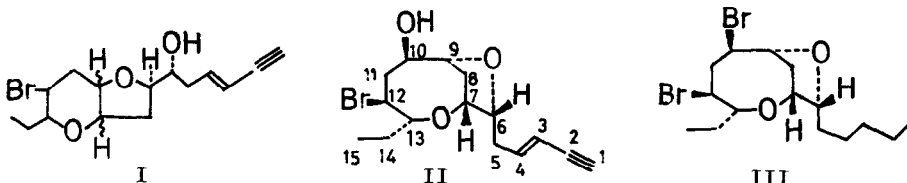


THE REVISED STRUCTURE AND ABSOLUTE CONFIGURATION OF LAUREFUCIN \*  
 FROM LAURENCIA NIPPONICA YAMADA

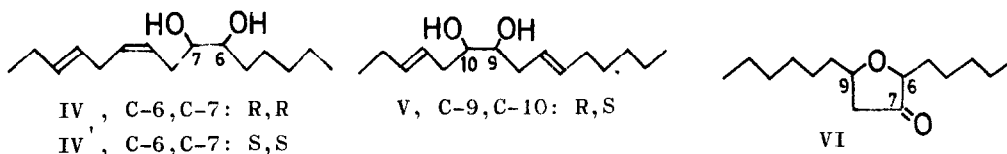
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In previous paper (1), the structure of laurefucin,  $C_{15}H_{21}O_3Br$ , isolated from the neutral essential oil of Laurencia nipponica Yamada, was represented by the formula I on the basis of its chemical and spectral properties. However, the chemical evidences afterwards have been interpreted in terms of new formula II, which are established by X-Ray crystallographic study as follows.



Treatment of hexahydrolaurefucin with  $SOBr_2$  in dry ether gave a dibromo compound (III),  $C_{15}H_{26}O_2Br_2$ ,  $m/e$  400, 398 and 396 ( $M^+$ ),  $\tau$  9.10 (3H, br. t), 9.06 (3H, t,  $J=7$ ), 7.1-8.1 (4H, m), 5.8-6.7 (5H, m) 5.47 (1H, dd,  $J=8,4$ ), contaminated with a small amount of impurity (TLC). III was then treated with Zn-acetic acid in ethanol yielding an unsaturated glycol (IV), which was an antipode of IV' derived from laureatin (2) or isolaureatin (3). On the column chromatography over silicic acid, raw material of III quantitatively converted to the rearrangement product \*\*,  $C_{15}H_{26}O_2Br_2$ , involving ring isomerization,  $m/e$  400, 398 and 396 ( $M^+$ ),  $\tau$  9.12 (3H, br. t), 9.04 (3H, t,  $J=7$ ), 7.94 (1H, m), 7.74 (2H, m), 7.42 (1H quintet), 6.4-5.8 (6H, m), which was then degraded to an unsaturated glycol (V) with Zn-acetic acid as described in previous report (1).



On the other hand, the oxolane ring in II has been confirmed by the chemical degradations of II to  $\beta$ -keto-oxolane (VI) ( $H_2/Pt$ ,  $SOCl_2$ ,  $Zn-AcOH$ ,  $H_2/Pt$ , Raney-Ni and  $Ag_2O$ ) (1). The compounds, IV and VI, show that the structure of laurefucin should be represented by the formula II, together with a biogenetical point of view (4) and it has been established by X-Ray crystallographic study including the absolute configuration.

