CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part XXI. Occurrence of Fallacinal in *Teloschistes flavicans*

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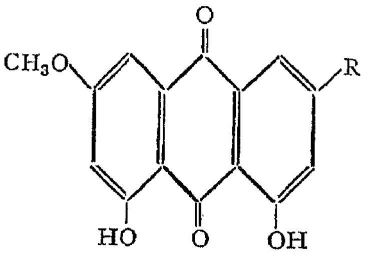
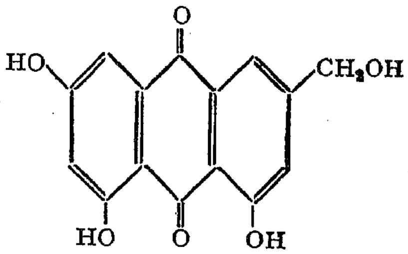
In an earlier study[1] of the Indian sample of *Teloschistes flavicans*, besides physcion (I) and a colourless substance, the existence of teloschistin was recorded and its constitution elucidated as ω-hydroxyphyscion (II).[1-2] Subsequently, its synthesis[3] was also effected by the action of N-bromosuccinimide on physcion diacetate followed by the action of silver acetate and final hydrolysis. The melting point of teloschistin, obtained from the lichen, was first recorded as 228–30° but the synthetic sample was found to melt higher (245–47°). However, purification of the natural sample by the preparation of its acetate and subsequent hydrolysis raised the melting point to 244–46° alone or mixed with the synthetic sample. The acetates of the synthetic and natural samples agreed closely and the mixed melting point was undepressed.

More recently, Murakami[4] examined the pigments of *Xanthoria fallax* and found that this lichen contains besides physcion (I) and teloschistin (II) the corresponding aldehyde, fallacinal (III). He also recorded the melting point of teloschistin as 235°. Consequently, we have repeated the study of *T. flavicans*; but the new collection made in 1955 appears to be somewhat different particularly in its colour. Adopting the procedure described in the earlier publications we have now obtained a product which even without purification through its acetate melted much higher (246°) and after purification by the acetate method, the melting point went up to 250–52°. Further, in all its properties it agreed with the description of the aldehyde, fallacinal (III). In order to have an effective separation of the components and have a quantitative idea of the composition, the aldehyde was removed as the 2:4-dinitrophenylhydrazone or by means of Girard's Reagent-T and the remaining portion examined. It was found to be almost pure physcion. In one experiment the mixture of components was subjected to oxidation with active manganese dioxide in order to oxidise any teloschistin that may be present. But it was noticed that this did not make an appreciable difference in the yield of fallacinal. The results of the present series of experiments lead to the conclusion that the sample of the lichen now examined contains physcion (I) (80%) and fallacinal (III) (20%) only as the coloured components and that teloschistin (II) is almost absent. It differs from the earlier sample which contained besides physcion (I), teloschistin (II).



I R=CH_3
II R=CH_2OH
III R=CHO



IV

In order to make sure of the melting point of teloschistin, we have now prepared it by the partial methylation of synthetic citreorosein[5] (ω-hydroxy-emodin) (IV). Earlier Anslow *et al.*[6] employed sodium methoxide and methyl iodide for this purpose and recorded a melting point of 229–31°. As a more convenient method, we have now employed a little less than one mole of dimethyl sulphate and excess of potassium carbonate. The product consisted of the monomethyl ether along with a small amount of the unchanged compound, which could be easily removed by extraction with sodium carbonate. Teloschistin (II) obtained by this method is easily purified and the pure compound is found to melt at 243–44°; this melting point has been checked a number of times and seems to be the most acceptable.

EXPERIMENTAL

The present sample of the lichen, *T. flavicans*, was collected in summer 1955 and it was found to be less coloured than the sample used earlier[1] (collected in 1947).

The air-dried lichen (500 g.), in coarse powder form, was extracted with hot chloroform (3 × 1 L) and filtered. The total extract was concentrated to about 200 c.c. and an equal volume of ethanol added. On allowing to stand overnight a red crystalline solid separated which was filtered (1·3 g., fraction A). The filtrate when worked up gave the colourless substance[1] along with a small quantity of physcion.

