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THE ABSOLUTE CONFIGURATIONS OF (+)-USNIC AND (+)-ISOUSNIC ACID. X-RAY ANALYSES OF THE (-)-α-PHENYLETHYLAMINE DERIVATIVE OF (+)-USNIC ACID AND OF (-)-PSEUDOPLACODIOLIC ACID, A NEW DIBENZOFURAN, FROM THE LICHEN RHIZOPLACA CHRYSOLEUCA.

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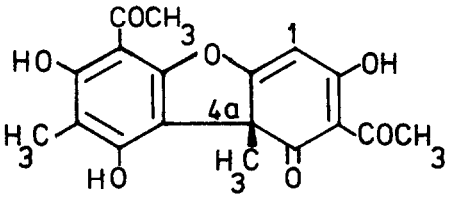
Summary. The absolute configuration of (+)-usnic acid has been shown to be (4aR) as in (1) by X-ray analysis of the (-)-α-phenylethylamine derivative (2). The structure and absolute stereochemistry of (-)-pseudoplacodiolic acid (4) have been established.

Despite the fact that usnic acid, a common constituent of lichens, has been known for many years in both its enantiomeric forms,[1] its absolute configuration has remained undetermined. We decided to approach this problem by X-ray analysis, using the direct method, of a derivative of usnic acid containing a second chiral centre of known configuration. Reaction of (+)-usnic acid with (-)-α-phenylethylamine afforded the imine (2) m.p. 162-163° $[\alpha]_D$ +391° (EtOAc), whose structure was shown to be (2) by X-ray analysis. Since the absolute configuration of (-)-α-phenylethylamine is known to be (S)[2] the absolute configuration at C-4a in (+)-usnic acid is (R).

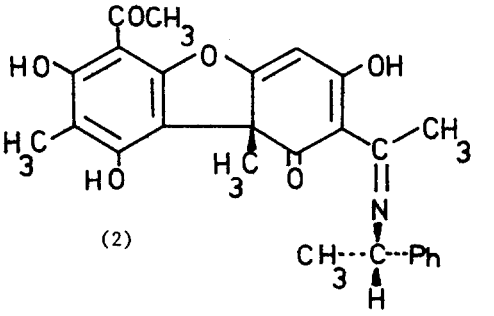
Certain chemical races of the lichen Rhizoplaca chrysoleuca (Smith) Zopf contain, in addition to (-)-usnic acid and (-)-placodiolic acid (3),[3] a third dibenzofuran derivative (-)-pseudoplacodiolic acid (4), m.p. 187-188°, $[\alpha]_D$ -209° ($CHCl_3$). The u.v. and mass spectra of (4) are very similar to those of (-)-placodiolic acid. The molecular formula $C_{19}H_{20}O_8$ corresponds to the addition of methanol to either usnic acid or isousnic acid and the expected features are readily identified in the 270 MHz ^1H n.m.r. spectrum which shows four C-methyl singlets (δ 1.45, 2.09, 2.64, 2.68), a methoxyl group (δ 3.25), a methylene group (δ 3.50 and 3.30, ABq, J 18.5 Hz, 2H-1), and three phenolic hydroxyl groups (δ 10.23, 13.25, and 18.12, exchangeable with D_2O). Reaction of (4) with hydrochloric acid in methanol afforded (-)-usnic acid. This result indicated that pseudoplacodiolic acid is an isomethoxide of usnic acid. The stereochemistry of the ring junction was established as trans by X-ray analysis. The absolute configuration at C-4a of both (-)-placodiolic acid (3)[3] and (-)-pseudoplacodiolic acid (4) follow from correlation with (-)-usnic acid.

(+)-Usnic acid and (+)-isousnic acid (5)[4] have been related via (-)-dihydrousnic acid, prepared either by hydrogenation of (+)-usnic acid or by thermal isomerisation of (+)-iso-dihydrousnic acid, the hydrogenation product of (+)-isousnic acid.[4] Hence (+)-isousnic acid has the absolute configuration shown in (5).

X-ray diffraction data for (2) and (4) were collected using computer-controlled four-circle diffractometers. Both structures were resolved by direct methods and have been refined by least-squares calculations which for (2) converged when R was 9.8% and for (4) converged when R was 4.9%.



(1)



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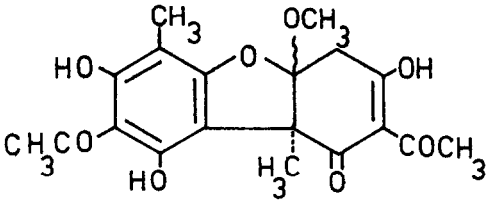

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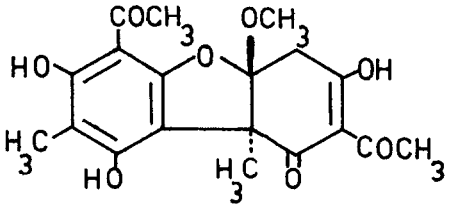
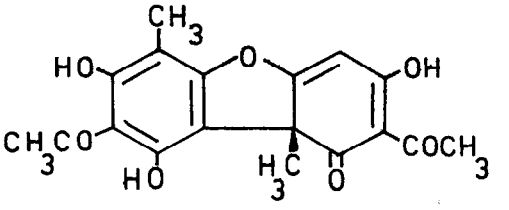


(4)



(5)

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