The crystals are orthorhombic, with four molecules in a unit cell with the dimensions of  $a = 13.161 \pm 0.003$ ,  $b = 14.444 \pm 0.004$ , and  $c = 8.389 \pm 0.003$  Å. The space group is  $P2_12_12_1$ . Intensities of reflections with  $2\theta$  values up to  $140^\circ$  were measured on a Rigaku automatic four-circle diffractometer using  $Cu K\alpha$  radiation monochromatized with a LiF crystal, and were corrected for the usual Lorentz and polarization factors. Out of the structure factors thus obtained, 1511 above  $2\sigma(F)$  were selected for the structural study. The structure was solved by the heavy-atom method on the basis of the bromine position derived from a sharpened Patterson function (5). After several cycles of the least-squares method were carried out using the atomic scattering factors of carbon for all the light atoms, the assignment of oxygen atoms was made by taking account of the isotropic temperature factors as well as the interatomic distances. The structure thus obtained was refined by the block-diagonal-matrix least-squares method, anisotropic thermal motions being assumed for all the atoms. At the stage of the R factor of 9.6%, the absolute configuration was determined by using the anomalous dispersion effect of the bromine atom for  $Cu K\alpha$  radiation. The observed and calculated Bijvoet inequalities for twenty pairs of reflections having the largest  $\left| |F_c(hkl)| - |F_c(\bar{h}\bar{k}l)| \right| / \sigma(F_o)$  values were in good agreement with each other, thus establishing the full structure of laurefucin including the absolute configuration as shown in Fig. 1. Further least-squares refinement including the anomalous dispersion effect of the bromine atom reduced the R factor to 9.4%. The final atomic parameters are listed in Table 1.

Table 1. The atomic parameters and their estimated standard deviations (  $\times 10^4$  )

The anisotropic thermal parameters are expressed as  
 $\exp( - B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{23}kl - B_{31}lh )$ .

	x/a	y/b	z/c	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>23</sub>	B <sub>31</sub>
Br	2322(2)	2349(1)	8880(1)	225(2)	114(1)	215(2)	-19(2)	-109(2)	118(3)
O1	1224(3)	4637(4)	2837(7)	53(2)	83(3)	215(8)	-20(4)	-71(8)	18(7)
O2	416(4)	3650(4)	5703(7)	69(3)	82(3)	192(8)	-24(5)	36(8)	-54(8)
O3	3322(3)	4742(4)	4660(7)	56(2)	79(3)	237(9)	-28(5)	-8(9)	-12(8)
C1	-4157(8)	4588(10)	4316(23)	85(6)	115(8)	490(39)	-6(11)	178(30)	-120(24)
C2	-3251(8)	4728(10)	4372(23)	79(5)	116(7)	478(36)	20(11)	158(29)	-81(22)
C3	-2211(9)	4943(14)	4480(34)	88(7)	160(13)	790(74)	-57(17)	432(56)	-174(37)
C4	-1520(7)	4796(12)	3920(40)	58(4)	125(9)	890(84)	22(10)	87(53)	-34(29)
C5	-411(6)	5059(7)	3832(18)	66(4)	92(5)	393(25)	16(8)	-1(21)	31(18)
C6	187(5)	4309(7)	3140(12)	52(3)	89(5)	260(14)	-15(6)	-55(15)	41(11)
C7	333(5)	3412(6)	4073(9)	66(4)	80(4)	185(10)	-34(6)	40(11)	-5(10)
C8	1347(5)	3045(5)	3382(8)	57(3)	73(3)	176(9)	-18(6)	39(9)	-5(9)
C9	1961(5)	3959(5)	3391(8)	58(3)	74(3)	155(8)	5(6)	-21(9)	-7(9)
C10	2402(4)	4248(4)	5024(8)	56(3)	58(3)	184(8)	-20(5)	-17(8)	-6(9)
C11	2630(6)	3471(5)	6193(9)	83(4)	74(3)	176(9)	-3(7)	-7(10)	38(12)
C12	1790(7)	3280(5)	7410(9)	109(5)	66(3)	158(9)	-30(8)	-1(9)	-14(12)
C13	786(7)	2960(7)	6802(9)	106(6)	91(5)	165(10)	-51(9)	16(12)	-52(13)
C14	-30(14)	2876(13)	8125(15)	183(14)	147(11)	226(16)	-148(22)	16(23)	-137(25)
C15	-1054(16)	2598(22)	7425(25)	166(15)	259(26)	409(38)	-250(37)	257(57)	-232(42)

