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CONSTITUTION OF VICANICIN FROM THE LICHEN TELOSCHISTES FLAVICANS

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TELOSCHISTES FLAVICANS has been found to contain besides anthraquinone pigments, a colourless substance. The former have been found to vary in composition,[1-3] but the colourless substance seems to have been the same in all the samples of the lichen and by employing column chromatography (magnesium carbonate) nearly 1% yield on the dry weight of the lichen could be secured. It has now been given the name "vicanicin" based on the species name of the lichen, omitting the first syllable in view of the compound being colourless.

Vicanicin crystallized from benzene as colourless stout needles, m.p. 248-250°. It had the molecular formula $C_{17}H_{14}O_5Cl_2$** with one methoxyl

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** Satisfactory analyses were obtained for all the compounds described here.

[1] W. Zopf, Ann. 340, 300 (1905).

[2] T. R. Seshadri and S. S. Subramanian, Proc. Indian Acad. Sci. 30A, 67 (1949).

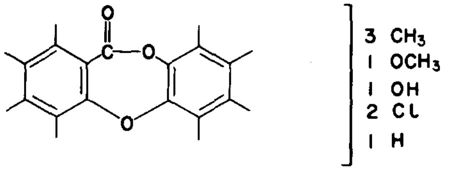
[3] T. R. Rajagopalan and T. R. Seshadri, Proc. Indian Acad. Sci. 49A, 1 (1959).

and three C-methyl groups. The crystalline solid did not readily dissolve in aqueous sodium hydroxide but a fine suspension of it, obtained by the dilution of an ethanolic solution with water, dissolved easily in the alkali and the solution turned pink on long standing. It did not give any prominent colour with either alcoholic ferric chloride or concentrated sulphuric acid.

The presence of a free hydroxyl group was shown by the ready formation of a monoacetate ($C_{19}H_{16}O_6Cl_2$), m.p. 213-214°, and of a monobenzoate ($C_{24}H_{18}O_6Cl_2$), m.p. 190-191°. This hydroxyl was phenolic in nature since it underwent easy methylation and ethylation with the appropriate alkyl iodide and potassium carbonate: monomethyl ether ($C_{18}H_{16}O_5Cl_2$), m.p. 193-194°; monoethyl ether ($C_{19}H_{18}O_5Cl_2$), m.p. 185-186°.

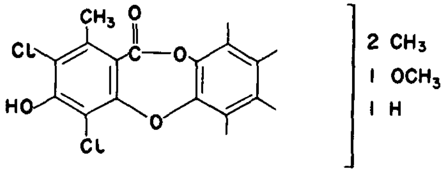
Vicanicin gave evidence for the presence of a lactone ring. By the action of aqueous 2 N-sodium hydroxide in dioxane solution, O-methylvicanicin formed a hydroxy acid (O-methylvicanicic acid, $C_{18}H_{18}O_6Cl_2$), m.p. 217-218°. On the other hand when refluxed with absolute methanolic sodium methoxide, a methyl ester (methyl O-methylvicanicate, $C_{19}H_{20}O_6Cl_2$), m.p. 155-156°, was formed. When this was further methylated, it gave rise to a neutral product ($C_{20}H_{22}O_6Cl_2$), m.p. 97-98, agreeing with the requirements of an ether-ester derived from the lactone.

Of the five oxygen atoms, four had been accounted for as one in the methoxyl, one in the hydroxyl and two in the lactone. The fifth oxygen was inert and could be placed in a diphenyl ether linkage. All these considerations suggested the possibility of vicanicin being a chlorodepsidone of the partial formula (I).



I

This was supported by spectral studies. In ultra-violet light, vicanicin had maximum absorption at 270 mμ and an inflexion at 324 mμ. For comparison, the ultra-violet spectrum of diploicin was taken and it had the maximum absorption at 270 mμ and an inflexion at 321 mμ. Robertson and co-workers[4] reported that nidulin had a maximum absorption at 267 mμ and an inflexion at 323 mμ and for nornidulin, the corresponding values were 266 mμ and 323 mμ. The infra-red spectra of vicanicin and diploicin were very similar. These data led to the development of the formula (II) indicating the common structure of the left half in all the four compounds, diploicin, nidulin, nornidulin and vicanicin.



II

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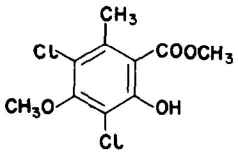
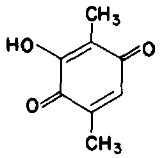
[4] F. M. Dean, J. C. Roberts and A. Robertson, J. Chem. Soc. 1432 (1954).

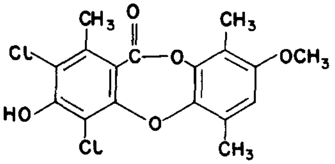
Two methods had been used in the past for splitting molecules of this type: (i) perchlorination of the methyl ester of the corresponding hydroxy acid followed by reduction and methanolysis;[5] (ii) oxidation of the ester with concentrated nitric acid and glacial acetic acid.[4] Using the second method and methyl O-methylvicanicate, methyl 3:5-dichloroeverninate (III), m.p. 78°, could be obtained as one product; this confirmed structure (II). In this oxidation, a small quantity of an orange-red quinone could be isolated from the sodium bicarbonate-soluble fraction. It gave a characteristic purple colour in alkaline solution (λ_{max} 532 mμ in buffer solution, pH 10.4) and was almost certainly 2-hydroxy-3:6-dimethyl-p-benzoquinone (IV) which was reported to have λ_{max} 530 mμ (in buffer solution, pH 10.4). On the basis of this result, the structure of vicanicin could be completed as in (V) which would also be in comformity with its possible formation from an orsellinic unit and a C-methylorsellinic unit.



III



IV



V

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[5] T. J. Nolan, J. Algar, E. P. McCann, W. A. Manahan and N. Nolan, Sci. Proc. R. Dublin Soc. **24**, 319 (1948).

[6] L. F. Fieser and M. I. Ardao, J. Amer. Chem. Soc. **78**, 776 (1956).