydroxypiperenone, $C_{24}H_{31}O_7Br$, has been determined by the X-ray diffraction method. The compound crystallized in the space group $P2_1$, with $a=8.296$, $b=13.247$, $c=11.400$ Å, and $\beta=102.8°$. The structure was solved by the heavy-atom method and refined to $R=0.075$ for 1614 reflections. The present analysis has established that the five- and six-membered rings are fused in the *cis* fashion. The absolute configuration of the molecule has been determined by using the anomalous dispersion effect of the bromine atom for Cu $K\alpha$ radiation.

Piperenone isolated from the leaves of *Piper futokadzura* Sieb. et Zucc. shows a distinct antifeeding activity in response to the larvae of *Spodoptera litura* F. The structural formula of piperenone has been shown to be (I),[1] and the configurations at the C(7) and C(8) atoms (refer to Fig. 1) have been presumed to be *S*-form[2] on the basis of chemical and spectroscopic methods. However, the configurations at the C(9) and C(14) atoms could not be determined by these methods. In order to confirm the presumption, and, further, in order to determine the absolute configuration, a bromoacetate of hydroxypiperenone (II) has now been investigated by means of the X-ray diffraction method.



(I)



(II)

Experimental

The bromoacetate of hydroxypiperenone was prepared by the reaction of bromoacetyl bromide and hydroxypiperenone, one of the epimers obtained by the reduction of piperenone with lithium aluminum hydride. The compound crystallized from the hexane–ethyl acetate solution in the form of colorless plates.

A preliminary photographic investigation showed that the crystals were monoclinic with the b axis along the most developed axis, and that the intensities fell off fairly rapidly with an increase in θ. The systematic absence ($0k0$ when k is odd) and optical activity indicated the space group to be $P2_1$. The unit-cell constants were obtained from the Bragg angles measured by a Toshiba four-circle diffractometer using Ni-filtered Cu$K\alpha$ radiation. The crystal data were as follows: $C_{24}H_{31}O_7Br$, mp 153—155 °C, $M=511.4$, monoclinic, $P2_1$, $a=8.296(5)$, $b=13.247(7)$, $c=11.400(6)$ Å, $\beta=102.8(1)°$, $V=1222$ Å^3, $Z=2$, $D_0=1.38$ g/cm^3, $D_x=1.39$ g/cm^3, $\mu=28.6$ cm^{-1} (for Cu$K\alpha$).

A crystal with dimensions of *ca.* $0.12\times0.35\times0.22$ mm^3 was mounted with its b axis parallel to the ϕ axis of the diffractometer. The stationary-crystal stationary-counter technique was applied, with a counting time of 30 s. The intensities of 1616 independent reflections were measured up to $\sin\theta/\lambda=0.53$, with Ni-filtered Cu$K\alpha$ radiation. The background for each reflection was taken from the plots of the background as a function of 2θ. The intensities were corrected for the Lorentz and polarization factors, but not for absorption.

Determination of the Structure

The coordinates of the bromine atom were easily determined from the Patterson map. The locations of the remaining non-hydrogen atoms were determined by successive Fourier syntheses. The coordinates and isotropic temperature factors were initially refined by a block-diagonal least-squares method, using carbon and bromine scattering factors. The atomic species were determined on the bases of the temperature factors and chemical sense. The refinement with anisotropic temperature factors reduced the R value to 0.08. Two

TABLE 1. DETERMINATION OF THE ABSOLUTE CONFIGURATION

h	k	l	$F_c(hkl)$	$F_c(\bar{h}\bar{k}\bar{l})$	$I_0(hkl)$ $I_0(\bar{h}\bar{k}\bar{l})$
0	1	1	486	533	<
0	3	1	564	513	>
1	1	−3	581	553	>
1	3	−3	414	390	>
1	1	−2	255	287	<
1	2	1	254	272	<
2	1	−4	436	470	<
2	4	−3	510	484	>
2	4	−2	290	306	<
2	5	−2	370	395	<
2	6	−2	273	255	>
2	2	−1	203	160	>
2	6	−1	278	302	<
2	3	0	322	304	>
2	5	0	316	297	>
2	1	3	273	246	>
3	1	−4	429	400	>
3	2	−1	357	379	<
4	1	0	391	417	<

The right-handed coordinate system is adopted.
The values of F_c are multiplied by 10.