The bond distances calculated with the final atomic coordinates are given in Fig. 1. Considering the estimated standard deviations, these values are reasonable except for the C3-C4 bond. Seeing that the thermal parameters of the C1, C2, C3, and C4 atoms are very large, the unusual shortening of the double bond may be due to either the special and vigorous thermal vibrations of these atoms or some disordering associated with the conformation of the long side chain. The oxa-

cyclooctane ring takes a somewhat distorted boat-chair form, while the tetrahydrofuran ring has an envelope form, with the C8 atom remarkably displaced from the mean plane of the other four atoms. As a result of such conformations of the rings, the O2 and C10 atoms are forced to approach each other at a distance of  $2.81 \pm 0.01 \text{ \AA}$ . The free hydroxyl group, O3-H, forms a hydrogen bond with the O1 atom of another molecule, the  $O \cdots O$  distance being  $2.88 + 0.01 \text{ \AA}$ .

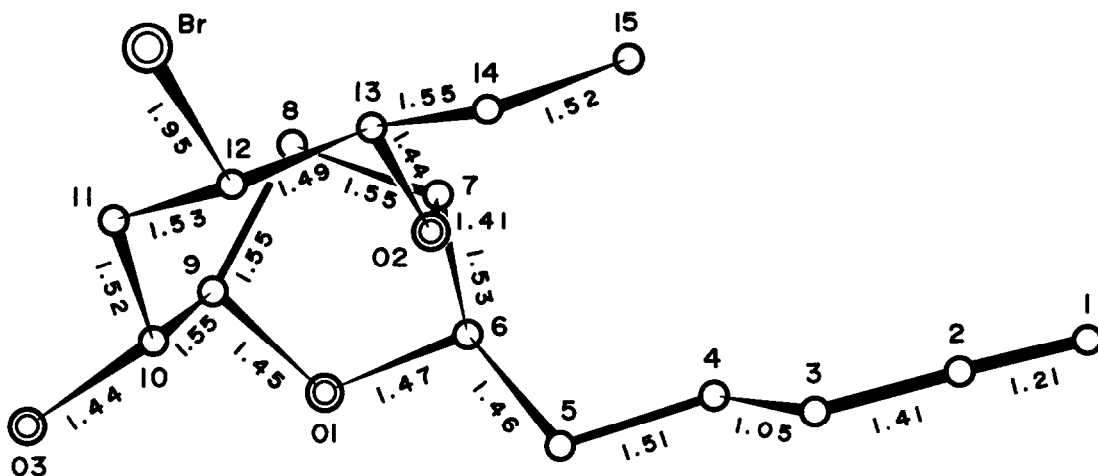


Fig. 1. The molecular conformation and the bond distances ( $\text{\AA}$ ). The estimated standard deviations are about  $0.02 \text{ \AA}$  for the C1-C2 and C2-C3 bonds,  $0.03 \text{ \AA}$  for the C3-C4 and C14-C15 bonds and  $0.01 \text{ \AA}$  for the other bonds.

#### References

- \* Part XXIII of "Constituents of marine plants". Part XXII; E. Kurosawa, A. Fukuzawa and T. Irie, Tetrahedron Letters, in press.
- \*\* The discussions for the structure of a rearrangement product and mechanism will be particularly reported in near future.
- (1) A. Fukuzawa, E. Kurosawa and T. Irie, Tetrahedron Letters, 3 (1972).
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- (3) T. Irie, M. Izawa and E. Kurosawa, Tetrahedron Letters, 2735 (1968); Tetrahedron, 26, 851 (1970); See also part XXI of this series, in press.
- (4) E. Kurosawa, A. Fukuzawa and T. Irie; See also part XXII of this series.
- (5) All calculations were performed on FACOM 230-60 computer at the Computer Center of Hokkaido University using our programs.