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Chemical Studies on Lichens

22.* Anthraquinones from the Lichen *Lasallia papulosa* var. *rubiginosa* and the Fungus *Valsaria rubricosa*

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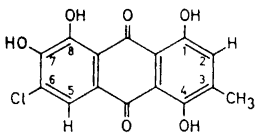
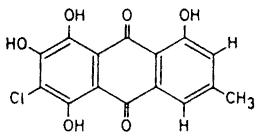
Two new anthraquinones have been isolated both from the lichen *Lasallia papulosa* (Ach.) Llano var. *rubiginosa* (Pers.) and the fungus *Valsaria rubricosa* (Fr.) Sacc. The pigments have tentatively been assigned the structures 7-chloro-4-hydroxyemodin (IV) and 7-chloro-5-hydroxyemodin (V).

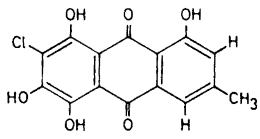
Three different anthraquinones have been isolated from the lichen *Lasallia papulosa* (Ach.) Llano var. *rubiginosa* (Pers.). Of these pigments, one has been identified as 7-chloroemodin. The identity was verified by mass spectrometry and co-chromatography. The other two anthraquinones were very similar to valsarin.



I



II



III

Valsarin has been investigated earlier by Briggs *et al.*[1] They isolated the new pigment as the main product from the fungus *Valsaria rubricosa* (Sphaeriales), isolated from New Zealand *Nothofagus* species and grown on potato/glucose media at room temperature. On the basis of chemical and physical examination the pigment was limited to the structures I–III.

* Part 21. *Arkiv Kemi* 31 (1969) 121.

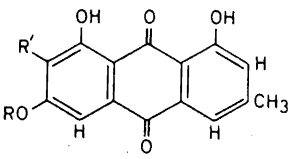
However, they could not ascertain the precise location of the different substituents.

Samples of *Valsaria rubricosa* (Fr.) Sacc. collected in five different places (Table 1) have been investigated in order to get valsarin as a reference compound to the lichen anthraquinones mentioned above. The samples showed considerable differences in their content of anthraquinones.

Because of the slight fragmentation of anthraquinones in the mass spectrometer, molecular peak = base peak, the identities of the molecular peaks in a "fungus mass spectrum" [2] give a rather good idea of the amounts of the different anthraquinones (Table 1).

Table 1. The molecular peaks of the anthraquinones from the "fungus mass spectrum" of *Valsaria rubricosa* expressed in percent of the base peak.

Locality	emodin *m/e* 270	parietin *m/e* 284	7-chloroemodin *m/e* 304 (306)	valsarin *m/e* 320 (322)
Denmark	100	—	18	—
N. America	100	26	11	1
France I	100	30	23	5
Czechoslovakia	100	31	28	22
France II	70	23	100	25



	R	R'
emodin:	H	H
parietin:	CH_3	H
7-chloroemodin:	H	Cl

The fungus collection from Denmark contains no traces of valsarin, only emodin and 7-chloroemodin, while the other four collections also contain parietin and valsarin. Emodin is the main component in all samples of fungus but one, which yields 7-chloroemodin as the main product.

The pigments were identified by mass spectrometry and co-chromatography.

As these specimens of *Valsaria rubricosa* were too small and few in number, it was not possible to draw any conclusions as to whether their anthraquinone contents varied because of the locality, stage of development or chemical strains.

By TLC it was possible to separate valsarin from *Valsaria rubricosa* from Czechoslovakia and France II into two different anthraquinones, valsarin I and II. Co-chromatography showed that valsarin I and II were identical with the two unknown anthraquinones from the lichen *Lasallia papulosa* var. *rubiginosa*.

Both of the pigments are excellent dyes and give violet spots on silica gel and violet acetone and concentrated sulphuric acid solutions. The dimethyl-

formamide solutions are violet at first but change after some hours to a reddish-brown colour.

Briggs found that the elemental analysis of valsarin indicated the formula $C_{15}H_9ClO_6$. This agrees with its mass spectrum, which shows a molecular peak at *m/e* 320, the relative intensity of M+2 to M being 34 %.

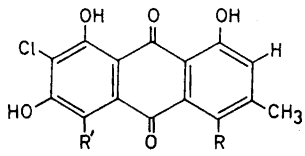
On the basis of Briggs' preparation of tetraacetyl valsarin and valsarin tetramethyl ether, the pigment ought to have four phenolic hydroxy groups. The remaining carbon atom is probably present as a methyl group.

Briggs suggested that valsarin has three hydroxy groups in α-positions, which was indicated by colour reactions, infrared and ultra-violet spectra.

According to biogenetic considerations for the formation of anthraquinone derivates [3,4] the fourth hydroxy group ought to be in the 6 position and the methyl group in the 3 position.

That the chlorine atom is situated in the β-position and not in the fourth α-position is indicated by Briggs' oxidation product of valsarin with manganese dioxide and concentrated sulphuric acid. He obtained an 1,4,5,8-tetrahydroxyanthraquinone, which still gave a positive halogen test.

As valsarin is soluble in sodium hydrogen carbonate it ought to have the chlorine atom in the 7 position because this would enhance the acidity of the β-hydroxyl.



	R	R'
IV:	OH	H
V:	H	OH

This suggests that the structure of valsarin could be 7-chloro-4-hydroxyemodin (IV) or 7-chloro-5-hydroxyemodin (V).

It seems plausible that valsarin I and II corresponds to the two structures IV and V.

Unfortunately, the very small amount of the pigments available was not enough to give an NMR spectrum, which presumably would have verified the structures of valsarin I and II.

The structures IV and V agree with those of all chlorinated anthraquinones hitherto isolated from lichens,[5] in being derivates of 7-chloroemodin.

A hydroxy group in the 4 or 5 position is rather uncommon in anthraquinones isolated from lichens. The only one hitherto found is xanthorin (5-hydroxyparietin) from the lichens *Xanthoria elegans* (Link) Th. Fr.[6] and *Laurera purpurina* (Nyl.) Zahlbr.[7]

According to the lichen mass spectrum one sample of *Lasallia papulosa* var. *rubiginosa* contains a chloro compound with a molecular peak at *m/e* 290 with a concomitant peak at *m/e* 292. However, it has not yet been possible to isolate this compound. It might be some precursor to the anthraquinones, for instance 7-chloro-1,6,8-trihydroxy-3-methylanthrone, which has earlier been found in a fungus [8] and probably also in the lichen *Nephroma laevigatum*.[5]

A colorless precipitate was obtained during the acetone extraction of *Lasallia papulosa* var. *rubiginosa*. The compound was identified by mass spectrometry as gyrophoric acid. This depside has earlier been found in *Lasallia*.

EXPERIMENTAL

The lichen *Lasallia papulosa* var. *rubiginosa*, collected in South Africa, and the different specimens of the fungus *Valsaria rubricosa* were dried and extracted with acetone.

The separation of the anthraquinones, with TLC, was carried out on Eastman "Chromagram sheets" type 6061 (chloroform-acetone, 4:3 v/v).

Parietin, emodin, 7-chloroemodin, and valsarin I and II were co-chromatographed with authentic specimens in chloroform-acetone, 4:3 v/v. [$R_F = 0.90$ (yellow), 0.83 (yellow), 0.63 (red-orange), 0.20 (violet) and 0.09 (violet), respectively.]

The gyrophoric acid precipitated during the acetone extraction of the lichen and was purified by recrystallisation from acetone.

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