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X-Ray Structure of (10*R*)-10-Bromo-10-deoxyhexahydrolaurefucin

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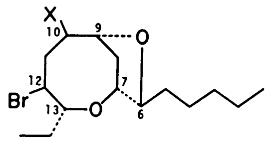
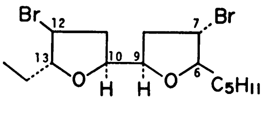
Synopsis. The main product of the bromination of hexahydrolaurefucin with sulfinyl bromide has been established as (10*R*)-10-bromo-10-deoxyhexahydrolaurefucin by X-ray crystal structure analysis.

In a previous paper, we reported that, when treated with silica gel, the dibromo compound **1** derived from hexahydrolaurefucin (**2**) was transformed into an isomerization product **3**.[1] Although the structure of **3** was recently elucidated,[2] that of **1** remained uncertain. Therefore, in order to confirm that no skeletal change occurred during the bromination of **2** and to establish the configuration of the bromine atom at the 10-position, we have now undertaken an X-ray crystal structure analysis of **1**.



1 : X=Br 2 : X=OH



3

Experimental

A colorless, single crystal with dimensions of about 0.3×0.4×0.4 mm^3 was used for the X-ray measurement. The crystal data are as follows: $C_{15}H_{26}O_2Br_2$, mp 36—37 °C, mol wt 398.18, orthorhombic, space group $P2_12_12_1$, $a=10.924(4)$, $b=17.642(7)$, $c=9.143(3)$ Å, $Z=4$, $D_c=1.501$ g cm^{-3}, $\mu(\text{Cu } K\alpha)=58.6$ cm^{-1}. The cell dimensions and diffraction intensities were measured on a Rigaku four-circle diffractometer at the High Energy X-Ray Diffraction Laboratory of Hokkaido University, using graphite-monochromated Cu *Kα* radiation ($\lambda=1.54178$ Å). The θ-2θ scan technique was applied at a θ scan rate of 4° min^{-1}; the background was measured for 5 s at each end of the scan range. Three standard reflections, measured at intervals or every 50 reflections, showed a gradual decrease in intensity with the course of data collection; the final-intensity/initial-intensity ratios were about 0.72—0.74. The intensities were corrected for this damage of the sample as well as for the Lorentz and polarization factors, but not for the absorption or the extinction effect. In the range of 2θ values up to 120°, 1354 independent structure factors above the $3\sigma(F)$ level were selected for the structure determination.

Structure Determination

The structure was solved by the Monte Carlo direct method,[3] using the 20 reflections with the greatest $|E|$ values as the starting set. The ninth-generated random phase set led to the correct solution; an *E*-map based on 459 phases revealed the locations of all the non-hydrogen atoms. After the structure had been well refined by the block-diagonal least-squares method with anisotropic temperature factors, the absolute configuration was determined by taking account of the anomalous dispersion of the bromine atoms for Cu *Kα* radiation. The *R* ratio for the two enantiomeric structures, 1.022, rejected one of them at the 99.5% confidence level.[4] Since a difference Fourier map afforded the 10 hydrogen atoms attached to the rings, further least-squares refinements were carried out including the hydrogen atoms. For these refinements, the following weighting scheme was used:

$$w = 1/\{\sigma(F)^2 \exp(AX^2+BY^2+CXY+DX+EY)\},$$

where $X=|F_o|$ and $Y=\sin\theta/\lambda$. The *A*, *B*, *C*, *D*, and *E* coefficients were evaluated from the $(\Delta F)^2$ distribution; $A=-0.107\times10^{-5}$, $B=-4.06$, $C=-0.757\times10^{-2}$, $D=-0.488\times10^{-3}$, and $E=1.75$. The final *R* value was 0.069. The final atomic parameters are listed in Table 1.[5]

The calculations were performed on a HITAC M-200H computer at the Hokkaido University Computing Center, using our own programs. The atomic scattering factors were taken from the International Tables.[6]

Results and Discussion

The molecular structure of **1** including the absolute configuration is shown in Fig. 1. This absolute configuration (6*R*, 7*R*, 9*R*, 10*R*, 12*S*, 13*R*) corresponds to that which has been already assigned to laurefucin by X-ray

Table 1. The final atomic parameters and estimated standard deviations

Atom	10^4x	10^4y	10^3z	$B_{eq}$$^{a)}$/Å^2
Br(1)	5196(1)	1550.0(7)	764.1(2)	8.41
Br(2)	9511(1)	549.7(6)	529.7(2)	7.34
O(1)	4704(5)	2310(3)	412.4(6)	4.83
O(2)	6765(5)	1477(3)	283.8(6)	4.20
C(1)	1577(11)	35(7)	−11(2)	13.31
C(2)	2389(12)	540(7)	105(2)	16.94
C(3)	2302(12)	1260(7)	62(1)	10.91
C(4)	3018(9)	1817(5)	182(1)	8.14
C(5)	4466(8)	1669(5)	183(1)	5.77
C(6)	5073(8)	2325(5)	263(1)	4.57
C(7)	6434(8)	2287(4)	264(1)	4.49
C(8)	6714(8)	2699(5)	403(1)	5.34
C(9)	5739(7)	2382(5)	508(1)	4.36
C(10)	6054(7)	1583(5)	576(1)	4.57
C(11)	7380(7)	1363(5)	593(1)	4.59
C(12)	7880(7)	935(4)	467(1)	5.13
C(13)	8019(7)	1287(5)	322(1)	4.61
C(14)	8505(8)	763(4)	198(1)	5.52
C(15)	8462(9)	1178(6)	40(1)	7.95

