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CRYSTAL AND MOLECULAR STRUCTURES OF (−)-ASARININ – A LIGNAN ISOLATED FROM *Asarum sieboldii*

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The lignan (−)-asarin (1), first isolated in 1935 [1], has not hitherto been investigated by the method of x-ray structural analysis. In the present communication we give information on the spatial structure of the (1) molecule and the coordinates of the atoms in the crystal (Table 1) obtained by the x-ray structural analysis of a single crystal of this compound.

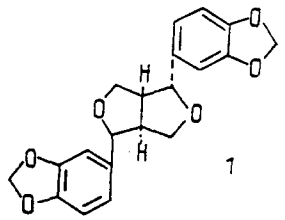

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TABLE 1. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$)

Atom	x/a	y/b	z/c	U_{eq}
C1	7715(10)	−594(19)	−770(6)	40(2)
C2	7246(10)	−2305(18)	−1427(6)	39(2)
C3	7438(11)	−1853(18)	−2236(6)	42(2)
C4	8048(10)	245(19)	−2446(6)	44(2)
C5	8533(11)	1894(19)	−1824(6)	50(2)
C6	8354(11)	1505(18)	−980(7)	52(2)
C7	7603(10)	−1070(18)	141(6)	41(2)
C8	7407(10)	1145(17)	709(6)	41(2)
C9	8789(10)	1914(19)	1335(6)	47(2)
C10	7661(14)	−2170(21)	−3632(8)	81(2)
O3	7055(8)	−3265(16)	−2982(5)	68(2)
O4	8070(8)	202(15)	−3329(4)	61(2)
O7	6393(7)	−2518(14)	143(4)	52(2)
O9	8857(7)	611(14)	2126(4)	44(1)
C1′	7253(10)	−1274(19)	2909(6)	44(2)
C2′	8372(10)	−2878(19)	3254(6)	43(2)
C3′	8111(11)	−4459(20)	3864(6)	48(2)
C4′	6847(11)	−4507(20)	4145(6)	52(2)
C5′	5755(11)	−2951(21)	3824(7)	69(2)
C6′	5999(11)	−1371(20)	3199(7)	59(2)
C7′	7418(10)	531(19)	2231(6)	45(2)
C8′	6463(10)	162(19)	1302(6)	44(2)
C9′	6158(12)	−2395(19)	1009(6)	57(2)
C10′	5307(12)	−7344(20)	4868(7)	69(2)
O3′	9046(8)	−6227(17)	4291(5)	70(2)
O4′	6927(9)	−6287(16)	4767(5)	72(2)

* $U_{eq} = 1/3(U_{11}+U_{22}+U_{33})$

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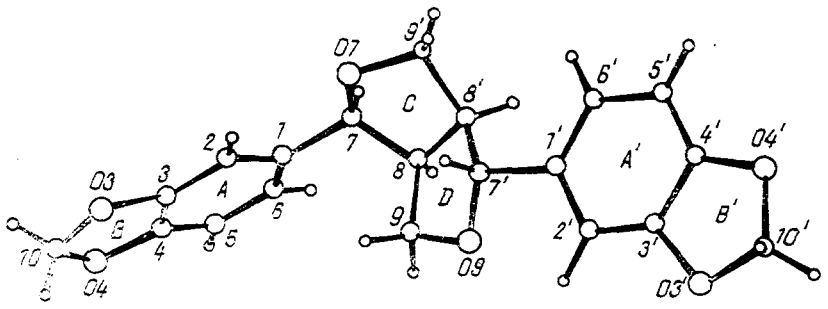

Fig. 1. Spatial structure of the (1) molecule and numbering of the atoms.

Figure 1 illustrates the spatial structure of the lignan (1). Rings A, A′, B′ are plain. Ring B has the conformation of a flattened 10β-envelope. Rings C and D are cis-linked. Different spatial orientations of the aromatic rings relative to rings C and D are shown by the values of the torsional angles C2−C1−C7−O7 and C2′−C1′−C7′−O9: −31.9° and 9.8°, respectively

In the two symmetrical parts of the molecule, the corresponding values of the bond lengths agree to within 3σ. So far as concerns the valence angles, the asymmetry of the molecule is shown in the values of only some of them. The greatest difference is observed in the values of the valence angles C7−C8−C9 and C7′−C8′−C9′ −4.1°. The maximum deviations of the values of the valence angles from the tetrahedral value are observed at the C8′, C7 and C7′ atoms (about 7°).

(−)-Asarin was isolated from an ethanolic extract of the bark of *Asarum sieboldii* Mig. by preparative chromatography on a column (20 × 200 mm) of silica gel L 40/100 in the C_6H_6—$CHCl_3$ (1:1) system. mp 120-122°C, R_f 0.78 (C_6H_6—CH_3CH_2OH (10:1)) on TLC in a fixed layer of KSK silica gel. The weight of the material isolated was 0.17% of the weight of the air-dry bark.

Single crystals of (1) ($C_{20}H_{18}O_6$, mol. mass 354.4) grown from solution in benzene were of the monoclinic system, sp. gr. $P2_1$, Z = 2. The parameters of the unit cell were measured and refined on an automatic Hilger−Watts four-circle diffractometer, and their values were: a = 9.613(1), b = 5.625(2), c = 15.664(3) Å, β = 103.65(2)°, V = 823.2(3) Å^3, d_{calc} = 1.44 g/cm^3, $\mu_{MoK\alpha}$ - 0.10 mm^{-1}. The integral intensities of 1140 reflections with $\sin\theta/\lambda \leq 0.63$ Å^{-1} were measured on a Hilger−Watts automatic x-ray diffractometer (MoK_α radiation, graphite monochromator, $\theta/2\theta$ method of scanning). The structure was determined by the direct method with refinement by the method of least squares in the full-matrix anisotropic approximation to R = 0.062. In refinement we used 882 reflections with $|E_0| \geq 2\sigma(|F_0|)$. The coordinates of the hydrogen atoms were given geometrically. The values of the equivalent thermal parameters of the nonhydrogen atoms are given in Table 1. All the calculations were made by the SHELX-76 and SHELX086 programs [2, 3]. The x-ray diffraction results were obtained in the Center for X-Ray Structural Investigations OOTKh, Russian Academy of Sciences.

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