

THE STRUCTURE OF ISOLACTARORUFIN

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(Received in UK 13 July 1977; accepted for publication 4 August 1977)

Isolactarorufin (syn. lactarorufin C), a metabolite of *Lactarius rufus*, is one of the sesquiterpenes isolated from the milky juice of that mushroom¹. The structure of the carbon skeleton of isolactarorufin was determined on the basis of NMR spectra of 2,3-anhydroisolactarorufin². As a result of the chemical transformation of isolactarorufin into its anhydroderivative two asymmetric centres were missing. Their relative configuration was suggested² on the analogy to the configuration of corresponding centres in the lactarorufin B derivative (III, R₃=p-Br-C₆H₄CO-)^{3,4}.

We have performed an X-ray analysis of the crystal structure of isolactarorufin p-bromobenzoate (IV). Crystals were grown from ethyl ether. Preliminary investigations were carried out on a precession camera.

Crystal data:

C₂₂H₂₅O₅Br, MW=449,

m.p. 208.5-210°C, tri-

gonal, space group P3₁

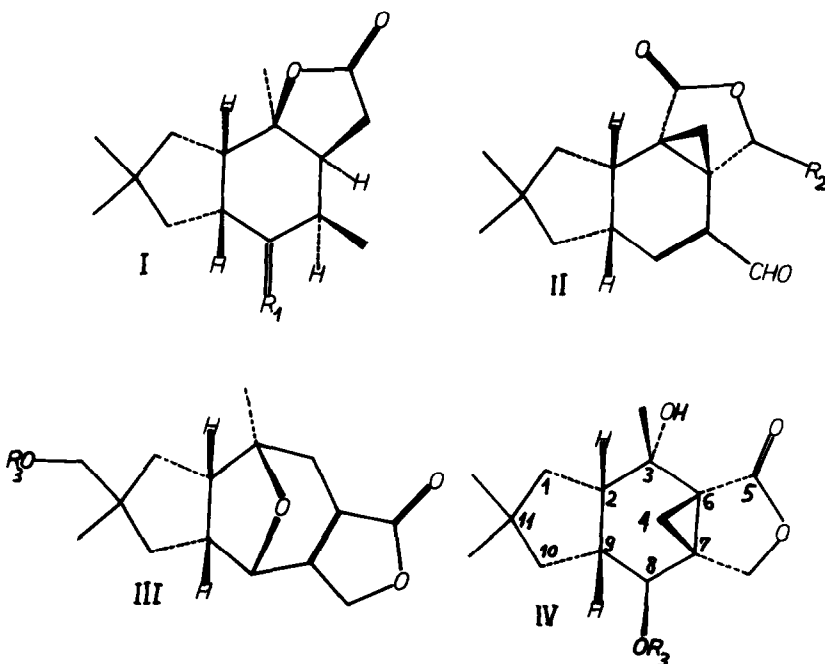
or P3₂, a=b= 15.58(2),

c= 7.73(1), V= 1534 Å³,

D_m= 1.47, D_x= 1.46 g/cm³

Z= 3, F(000)= 696.

Intensities were measured on a Syntex P2₁ diffractometer.



The structure (IV, $R_3 = p\text{-Br-C}_6\text{H}_4\text{CO-}$) was solved by the heavy-atom method. Final R-factor = 5.1% for 176 reflections. Standard deviations of the bond lengths are less than 0.02 Å, valency angles are less than 1.5°. The mean $sp^3\text{-}sp^3$ bond length is 1.546 Å; the aromatic $sp^2\text{-}sp^2$ is 1.385 Å.

The relative configuration of (IV) at C(2) and C(9) is identical with that of the corresponding centres in the terpene illudol (I, $R_1 = p\text{-Br-C}_6\text{H}_4\text{NHN=}$) and marasmic acid (II, $R_2 = \text{Cl-}$) derivatives⁵. On the basis of the known absolute configuration of C(2) and C(9) in (I) and (II) and the common biogenesis of illudoids, we propose the absolute configuration for (IV). The configuration of (IV) at C(3) is reverse to that suggested earlier².

The intermolecular hydrogen bond between lactone carbonyl oxygen at C(5) and hydroxyl oxygen at C(3) in crystal of (IV) forms a helicoidal system around $P3_1$ axis.

ACKNOWLEDGMENTS

The authors thank Prof. M.Kocór and Dr. W.Daniewski from the Institute of Organic Chemistry of the Pol.Acad.Sci. for preparing isolactarorufin p-bromobezoate and Dr. T. Głowiak from the University of Wrocław for measuring the diffraction data. We also express appreciation to the Institute of Organic Chemistry of the Pol.Acad.Sci. in Warsaw for a grant in support of this work.

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