a) $B_{eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where u_i is the root-mean-square deviation in the *i*th principal axis of the thermal ellipsoid.

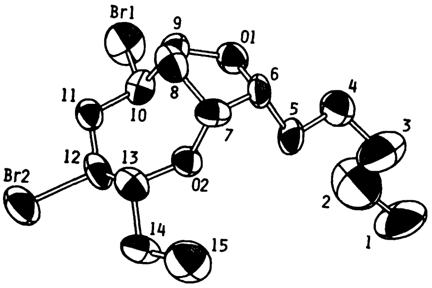


Fig. 1. A perspective view of the **1** molecule. Each non-hydrogen atom is represented as a thermal ellipsoid enclosing a 50% probability. The symbol C for carbon atoms is omitted.

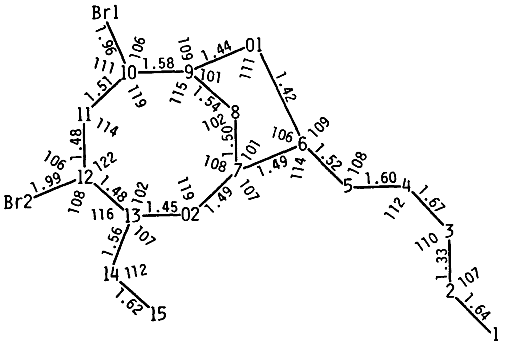


Fig. 2. The bond distances (l/Å) and angles (θ/°). The e.s.d.'s are 0.01—0.02 Å and 0.6—1.3° respectively.

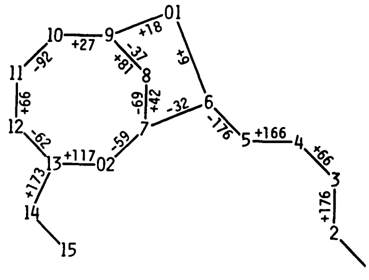


Fig. 3. The torsion angles (ϕ/°). The torsion angles relevant to atoms which form the same ring are given in the ring. The values given near the C(5)–C(6) and C(13)–C(14) bonds show the C(4)–C(5)–C(6)–C(7) and C(12)–C(13)–C(14)–C(15) torsion angles respectively.

methods.[1] Figure 1 demonstrates that **1** has the same skeleton as **2**, and that the Br(1) and Br(2) atoms are *cis* to each other. Thus, it has been confirmed that **2** undergoes no skeleton rearrangement during its bromination with sulfinyl bromide. It has also been revealed that this bromination proceeds with retention of the original configuration at the C(10) atom.

The bond distances and angles and the torsion angles are given in Figs. 2 and 3 respectively. If the standard deviations are considered, all the bond distances, except the C(1)–C(2), C(2)–C(3), and C(3)–C(4) distances, are normal. Of these three bond distances, the second is much shorter than the standard C–C single-bond distance, while the remaining two are considerably longer. Since the spectroscopic data show the absence of a C=C double bond in **1**, these abnormal bond distances may be due to a special and vigorous thermal motion or a disordering of the pentyl group. The eight-membered ether ring takes on a boat-chair conformation with an approximate mirror plane through the C(8) and C(12) atoms; the Br(1) and Br(2) atoms and the C(14)H$_2$–C(15)H$_3$ ethyl group are equatorially oriented, while the O(1) and C(6) atoms are axially placed. The five-membered ether ring adopts a conformation intermediate between the envelope form with an approximate mirror plane through the C(8) atom and the half-chair form with an approximate two-fold rotation axis through the O(1) atom. This deformation from the envelope form somewhat relieves the severe steric repulsion between the O(2) atom and the C(5)H$_2$ group; the O(2)···C(5) distance is 2.70(1) Å.

The molecules are held together mainly by the van der Waals interactions; there are no unusual intermolecular distances.

References

1) A. Furusaki, E. Kurosawa, A. Fukuzawa, and T. Irie, *Tetrahedron Lett.*, **1973**, 4579.

2) The details of the structure elucidation of **3** will be reported elsewhere.

3) A. Furusaki, *Acta Crystallogr.*, *Sect. A*, **35**, 220 (1979).

4) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

5) The tables of the anisotropic temperature factors and hydrogen parameters and the F_o-F_c table are kept at the Chemical Society of Japan (Document No. 8326).

6) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1974), Vol. IV.