Table 2. Final atomic parameters and e.s.d.'s ($\times 10^4$) for non-hydrogen atoms
The anisotropic temperature factors are of the form; $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	698(2)	2500(2)	7354(1)	232(2)	100(1)	182(2)	61(3)	103(3)	25(3)
C(1)	6604(14)	1517(9)	3363(10)	192(21)	68(8)	101(11)	28(22)	64(23)	−19(16)
C(2)	5178(16)	1382(10)	2459(11)	249(24)	73(9)	105(11)	−5(26)	39(26)	0(17)
C(3)	4945(20)	1897(13)	1389(12)	343(35)	99(11)	107(12)	−36(33)	83(33)	1(20)
C(4)	6163(16)	2587(13)	1174(10)	300(26)	81(9)	115(11)	−16(35)	122(27)	−20(23)
C(5)	7541(18)	2766(10)	2084(13)	293(28)	65(11)	157(14)	−6(26)	185(34)	−23(19)
C(6)	7737(15)	2232(9)	3179(11)	216(22)	70(10)	116(12)	1(22)	98(25)	−17(16)
C(7)	6912(13)	928(9)	4504(11)	141(18)	61(8)	136(13)	3(19)	64(25)	17(16)
C(8)	7983(13)	−15(10)	4488(10)	126(17)	76(8)	122(12)	−2(20)	58(22)	4(17)
C(9)	7438(13)	−663(9)	5463(11)	152(18)	69(8)	123(12)	10(20)	74(23)	−14(16)
C(10)	8159(13)	−291(10)	6709(11)	131(17)	71(8)	129(12)	18(20)	43(23)	1(17)
C(11)	7320(14)	27(11)	7478(12)	154(19)	79(9)	147(14)	−20(23)	−5(26)	17(19)
C(12)	5458(13)	−51(10)	7260(10)	154(19)	74(8)	119(12)	−18(21)	50(24)	−5(17)
C(13)	4654(13)	−627(10)	6142(10)	161(19)	82(9)	96(10)	14(22)	75(22)	−12(16)
C(14)	5558(12)	−510(10)	5113(10)	127(17)	77(9)	110(11)	4(21)	15(22)	0(17)
C(15)	3377(15)	1131(9)	7471(10)	208(22)	71(9)	99(11)	74(23)	39(25)	−4(16)
C(16)	3010(14)	2272(10)	7488(11)	169(19)	94(13)	127(12)	60(24)	64(24)	2(18)
C(17)	3166(15)	−1198(15)	3655(13)	146(20)	155(16)	148(15)	−63(31)	70(28)	−90(27)
C(18)	2130(19)	1413(14)	661(14)	258(29)	125(14)	145(16)	−73(36)	4(34)	−11(26)
C(19)	7153(33)	3737(17)	−124(17)	754(76)	132(17)	152(19)	−280(64)	264(61)	−6(30)
C(20)	9865(16)	195(11)	4705(12)	163(20)	97(12)	142(16)	−14(25)	113(30)	13(21)
C(21)	7521(17)	−2448(16)	6021(14)	271(27)	95(11)	198(17)	39(40)	169(35)	63(32)
C(22)	8156(16)	422(12)	8724(10)	229(24)	122(12)	92(11)	−73(30)	−7(26)	−5(21)
C(23)	8136(20)	−307(15)	9716(14)	305(32)	130(15)	135(15)	35(37)	−13(35)	27(25)
C(24)	7672(37)	−48(20)	10722(18)	831(91)	157(20)	152(21)	−60(77)	246(68)	29(36)
O(1)	5349(8)	522(6)	4703(6)	146(12)	77(6)	109(7)	24(14)	61(14)	10(11)
O(2)	4966(9)	−1170(7)	4161(7)	141(12)	109(7)	129(8)	−14(16)	78(16)	−67(14)
O(3)	3556(14)	1845(10)	442(8)	355(25)	166(11)	101(8)	−111(28)	−58(23)	48(17)
O(4)	5884(17)	3047(9)	76(9)	562(37)	116(9)	123(10)	−89(30)	107(32)	60(16)
O(5)	7999(10)	−1668(7)	5318(8)	180(14)	67(5)	156(9)	23(14)	102(18)	8(12)
O(6)	4849(9)	995(6)	7224(7)	182(14)	67(6)	121(8)	5(14)	73(17)	−4(11)
O(7)	2504(10)	486(7)	7719(8)	180(14)	71(6)	170(10)	−1(15)	111(19)	14(13)

intense reflections, -121 and 013, were rejected from the subsequent calculations.

