CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part III. The Isolation of Montagnetol, A New Phenolic Compound from *Roccella montagnei*

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IN a previous communication[1] it was stated that the lichen *Roccella montagnei* differs markedly in chemical composition, depending upon the season. Erythrin, erythritol, lecanoric acid, roccellic acid and orcinol were found to be the main components along with isolichenin. It was further recorded that orcinol which was obtained from the ether and acetone extracts was contaminated with a tenacious impurity which rendered purification extremely difficult and wasteful. This was obviously due to the close similarity that existed between the contaminating impurity and orcinol, particularly in regard to their solubility in ordinary solvents. However, as the result of repeated attempts using a combination of solvents, it has now become possible to separate the crude orcinol mixture into two components, (1) orcinol and (2) montagnetol, a new crystalline compound. The details of the procedure are described in the experimental part.

The name 'Montagnetol' has been given to the new compound with a view to indicate its occurrence in *Roccella montagnei* and its nature as a phenol. It resembles orcinol in regard to its ready solubility in water, alcohol and acetone, and in its colour reaction with ferric chloride and bleaching powder, but it differs from orcinol in its high melting point (154–56°) its sparing solubility in ether, benzene and chloroform, and in not giving the homofluorescein reaction. It seems to have the molecular formula $C_{13}H_{20}O_7$. Montagnetol has been all along accompanying orcinol in the several samples examined during the years 1938–39, the quantity present being small. In a number of samples collected during August, September and October 1940 it has been found to be the major component, the other substances being orcinol, roccellic acid and erythritol. These samples contained neither erythrin nor lecanoric acid in any detectable quantity.

Experimental

Separation of montagnetol and orcinol.—The crude orcinol mixture was dissolved in the minimum quantity of acetone and after filtering off any undissolved impurity, the solution was diluted with an equal volume of ether. This mixture was then treated with chloroform or benzene until

turbidity was produced and allowed to stand overnight. A colourless crystalline solid (montagnetol) in the form of lens-shaped crystals separated out. Very often a semi-solid mass was obtained and it turned crystalline after further repetition of the treatment or allowing to stand for a considerable length of time. The solid was separated and the mother liquor slowly concentrated, further quantities of the substance being collected at different stages if possible. It was again recrystallised using the mixture of solvents, acetone, ether and benzene or chloroform. Final concentration of the mother liquors yielded pure orcinol melting at 57–58° and it was found to be identical with an authentic sample of the monohydrate.

The separation of the crude mixture could also be effected in the following manner though it involved some loss of material and could not be adopted with larger quantities. A small quantity of it was placed on a porous tile and a few drops of water slowly added. Orcinol dissolved readily and the solution was absorbed by the tile almost immediately leaving montagnetol almost pure and colourless. The sample thus obtained could be easily crystallised from a mixture of acetone, ether and benzene. By extracting the porous tile with hot water, orcinol could be recovered, but it was always contaminated with small amounts of montagnetol.

The new compound montagnetol is easily soluble in water, alcohol and acetone and insoluble in benzene, chloroform and solvent spirit. Even though it is extracted along with orcinol from the lichen by means of ether, the purified compound is only sparingly soluble in this solvent. An aqueous solution of the substance gave a bright violet colour with ferric chloride and an orange red colour with bleaching powder. It is neutral to litmus and does not evolve carbon dioxide with sodium bicarbonate. When treated with chloroform and alkali it does not give the greenish-yellow fluorescence characteristic of orcinol (Found : C, 53·9; H, 6·4 ; molecular wt. by Rast's method 314 ; $C_{13}H_{20}O_7$ requires C, 54·2 ; H, 6·9% and molecular weight 288).

The following is a description of a third representative extraction relating to the samples of the lichen collected during the months of August, September and October, 1940. They contained montagnetol, roccellic acid, erythritol and orcinol.

