Phytochemistry, Vol. 23, No. 3, p. 702, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

CRYSTAL STRUCTURE OF (−)-PLACODIOLIC ACID, A DIBENZOFURAN DERIVATIVE FROM THE LICHEN *RHIZOPLACA CHRYSOLEUCA*

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(*Received* 14 *June* 1983)

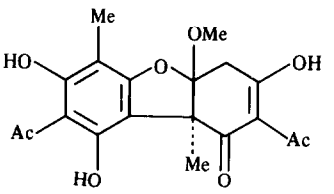
Key Word Index—*Rhizoplaca chrysoleuca*; lichen; X-ray; dibenzofuran; (−)-placodiolic acid.

Abstract—The stereochemistry of placodiolic acid has been established by crystal structure analysis. The ring junction is *trans*.

Certain chemical races of the lichen (*Rhizoplaca chrysoleuca* (Smith) Zopf [syn. *Lecanora rubina* (Vill.) Ach.] contain two further dibenzofuran derivatives, (−)-placodiolic acid and (−)-pseudoplacodiolic acid, in addition to (−)-usnic acid. (−)-Pseudoplacodiolic acid has been shown [1] to be the isomethoxide of (−)-usnic acid with a *trans* ring junction. The structure of (−)-placodiolic acid was assigned by Huneck [2] as (−)-isousnic acid isomethoxide (**1**) but definitive proof for the stereochemistry of the ring junction was lacking.

An X-ray crystal structure analysis of (−)-placodiolic acid has been carried out and establishes its stereochemistry as in **1** with a *trans*-ring junction. The absolute configuration of **1** has already been determined [1]. An ORTEP diagram of the enantiomeric form of **1** is shown in Fig. 1.

This paper resolves the long standing uncertainty concerning the relative stereochemistry of (−)-placodiolic acid (**1**) and completes the stereochemical studies on usnic acid and isousnic acid and their respective isomethoxides,



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placodiolic acid (**1**) and pseudoplacodiolic acid. The formation of these isomethoxides presumably involves hydration of the enol ether system of the parent compounds followed by *O*-methylation. The thermodynamically more stable *trans*-form is produced exclusively since it lacks the steric interaction between the C-4a tertiary methyl group and the C-1a oxygen function which would destabilize the *cis*-form.

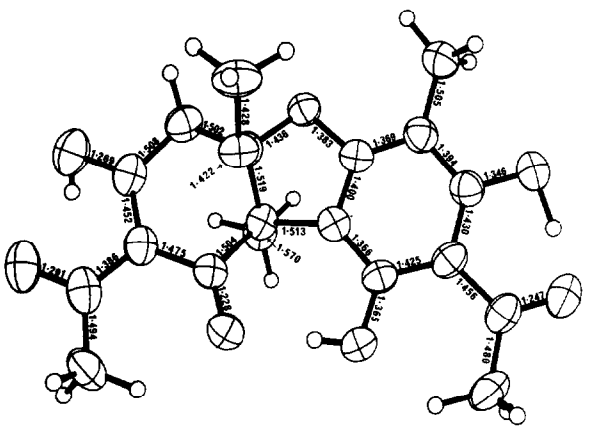

Fig. 1. ORTEP diagram of placodiolic acid.

EXPERIMENTAL

Crystal data. $C_{19}H_{20}O_8$, $M = 376.4$, monoclinic, $P2_1$ with two molecules per asymmetric unit, $a = 9.500$, $b = 10.156$, $c = 18.657$ Å, $\beta = 92.14°$, $U = 1798.8$ Å^3, F (000) = 2472, $D_c = 1.38$ g/ml, $Z = 4$. 2787 independent reflections ($I > 2.5\,\sigma_I$) were collected on an Enraf-Nonius CAD-4 automatic diffractometer. The structure was elucidated by direct *phasing* techniques (MULTAN) and refined by least squares calculations to a final R of 0.05. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW.

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