Structure of Gangaleoidin

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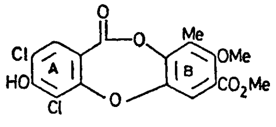
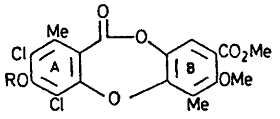
Summary The structure of the lichen depsidone gangaleoidin is revised to 3,5-dichloro-4-hydroxy-1′-methoxycarbonyl-2′-methoxy-6,6′-dimethyldepsidone (**2**).

The structure (**1**), of the lichen depsidone gangaleoidin, proposed by Nolan[1] is highly unusual since ring B appears to be derived biogenetically from β-orcinol carboxylic acid by loss of a methyl group.[2] Hendrickson[3] has suggested that structure (**2**), in which ring B is similar to that of notatic acid,[4] would be biogenetically more normal. He was, however, unable to vindicate his proposal.[3]

We have, therefore, resolved the question by the syn-

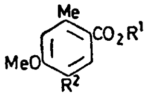


(1)



(2) R = H

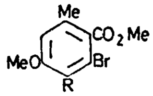
(3) R = Me



(4) $R^1 = R^2 = H$

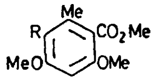
(5) $R^1 = Me, R^2 = NO_2$

(6) $R^1 = Me, R^2 = NH_2$



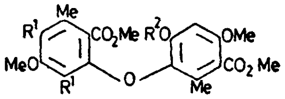
(7) R = NH_2

(8) R = H



(9) R = CHO

(10) R = OH



(11) $R^1 = H, R^2 = Me$

(12) $R^1 = Cl, R^2 = H$

(13) $R^1 = Cl, R^2 = Me$

thesis of the diaryl ether (**11**). Nitration of the acid (**4**)[5] followed by esterification of the acidic products gave a mixture from which the ester (**5**), m.p. 132—133°, was separated by fractional crystallisation. Reduction (SnCl$_2$–HCl) of the latter gave the amine (**6**), m.p. 82°, which on bromination gave the oily amine (**7**) (*N*-benzoyl derivative m.p. 217·5—218°). Treatment of the diazonium salt of (**7**) with hypophosphorous acid gave the bromo-ester (**8**), m.p. 31°. Baeyer–Villiger oxidation[6] of the aldehyde (**9**)[7] followed by base hydrolysis of the resultant formate gave the phenol (**10**), m.p. 112—113°. Ullmann reaction of (**8**) and (**10**) then gave (**11**) (*ca.* 70%), m.p. 127—128°.

Diazomethane treatment of gangaleoidin gave the methyl ether (**3**), m.p. 180—181°, which was methanolysed to the phenolic ester (**12**). Methylation (CH$_2$N$_2$) of (**12**) then gave the ether (**13**), which on hydrogenolysis over palladised charcoal in MeOH–Et$_3$N at 3 atm. gave the diaryl ether (**11**) identical with the synthetic product. Gangaleoidin therefore has structure (**2**).

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