The absolute configuration of the molecule was determined using the anomalous dispersion effect of the bromine atom ($\Delta f' = -0.9$ and $\Delta f'' = 1.5$) for Cu$K\alpha$ radiation. The intensities of the Friedel-pair reflections were measured by the ω-2θ scan technique, using Ni-filtered Cu $K\alpha$ radiation with a specimen with dimensions of *ca.* $0.08 \times 0.20 \times 0.10$ mm^3. A comparison of the observed and calculated intensities between the Friedel-pair reflections is given in Table 1. Of the 31 hydrogen atoms in the molecule, twelve atoms were located from a difference Fourier map. The final refinement was made by including these hydrogen atoms with fixed parameters and the anomalous dispersion effect of the bromine atom, and by using the following weighting scheme; $w=0.34$ for $F_o=0.0$, $w=1.0$ for $0<F_o\leqq 15$, and $w=1.0/(1.0+0.1(F_o-15))$ for $15<F_o$. The final R value was 0.075 for 1614 independent reflections. The final atomic parameters are given in Table 2.***

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[3] The computations were performed on a TOSBAC-3400 computer at the Tottori University Computing Center, and on a NEAC 2200-N700 computer at the Computation Center of Osaka University.

Results and Discussion

The structural formula and the absolute configuration of the molecule have been established by the present

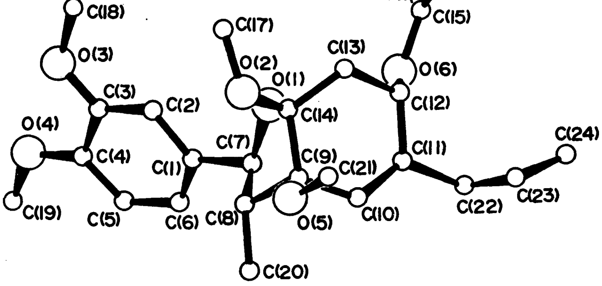


Fig. 1. Perspective view of the molecule and the scheme of atomic numbering.

*** A list of the observed and calculated structure factors is kept by the office of the Chemical Society of Japan (Document No. 7602).

X-ray analysis. The absolute configuration of the molecule is correctly represented by the parameters in Table 2 if the right-handed coordinate system is adopted. A perspective drawing of the molecule and the numbering of atoms are shown in Fig. 1, and a stereoscopic view of the molecule, in Fig. 2. Both figures are drawn with a correct absolute configuration. The least-squares planes and the deviations of atoms from each plane are listed in Table 3. The two methoxy groups bonded to the C(9) and C(14) atoms are in the *cis*-form to each other; the torsion angles† of O(2)–C(14)–C(9)–O(5) and C(8)–C(9)–C(14)–O(1) are −33° and −36° respectively. The torsion angle of H–C(7)–C(8)–

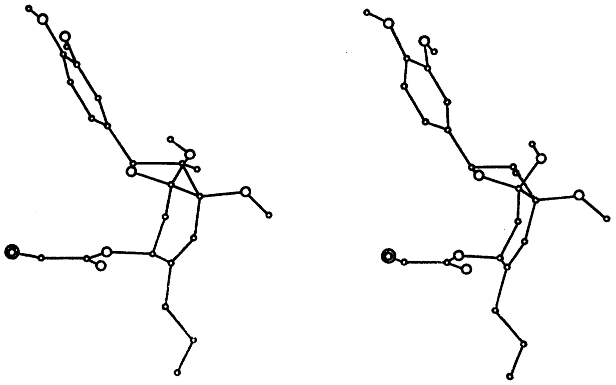


Fig. 2. Stereoscopic drawing of the molecule.

Table 3(a). Least-squares planes and deviations of atoms

In the equation of each plane, X, Y, and Z are defined to be $ax+cz\cos\beta$, by, and $cz\sin\beta$, respectively.

