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SHORT COMMUNICATION

LOXODIN, A DEPSIDONE OF LICHENS OF *PARMELIA* SPECIES

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Abstract—Loxodin isolated from *Parmelia flavescentireagens* Gyel. and some other lichens of *Parmelia* spp. was shown to be methyl norlobarate (I).

In a taxonomic and microchemical survey on lichens of *Parmelia* species, Kurokawa[1] found a new compound tentatively named "neoloxodic acid" occurring along with norlobaridone (III)[2] in fourteen species of that genus.

From *Parmelia flavescentireagens* Gyel.* "neoloxodic acid", m.p. 132–133·5°, was isolated in a crystalline form. Mass spectral analysis showed it to be a depsidone having a molecular formula, $C_{25}H_{28}O_8$, M^+ 456 (100%).

The mass spectral peak at *m/e* 424 (54%) indicated the presence of COOMe and OH at a vicinal disposition. The NMR spectrum of "neoloxodic acid" (in $CDCl_3$) indicated the presence of two aliphatic end methyls (δ 0.93, 6H (t, $J=3$ c/s)), five methylenes in the side-chains (δ 1·46, 10H (m)), one end methylene attached to a benzene ring (δ 3·10, 2H (t, $J=7$ c/s), one end methylene attached to a carbonyl group (Δ 2·74, 2H (t, $J=7$ c/s)), three aromatic protons (δ 6·61, 6·70, 1H each (d, $J=2{\cdot}5$ c/s) and δ 6·76, 1H (s)) and one methoxyl group (δ 3·96, 3H (s)).

Thus "neoloxodic acid" was regarded to be a methyl ester of an orcinol-type depsidone having an acyl and an alkyl side-chain, which would be assumed biogenetically to be n-C_4H_9CO and n-C_5H_{11}, respectively, as shown in norlobaridone (III).

Finally the methylated product, m.p. 102° (from methanol), prepared from "neoloxodic acid" with diazomethane, was identified as methyl lobarate methyl ether (II) by a mixed fusion and comparison of i.r. spectra with the authentic sample. Thus it is concluded that "neoloxodic acid" is methyl norlobarate (I). The name of "neoloxodic acid" is unsuitable, since the compound is not a free carboxylic acid, and we suggest the compound should be called loxodin.

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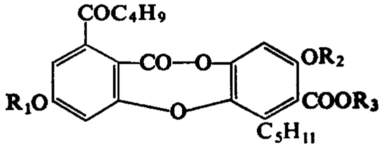
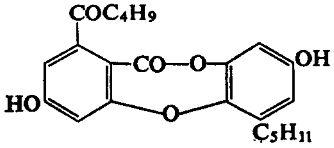
* Collected at Charlottes pass, Mt. Kosciusko, N.S.W., Australia, by S. Kurokawa (No. 6481); the specimen is kept in TNS and the duplicates in MEL and UPS.

[1] S. Kurokawa, *J. Hattori Bot. Lab.* 32, 205 (1969).

[2] G. P. Briner, G. E. Grean and N. V. Riggs, *Australian J. Chem.* 13, 277 (1960); G. E. Grean and N. V. Riggs, *Australian J. Chem.* 13, 285 (1960).



(I) $R_1 = R_2 = H$ $R_3 = CH_3$
(II) $R_1 = R_2 = R_3 = CH_3$



(III)

According to Kurokawa's survey experiments,[1] loxodin ("neoloxodic acid") occurs in the following lichens of *Parmelia* always accompanied by norlobaridone (III): *P. abessinica* Krempelh., *P. australiensis* Cromb., *P. dichotoma* Müll. Arg., *P. flavescentrireagens* Gyel., *P. furcata* Müll. Arg., *P. hababiana* Gyel., *P. metamorphosa* Gyel., *P. paulensis* Zahlbr., *P. recipienda* Nyl., *P. scabrosa* Tayl., *P. subdistorta* Kurok., *P. subtinctoria* Zahlbr., *P. thamnoides* Kurok., and *P. tortula Kurok.*

EXPERIMENTAL

Isolation of Loxodin

The thalli of *Parmelia flavescentireagens* Gyel. (22 g) were extracted with ether, and the extracts were evaporated to dryness to obtain a yellowish solid (1·6 g), which was extracted with benzene to isolate yellow crystals of usnic acid (0·14 g) on concentration. The mother liquor separated from usnic acid was chromatographed repeatedly on a silica gel column (impregnated with 0·5N oxalic acid) eluting with benzene and benzene–acetone successively to obtain loxodin in a colourless crystalline form, m.p. 132–133·5° (from $CHCl_3$) (yield: 29 mg). U.v. absorption: $^{\mathrm{EtOH}}_{\mathrm{max}}$ 289 (3·98), 320 (3·93) nm (log ϵ); i.r. absorption: $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1} 1713, 1672, 1608, 1578, 1437; mass spectrum: *m/e* 456 (100%), 428 (32%), 424 (54%), 398 (22%), 396 (18%), 367 (19%), 341 (53%), 221 (27%).

Methylation of Loxodin with Diazomethane

An excess of CH_2N_2 in ether was added to the ethereal solution of loxodin (20 mg), and the mixture was allowed to stand for 3 days. An oily residue obtained on evaporation was chromatographed on a silica gel column (impregnated with 0·5 N oxalic acid) eluting with benzene to yield colourless needles (from MeOH), m.p. 102° (16 mg). The methylated product was proved to be identical with methyl lobarate methyl ether (II) by a mixed fusion and an i.r. and mass spectral comparison with an authentic sample.

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