ACTA CHEMICA SCANDINAVICA 19 (1965) 1185–1187

Studies on the Chemistry of Lichens

20* The Chemistry of the *Ramalina ceruchis* Group

GERD BENDZ, JOHAN SANTESSON and
CARL AXEL WACHTMEISTER

The Institute of Chemistry, University of Uppsala, Uppsala, and
The Institute of Organic Chemistry, University of Stockholm, Stockholm, Sweden

Five species of the *Ramalina ceruchis* group have been investigated mainly with regard to their contents of aromatic lichen compounds. From all but one of these species we have isolated an unknown diol named ceruchdiol with a suggested formula of $C_{30}H_{52}O_2$ and from two of the species we have isolated an unknown depside.

The fruticose lichen species *Ramalina ceruchis* (Ach.) DNot. *R. combeoides* Nyl., *R. flaccescens* Nyl., *R. homalea* Ach., and the yet undescribed *R. ceruchoides* HMagn. form a distinct group in the genus *Ramalina*.[1] The distribution is limited to the American Pacific coast, from California in the north to Chile in the south.

When specimens of *R. ceruchis* are kept in a herbarium for a couple of years, a white deposit often appears on the surface giving the lichen a mouldy appearance. The same type of deposit, although far less abundant, is sometimes also observed on specimens of *R. combeoides*, *R. homalea*, and *R. ceruchoides*.

From the chloroform extract of *R. ceruchis*, a well crystallizing compound named ceruchdiol was easily isolated. After sublimation *in vacuo* it melted at 217–217.5° (subl. from 190°), $[\alpha]_D^{25} = -44°$ (in chloroform). It also was possible, simply by carefully brushing of the downy specimens, to isolate practically pure microscrystalline ceruchdiol. Even the specimens of *R. ceruchis* without any deposit on the surface were found to contain ceruchdiol, although in smaller quantities.

If due regard is taken of the high melting point of ceruchdiol the analytical values suggested an empirical formula of $C_{30}H_{52}O_2$. The compound showed no significant absorption in the ultraviolet region. The infrared spectrum as measured in chloroform solution indicated the absence of carbonyl functions as well as of ethylenic double bonds except, possibly, tetrasubstituted double

---

* Part 19. *Acta Chem. Scand.* 18 (1964) 213.

bonds. Absorption maxima in the hydroxyl region gave evidence for the presence of two different kinds of hydroxyl groups.

Moreover, ceruchdiol does not seem to be identical with any previously described diol of known composition,[2,3] such as zeorin ($C_{30}H_{52}O_2$ m.p. 223—227°; $[\alpha]_D^{25} = +54°$),[4] already found in 16 lichen species by Zopf.[5]

All the species of the *Ramalina ceruchis* group, with the exception of *R. flaccescens*, contained ceruchdiol in about the same quantities. In order to find out if this taxonomically well-defined group showed the same homogeneity with regard to aromatic lichen compounds we have examined chloroform extracts from all the species by means of thin layer and paper chromatography. Table 1 shows the different compounds that we have identified with reasonable certainty by co-chromatography with authentic samples.

Table 1.

	Ceruchdiol	Usnic acid	Stictic acid	Divaricatic acid[a]	Atranorine	Unknown depside[b]
R. ceruchis (deposit)	×	×				0
» » (no deposit)	×	×				×
R. ceruchoides	×	×				
R. combeoides	×	×	×		×	
R. flaccescens	0	×				×
R. homalea (deposit)	×	×		×		
» » (no deposit)	×	×		0		

[a] Divaricatic acid has been reported from *R. homalea*.[6]

[b] This unknown depside has been identified as methyl 3,5-dichlorolecanorate.[7]

In 1898 Hesse [8] published an investigation of *R. ceruchis*. He isolated and identified usnic acid along with other compounds but characterised them only by their melting points. Judging from our data, however, the investigation was probably carried out on a different lichen.

EXPERIMENTAL

All melting points are uncorrected. The analyses were made by the Analytical Department of the Institute of Chemistry, Uppsala.

The lichen material. Quotation specimens are to be found in the herbarium of Uppsala Botanical Museum.

R. ceruchis (deposit on the surface) from Chile, collected in 1940, quotation number RSant 2452; *R. ceruchis* (no deposit) Chile 1940, RSant 2512; *R. ceruchoides*, Chile 1940 RSant 2660; *R. combeoides*, USA, Calif., 1905? Kryptogamæ Exsiccatae editae a Museo Palatio Vindobonensi 1369; *R. flaccescens*, Chile, 1940, RSant 2511; *R. homalea* (deposit on the surface), USA, Calif., 1874, 440; *R. homalea* (no deposit) USA, Calif., 1874, 442.