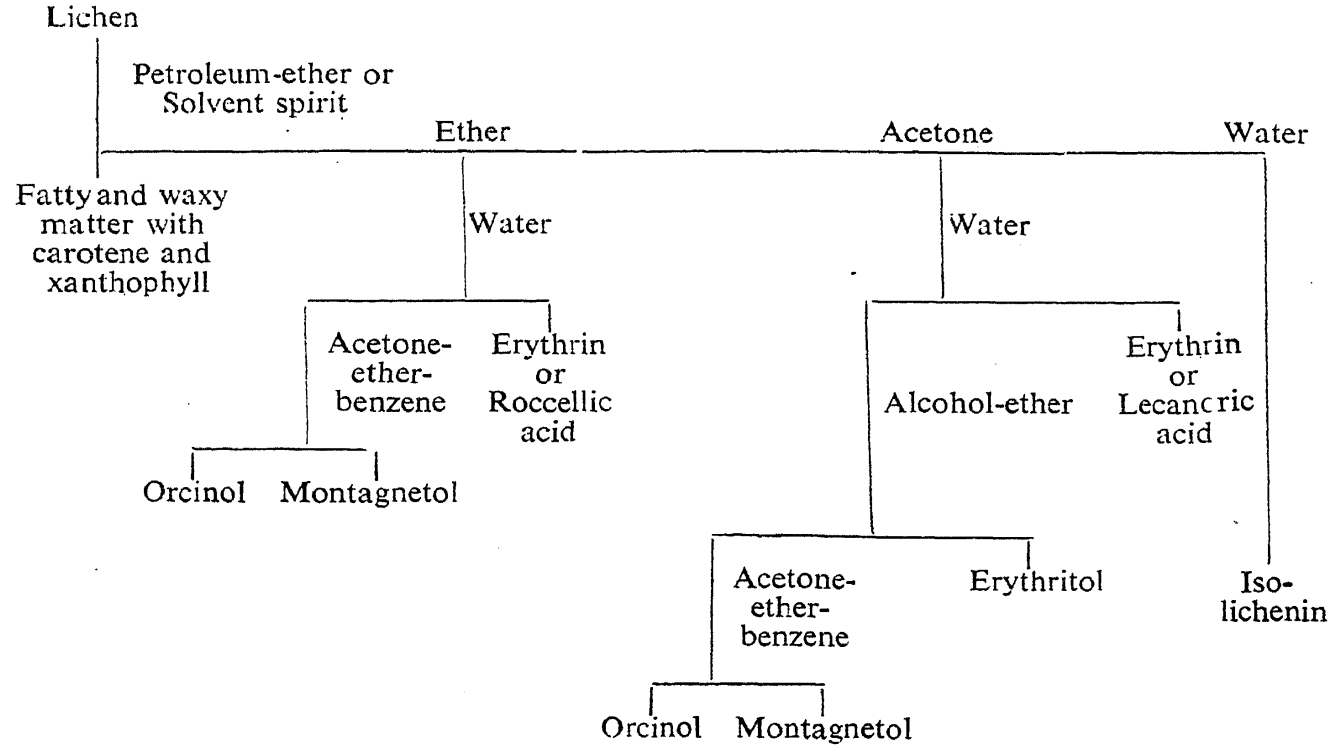
Extraction with solvent spirits for 24 hours yielded fatty and waxy matter along with some carotenoid pigments as found before. On subsequent extraction with ether for 48 hours a crystalline solid separated in the receiver the supernatant liquid being deeply coloured. The clear solution (*c*) was carefully poured out, the solid washed with small quantities of ether and the washings added to the original solution (*c*). The solid residue was then

crystallised from a mixture of acetone, ether and benzene and was found to be identical with a pure sample of montagnetol. From the coloured solution (*c*) ether was distilled off and thereby a green-coloured sticky residue was obtained. It was treated with water which dissolved a portion. From the water-insoluble residue pure roccellic acid was obtained after one recrystallisation from alcohol. On evaporating the aqueous solution a mixture of orcinol and montagnetol was left in the residue and was separated as already described.

The lichen sample was next extracted with acetone for 48 hours. On distilling off the solvent from the extract a reddish-brown solid was left and it was almost completely soluble in water yielding a red aqueous solution. The water-insoluble residue was very small. It was green in colour and did not give any crystalline product on purification. The aqueous solution was evaporated to dryness on a water-bath and the reddish-brown crystalline residue washed repeatedly with small quantities of a mixture of alcohol and ether (1 : 1). A colourless crystalline solid melting at 120–21° was thus obtained and was identified as erythritol. The alcohol-ether solution on evaporation yielded a mixture of orcinol and montagnetol.

The yields of the pure crystalline compounds obtained from this sample of the lichen were montagnetol 1·8%, erythritol 1·6%, roccellic acid 0·8% and orcinol 0·1%.

In view of the discovery of montagnetol, the following table has been drawn up in order to summarise comprehensively the processes adopted for the separation of the components of the lichen.



Summary

The isolation of a new phenolic compound, 'Montagnetol' from the lichen *Roccella montagnei* and its properties are described. The details of the extraction of a sample of the lichen which contained it as the major component are given.

LITERATURE REFERENCE

1. Subba Rao and Seshadri .. *Proc. Ind. Acad. Sci.* (A), 1940, 5, 466.