(1) Benzene ring

$0.568X-0.730Y-0.381Z=-0.288$ (I)

C (1)	0.03 Å	C (2)	0.00 Å
C (3)	0.00	C (4)	0.03
C (5)	−0.01	C (6)	−0.03
C (7)*	0.10	O (3)*	−0.07
O (4)*	0.07	C (18)*	−0.45
C (19)*	0.12		

(2) The plane through the C(7), C(8), C(9), C(14), and O(1) atoms

$0.143X+0.400Y+0.905Z=5.533$ (II)

C (7)	−0.15 Å	C (8)	0.24 Å
C (9)	−0.30	C (14)	0.18
O (1)	0.06	C (1)*	0.68
C (20)*	−0.31	O (5)*	0.31
O (2)*	1.53	C (10)*	−1.79
C (13)*	−0.65		

(3) The plane through the C(9), C(10), C(11), C(12), and C(22) atoms

$0.019X+0.928Y-0.371Z=-2.995$ (III)

C (9)	0.02 Å	C (10)	−0.03 Å
C (11)	0.02	C (12)	−0.01
C (22)	0.00	C (13)*	−0.26
C (14)*	0.32		

(4) The plane through the C(15), C(16), O(6), and O(7) atoms

$0.238X+0.056Y+0.970Z=8.377$ (IV)

C (15)	0.02 Å	C (16)	−0.01 Å
O (6)	−0.01	O (7)	−0.01
C (12)*	−0.09	Br*	0.57

*) Not included in least-squares calculation.

(b) Dihedral angles

	I	II	III
II	56°	—	—
III	122°	92°	—
IV	74°	21°	72°

Table 4(a). Bond lengths and their estimated standard deviations

Br–C(16)	1.92(1) Å	O(1)–C(7)	1.47(2) Å
O(1)–C(14)	1.44(2)	O(2)–C(14)	1.40(2)
O(2)–C(17)	1.48(2)	O(3)–C(3)	1.40(2)
O(3)–C(18)	1.39(2)	O(4)–C(4)	1.37(2)
O(4)–C(19)	1.45(3)	O(5)–C(9)	1.43(2)
O(5)–C(21)	1.42(2)	O(6)–C(12)	1.47(2)
O(6)–C(15)	1.33(2)	O(7)–C(15)	1.19(2)
C(1)–C(2)	1.40(2)	C(1)–C(6)	1.38(2)
C(1)–C(7)	1.49(2)	C(2)–C(3)	1.37(2)
C(3)–C(4)	1.42(2)	C(4)–C(5)	1.38(2)
C(5)–C(6)	1.41(2)	C(7)–C(8)	1.54(2)
C(8)–C(9)	1.55(2)	C(8)–C(20)	1.55(2)
C(9)–C(10)	1.50(2)	C(9)–C(14)	1.54(2)
C(10)–C(11)	1.30(2)	C(11)–C(12)	1.51(2)
C(11)–C(22)	1.53(2)	C(12)–C(13)	1.51(2)
C(13)–C(14)	1.53(2)	C(15)–C(16)	1.54(2)
C(22)–C(23)	1.49(3)	C(23)–C(24)	1.33(4)

Table 4(b). Bond angles and their estimated standard deviations

C(7)–O(1)–C(14)	111(1)°	C(14)–O(2)–C(17)	118(1)°
C(3)–O(3)–C(18)	118(1)	C(4)–O(4)–C(19)	116(2)
C(9)–O(5)–C(21)	118(1)	C(12)–O(6)–C(15)	117(1)
C(2)–C(1)–C(6)	118(1)	C(2)–C(1)–C(7)	122(1)
C(6)–C(1)–C(7)	120(1)	C(1)–C(2)–C(3)	121(1)
O(3)–C(3)–C(2)	126(1)	O(3)–C(3)–C(4)	113(1)
C(2)–C(3)–C(4)	120(2)	O(4)–C(4)–C(3)	117(2)
O(4)–C(4)–C(5)	124(2)	C(3)–C(4)–C(5)	119(2)
C(4)–C(5)–C(6)	119(1)	C(1)–C(6)–C(5)	122(1)
O(1)–C(7)–C(1)	110(1)	O(1)–C(7)–C(8)	104(1)
C(1)–C(7)–C(8)	114(1)	C(7)–C(8)–C(9)	100(1)
C(7)–C(8)–C(20)	115(1)	C(9)–C(8)–C(20)	115(1)
O(5)–C(9)–C(8)	106(1)	O(5)–C(9)–C(10)	110(1)
O(5)–C(9)–C(14)	115(1)	C(8)–C(9)–C(10)	112(1)
C(8)–C(9)–C(14)	100(1)	C(10)–C(9)–C(14)	112(1)
C(9)–C(10)–C(11)	126(1)	C(10)–C(11)–C(12)	123(1)
C(10)–C(11)–C(22)	122(1)	C(12)–C(11)–C(22)	114(1)
O(6)–C(12)–C(11)	106(1)	O(6)–C(12)–C(13)	112(1)
C(11)–C(12)–C(13)	115(1)	C(12)–C(13)–C(14)	113(1)
O(1)–C(14)–O(2)	110(1)	O(1)–C(14)–C(9)	105(1)
O(1)–C(14)–C(13)	107(1)	O(2)–C(14)–C(9)	106(1)
O(2)–C(14)–C(13)	113(1)	C(9)–C(14)–C(13)	115(1)
O(6)–C(15)–O(7)	126(1)	O(6)–C(15)–C(16)	109(1)
O(7)–C(15)–C(16)	125(1)	Br–C(16)–C(15)	111(1)
C(11)–C(22)–C(23)	114(1)	C(22)–C(23)–C(24)	123(2)