Isolation of the diol. Air-dried *R. ceruchis* (deposit on the surface) (8.45 g) was extracted with chloroform (2 × 250 ml) for 1 h at 60°. Upon evaporation, the extract yielded a crystalline residue (1.23 g; 14.6 %). Crystallisation from chloroform afforded the diol (0.31 g), m.p. 212.5—214°. It was purified for analysis by sublimation at 130°, 12 mm Hg and melted then at 217—217.5°-(subl. from 190°). (Found: C 81.0; H 11.63. $C_{30}H_{52}O_2$ requires: C 81.0; H 11.79).

The diol was soluble in concentrated sulphuric acid, forming a faint yellow solution, which turned reddish-brown. Upon addition of acetic anhydride, no colour change was observed. It was optically active $[\alpha]_D^{25} = -44°$ (chloroform, $c = 0.47$), $[\alpha]_D^{25} = -44°$ (99.5 % ethanol, $c = 0.90$), $[\alpha]_D^{25} = -42°$ (pyridine, $c = 0.86$). The infrared spectrum (chloroform) gave strong bands at 3597; 3306; 3255 (broad); 2986–2837 (5 bands); 1465; 1371; 1177; 871 cm^{-1} (Unicam 100).

When treated in the same way *R. ceruchis* (no deposit) (2.45 g) yielded a residue (0.28 g = 11.1 %) which after crystallisation afforded the above diol (0.08 g = 2.8 %) established by mixed melting point determination and comparison of the infrared spectra.

R. homalea, *R. ceruchoides*, and *R. combeoides* were treated as follows: The dry lichen (0.10–0.12 g) was extracted with chloroform (10 ml) at 50° for 1 h. Evaporation of the extract gave a residue which after crystallisation from chloroform afforded the above diol (mixed m.p., IR) (Yield: 0.002–0.004 g pure diol).

Specimens of *R. ceruchis* (deposit on the surface) (0.35 g) were carefully brushed leaving a white microcrystalline compound (0.008 g) m.p. 214.5–215.5° undepressed on admixture with ceruchdiol.

Chromatographical investigation. Stictic acid, divaricatic acid, atranorine, and an unknown depside were identified by thin layer chromatography including co-chromatography with authentic samples using silica gel G [9] as adsorbent and benzene-dioxane-acetic acid (90:25:4, v/v/v) or chloroform-acetone (1:1, v/v) as solvents.[10]

Usnic acid was identified by paper chromatography (Whatman No. 1) using butanol-conc. ammonia (4:1, v/v) and butanol-ethanol-water (5:1:4, v/v/v) as solvents. [11] The spots were made visible by Chloramin T (usnic acid), *p*-phenylenediamine (stictic acid and atranorine) and bis-diazotized benzidine (divaricatic acid and the unknown depside).

Acknowledgements. Our thanks are due to Professor Arne Fredga for the facilities put at our disposal and to Dr. Rolf Santesson for the generous supply of identified lichen material.

REFERENCES

1. Howe, R. H., Jr. *Bryologist* **16** (1913) 65.
2. Shibata, S. In Linskens, H. F. *Modern Methods of Plant Analysis*, Vol. VI, Berlin 1963.
3. Ourisson, G. and Crabbé, P. *Les triterpènes tétracycliques*, Paris 1961.
4. Neelakantan, S., Rangaswami, S. and Rao, V. S. *Indian J. Pharm.* **16** (1954) 173.
5. Zopf, W. *Die Flechtenstoffe*, Jena 1907.
6. Hale, M. E., Jr. *Lichen Handbook*, Washington D. C. 1961.
7. Bendz, G., Santesson, J. and Wachtmeister, C. A. *Acta Chem. Scand.* **19** (1965) 1188.
8. Hesse, O. *J. prakt. Chem.* **57** (1898) 232.
9. Waldi, D. In Stahl, E. *Dünnschicht-Chromatographie*, Berlin 1962.
10. Ramaut, J. L. *Bull. Soc. Chim. Belges* **72** (1963) 97.
11. Wachtmeister, C. A. In Linskens, H. F. *Papierchromatographie in der Botanik*, 2. Aufl., Berlin 1959.

Received March 25, 1965.