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THE STRUCTURE OF LACTARORUFIN B -3,8-ETHER 14-p-BROMOBENZOATE

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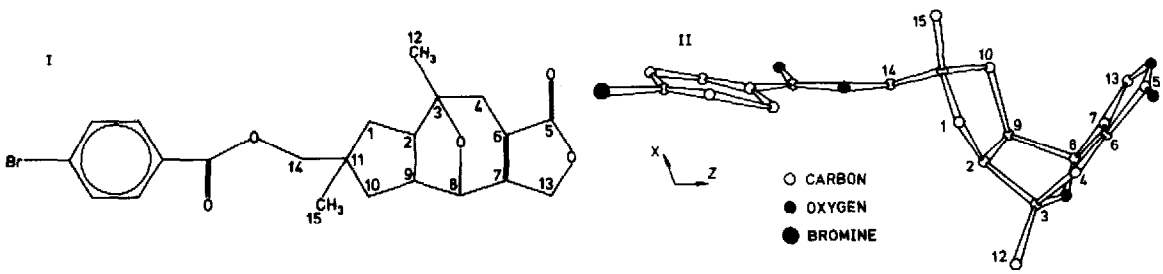
Lactarorufin B, a metabolite of the mushroom Lactarius rufus, is a novel sesquiterpene. Its structure and relative configuration have been established on the basis of chemical and spectroscopic evidence.[1] In our present studies the structure of the title compound has been verified by X-ray crystal structure analysis of (I). The results indicate that the lactone carbonyl oxygen occurs at C(5) and not at C(13) as postulated earlier.[1] Our findings may also imply that the same change of the position of the lactone carbonyl should be introduced in the closely related lactarorufin A,[2] because the chemical evidence on the structure of lactarorufin B was largely based on the correlation of its transformation products with the compounds obtained from lactarorufin A whose structure was elucidated earlier.

Suitable crystals of (I) were grown from isobutanol-ethanol in a hexane atmosphere in the form of colourless prisms elongated along b. Preliminary crystallographic investigations were performed on Weissenberg and precession cameras.

Crystal data: $C_{22}H_{23}O_5Br$, MW=447, m.p. 162-165°C, Monoclinic, space group C2, a=16.55(2), b=6.75(1), c=20.07(2)Å, β=111.73(5)°, V=2081 Å^3, D_m=1.41, D_x=1.42 g.cm^{-3}, Z=4, F(000)=1080.

A crystal, 0.3x2.2x0.2 mm^3 was mounted with b parallel to the axis of the goniostat. Intensities were collected on a Hilger-Watts four-circle automatic

diffractometer with graphite-monochromatized CuK_α radiation. Of the 1728 reflexions measured by the θ-2θ scan, 1584 had measurable intensities. The intensities were corrected for Lorentz and polarisation factor, but not for absorption. NRC crystallographic programmes adapted for an ICL 4/70 were used. The structure was solved by the heavy-atom method. Three cycles of least-squares (block-diagonal isotropic) gave an R of 22.3%. Three more cycles were applied but R did not decrease. Finally it became apparent that the lactone O atom was attached to C(5) not C(13). Full-matrix refinement with the thermal motion of the non-hydrogen atoms described by anisotropic ellipsoids then reduced R to 9.2%. The H atoms were found from difference map, on which no other atoms were visible. The final R value obtained is 7.9% for 1538 reflexions. The structure is shown in (II). The H atoms are not included. Full details of this work will be published elsewhere.



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