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† In this paper, the torsion angle A–B–C–D is a projected angle between the A–B and C–D bonds. When viewed down the B–C bond, the clockwise rotation of the C–D bond with reference to the A–B bond is taken to be positive.

Table 5. Intermolecular contacts for non-hydrogen atoms (<3.8 Å)

O (7) ···C (10)$^{\text{i}}$	3.68 Å	O (7) ···C (20)$^{\text{i}}$	3.66 Å
C (17)···C (20)$^{\text{i}}$	3.71	Br·········O (5)$^{\text{ii}}$	3.62
O (1) ···C (21)$^{\text{ii}}$	3.57	C (2) ···C (21)$^{\text{ii}}$	3.49
C (5) ···O (7)$^{\text{ii}}$	3.61	C (5) ···C (13)$^{\text{ii}}$	3.68
C (6) ···C (13)$^{\text{ii}}$	3.64	C (16)···O (2)$^{\text{ii}}$	3.47
C (16)···O (5)$^{\text{ii}}$	3.42	C (19)···O (7)$^{\text{ii}}$	3.55
O (7) ···O (3)$^{\text{iii}}$	3.53	O (7) ···C (18)$^{\text{iii}}$	3.65
C (15)···O (3)$^{\text{iii}}$	3.49	C (16)···O (3)$^{\text{iii}}$	3.35
C (16)···O (4)$^{\text{iii}}$	3.51	C (24)···C (2)$^{\text{iii}}$	3.69
C (24)···C (3)$^{\text{iii}}$	3.62	C (24)···C (4)$^{\text{iii}}$	3.78
C (19)···C (18)$^{\text{iv}}$	3.67		

Symmetry code: (i) $-1+x, y, z$ (ii) $1-x, 1/2+y, 1-z$ (iii) $x, y, 1+z$ (iv) $1-x, 1/2+y, -z$.

H derived from the X-ray analysis is about −168°. This value can be correlated with the coupling constant (11 Hz) of these hydrogen atoms, derived by an analysis of the NMR spectrum.[4] The five-membered ring comprising the C(7), C(8), C(9), C(14), and O(1) atoms takes a half-chair conformation, and the C_2 axis lies on a line connecting the midpoint of the C(8)–C(9) bond and the O(1) atom. This is one of two conformations of the cyclopentane. As is usually found in the cyclohexene and the heterocyclic rings,[5,6] the six-membered ring comprising the C(9), C(10), C(11), C(12), C(13), and C(14) atoms is also in the form of a half-chair. The ethylenic carbon atoms (C(10) and C(11)) and the two adjacent allylic carbon atoms (C(9) and C(12)) lie approximately on a plane, while the C(13) and C(14) atoms on the other side deviate by 0.26 Å above and 0.32 Å below the plane respectively. The torsion angles in the ring, C(13)–C(14)–C(9)–C(10), C(12)–C(13)–C(14)–C(9), and C(11)–C(12)–C(13)–C(14), are calculated to be −34°, 48°, and −33° respectively. One of the two methoxy groups attached to the benzene ring is approximately coplanar with the benzene ring; the torsion angles of C(5)–C(4)–O(4)–C(19) and C(2)–C(3)–O(3)–C(18) are 2° and 15° respectively. The bond lengths and angles of the molecule are listed in Table 4. They seem to be normal for the respective bond types within the limits of experimental error. The intermolecular distances between the non-hydrogen atoms less than 3.8 Å are listed in Table 5; the table indicates the absence of any abnormally short contact.

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