

CHEMICAL STUDIES ON LICHENS.

25.\* A NEW ANTHRAQUINONE FROM MYCOBLASTUS SANGUINARIUS.

Gerd Bohman

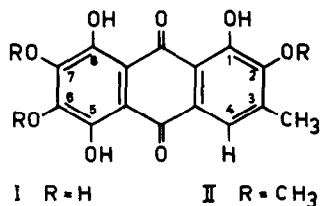
Institute of Chemistry, University of Uppsala,

Box 531, S-751 21 Uppsala 1, Sweden.

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The lichen Mycoblastus sanguinarius (L.) Norm. was investigated by Zopf, who isolated atranorin and caperatic acid, and reported the presence of an unextractable red pigment (1). J. Santesson isolated this pigment and suggested it to be an anthraquinone.

Two weeks' extraction of M. sanguinarius apothecia with acetone (Soxhlet), treatment of the extract with aqueous sodium bicarbonate, repeated recrystallisation (acetone), and sublimation (150-160° at 0,8 mm Hg) afforded the red pigment 2,5,7-trihydroxyemodin (I), C<sub>15</sub>H<sub>10</sub>O<sub>8</sub> (high resolution MS), m.p. above 365°.



UV:  $\lambda_{\max}^{\text{EtOH}}$  nm (rel. %): 294 (100), 497 (33),

$\lambda_{\text{inflexion}}$ : 313 (91), 350 (63),  $\lambda_{\min}$ : 397

(14). IR:  $\nu_{\max}^{\text{C=O}}$ : 1631 and 1614 cm<sup>-1</sup>. NMR

[in (CD<sub>3</sub>)<sub>2</sub>SO]:  $\delta$  2.17 (s, ArCH<sub>3</sub>) and 7.42

(s, ArH) ppm.

The presence of a hydroxylated anthraquinone structure is evident from the UV spectrum (2) and corroborated by the red violet colour reaction obtained with aqueous potassium hydroxide. The position of the UV absorption above 350 nm is dependent upon the number of  $\alpha$ -hydroxy groups present,  $\beta$ -hydroxy groups having little influence (2). In the case of I, the maximum at 497 nm is indicative of three  $\alpha$ -hydroxy groups (2).

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Methylation of I with diazomethane afforded a tri-O-methyl derivative (II), ( $M^+ = 360$  m/e). Since  $\alpha$ -hydroxy groups normally are too strongly hydrogen bonded to be methylated by diazomethane, the compound I ought to have three  $\beta$ -hydroxy groups (a carboxy group is contradicted by the IR spectrum).

The methyl group, established by a Kuhn-Roth determination, must be placed at the remaining  $\beta$ -position, because of both the chemical shift in the NMR spectrum (3) and biogenetic considerations (4,5).

The only aromatic proton ought to be placed at C<sub>4</sub>, due to the very low field shift in the NMR spectrum, which is consistent with an  $\alpha$ -proton adjacent to a methyl group (3).

The data given above indicate the structure of the Mycoblastus pigment as 1,2,5,6,7,8-hexahydroxy-3-methylanthraquinone (I).

To our knowledge no anthraquinone with six nucleic hydroxy groups has previously been found in nature. Two highly hydroxylated anthraquinones have been found in fungi: asperthecin, 1,2,5,6,8-pentahydroxy-3-hydroxymethylanthraquinone, isolated from a strain of Aspergillus nidulans (6) and dermocybin, 1,5,7,8-tetrahydroxy-6-O-methyl-3-methylanthraquinone, isolated from Cortinarius (Dermocybe) sanguineus (7,8).

An unusual feature of both the Mycoblastus and the Cortinarius pigment is the complete oxygenation of one of the anthraquinone rings.

#### REFERENCES

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