

# CHEMICAL EXAMINATION OF INDIAN LICHENS

## Part V. Occurrence of Active Montagnetol in *Roccella montagnei*

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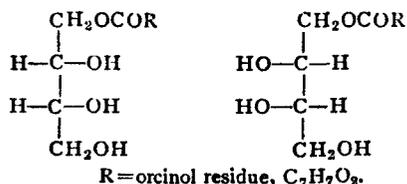
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THE isolation of montagnetol, a new phenolic component of *Roccella montagnei* and the establishment of its constitution as the erythrityl ester of orsellinic acid were described in two previous publications.<sup>1</sup> In the course of our attempts to prepare large quantities of this substance, a sample of montagnetol was obtained which melted sharp at 135–36° and the melting point could not be raised by repeated purification by the methods already described. Further, crystal form was different, being very small truncated prisms and triangular plates. Otherwise it had the same composition as montagnetol and resembled it very closely in all properties and reactions, and gave the same products of decomposition and synthesis. Thus with hot baryta or dilute sulphuric acid it gave orcinol and erythritol ; it condensed with ethylacetoacetate to form 4 : 7-dimethyl-5-OH-coumarin ; with concentrated sulphuric acid it formed orsellinic acid and erythritol and with methyl alcoholic potash methyl orsellinate and erythritol, and finally as a result of methylation with diazomethane and treatment with alcoholic potash the dimethyl ether of methyl orsellinate and subsequently the dimethyl ether of orsellinic acid could be prepared. It was obvious therefore that the new compound is a stereoisomer of montagnetol, and this idea was confirmed by an examination of the optical activity of the two compounds. The lower melting compound was dextrorotatory,  $[\alpha]_D +16.0^\circ$  in water and  $+12.6^\circ$  in acetone whereas the higher melting substance was optically inactive. Hence it has been concluded that the former is *d*-montagnetol, and the latter is the racemic variety. The final proof of this relationship was obtained when *d*-montagnetol was converted into the racemic variety by boiling with water for 3 hours. It may be mentioned at this stage that on a few occasions we met with samples of montagnetol having indefinite melting points and with low rotatory power being obviously mixtures of the active and racemic montagnetols. They could be readily converted into the higher melting inactive compound by heating with water as mentioned above.

Though the erythritol present in the two montagnetols belongs to the inactive meso variety the occurrence of optical activity in montagnetol s

easily explicable since dissymmetry is introduced due to esterification of one of the hydroxyl groups of the alcohol as represented below. For the sake of simplicity the hydroxyl involved is arbitrarily taken as that attached to carbon atom number one. The position is in no way affected even if any other hydroxyl were involved.



In most cases of plant products the optically active compound is of common occurrence and racemisation is brought about during extraction and subsequent treatment. With a view to be precise on this point in regard to montagnetol a number of lichen samples of *Rocella montagnei* were analysed carefully. From some the *d*-variety was isolated with ease. Hence it could be concluded that the method of extraction had no racemising influence. In some other cases a mixture was obtained and the racemic sample was also isolated in some others. It looks therefore that racemisation of montagnetol is taking place even in the plant.

### Experimental

The isolation of *d*-montagnetol was made following the same procedure as was adopted for the racemic compound. When obtained from the mixture of solvents, acetone-ether-benzene, the crystals were very small and the structure was not definite. The substance, however, crystallised from acetone on careful addition of benzene in the form of colourless truncated prisms and triangular plates. When mounted on a slide with a drop of water it quickly dissolved and when the solvent evaporated it crystallised as soft fibrous needles. In contrast to this *r*-montagnetol was less soluble and exhibited great tendency to come out in the form of big crystals; it appeared as big rectangular tablets when crystallised from acetone and as lens-shaped crystals when mounted with water. *d*-Montagnetol melted at 135-36° and repeated purification and crystallisation did not raise the melting point. A mixture of it with the higher melting montagnetol melted indefinitely between 130° and 150°. (Found: C, 53.4; H, 6.4; and molecular weight 285. C<sub>12</sub>H<sub>16</sub>O<sub>7</sub> required C, 52.9; H, 5.9% and molecular weight 272.) Its chemical properties and reactions were just the same as those of *r*-montagnetol.

*Optical activity of the two montagnetols.*—0.5875 g. of the lower melting montagnetol was dissolved in 25 c.c. of distilled water, a part of the solution

taken in 100 mm. tube and the rotation observed. It was found to be dextro-rotatory, and the specific rotation was  $+16.2^\circ$ . A similar solution in acetone gave  $[\alpha]_D +12.6^\circ$ .

0.5112 g. of the higher melting montagnetol was dissolved in 25 c.c. of distilled water, and a part of the solution taken in a 100 mm. tube. There was no rotation.

*Conversion of d-montagnetol into the racemic compound.*—A solution of the lower melting montagnetol (*d*), (0.8 g. in 25 c.c. of water) was boiled for 3 hours. Racemisation was complete by this time since optical activity disappeared. It was then concentrated when an almost pure sample of the higher melting montagnetol was obtained in a quantitative yield. After one crystallisation from acetone-ether-benzene mixture it melted at  $155-56^\circ$ . Mixed melting point with an authentic specimen of the higher melting compound showed them to be identical.

#### Summary

A lower melting sample of montagnetol has been isolated from *Roccella montagnei*. It gives all the reactions of montagnetol, but differs in having a lower melting point and a different crystal structure, and in being dextro-rotatory. Hence it is identified as *d*-montagnetol. The higher melting compound is the racemic variety having no optical activity. The general results indicate that racemisation takes place even in the plant.

#### REFERENCES

1. Rao and Seshadri  
..... ..  
.. *Proc. Ind. Acad. Sci.*, (A), 1941, 13, 199.  
.. *Ibid.*, 1942, 15, 18.