Separation of fraction A

(i) *By crystallisation.*—When crystallised from benzene or a mixture of chloroform and ethanol orange-red needles, m.p. 245–46°, were obtained. This solid was insoluble in aqueous sodium bicarbonate and sodium carbonate, but soluble in aqueous sodium hydroxide giving a purple-red solution from which a violet precipitate separated on standing. It gave a reddish brown colour with alcoholic ferric chloride and an orange-red solution with concentrated sulphuric acid. With 2:4-dinitrophenylhydrazine, it formed the hydrazone, m.p. 320–22°. It closely agreed in its properties with fallacinal.[4] The lower melting point was due to contamination with a trace of physcion, the presence of which was shown by vertical paper chromatography. The sample was therefore acetylated using acetic anhydride and concentrated sulphuric acid. The acetate was purified by crystallisation from ethyl acetate when it melted at 181–83° (Murakami[4] reported a melting point of 179–81° for fallacinal tetra acetate). On deacetylation with methanolic sulphuric acid it yielded pure fallacinal, m.p. 250–52°. The infra-red spectrum of this sample was found to agree with that of fallacinal isolated by Murakami.[4]

The chloroform-ethanol mother liquor from the crystallisation of the aldehyde was concentrated to a small bulk, when physcion was obtained as orange-red needles and plates. It was purified by crystallisation from a mixture of chloroform and ethanol, m.p. 204–06°. Yield, 1·0 g.

(ii) *By using* 2:4-*dinitrophenylhydrazine*.—The mixture (0·25 g.) was dissolved in ethanol and chloroform (1:2, 180 c.c.) at room temperature and to the orange-red solution an ethanolic solution of 2:4-dinitrophenylhydrazine (0·17 g.) was added. The mixture was refluxed for 15 min. and allowed to stand at room temperature for several hours to complete the separation of the hydrazone. It was filtered, washed with sulphuric acid (5 N) and then with water, m.p. 320–22° agreeing with fallacinal dinitrophenylhydrazone.[4] Yield, 0·085 g.

The filtrate was concentrated to $\frac{1}{3}$ vol. by distilling off the organic solvents under reduced pressure when orange-red needles were obtained. This solid was filtered, washed with sulphuric acid (5 N) and then with water. It crystallised from chloroform-ethanol mixture, m.p. 204–06° (0·18 g.). It agreed with physcion in every respect. In order to test for the possible presence of teloschistin, it (0·17 g.) was dissolved in benzene (30 c.c.) and active manganese dioxide (0·35 g.) was added and the mixture refluxed for 16 hours. The hot solution was filtered from manganese dioxide which was washed several times with hot benzene. The filtrate and the washings were collected and benzene was evaporated off completely. The residue was found to melt at 204–06° and did not give any hydrazone with 2:4-dinitrophenylhydrazine and further crystallisation did not raise the melting point.

In another experiment the separation of fraction A was effected after treatment of the mixture (fraction A) with active manganese dioxide as given above. The quantities of the hydrazone and physcion obtained were found to be approximately the same.

(iii) *By using Girard's Reagent-T.*—The mixture (0·5 g.) was dissolved in dioxan (20 c.c.) containing glacial acetic acid (2 c.c.) and a solution of Girard's Reagent-T (0·28 g. in 1 c.c. of water) was added. The mixture was refluxed for an hour, water added to the cooled solution and left overnight in the refrigerator. The precipitated orange-yellow solid was filtered, washed well with water and dried (0·35 g.). It was free from the aldehyde and did not give the dinitrophenylhydrazone. It had however an indefinite m.p. and hence it was methylated in dry acetone medium using excess of dimethyl sulphate (3 c.c.) and anhydrous potassium carbonate (6 g.) by refluxing for 30 hours. The crude dry methyl ether was dissolved in chloroform and chromatographed on alumina, when two bands were obtained. The lower band which was yellow in colour was eluted with chloroform. On evaporating off the solvent, a crystalline yellow solid was obtained which on crystallisation from a mixture of chloroform and ethyl acetate yielded bright yellow-needles, m.p. 224–25° (0·30 g.) undepressed by admixture with physcion dimethyl ether.

The light-red upper band could not be eluted with any solvent. Hence it was taken out and extracted with hot chloroform after treatment with hydrochloric acid. The residue obtained after evaporating the pale yellow chloroform extract was too small for characterisation, but was found to give a brown colour with alcoholic ferric chloride. The red band may therefore be due to a very small quantity of incompletely methylated product from physcion.

Partial methylation of citreorosein (ω-hydroxyemodin) (IV)

To a solution of citreorosein[5] (m.p. 288°, 0·17 g.) in dry acetone (25 c.c.), potassium carbonate (0·5 g.) and dimethyl sulphate (0·05 c.c.) were added and the mixture refluxed for 4 hours on a water-bath. The original intensely purple-red solution gradually changed to reddish brown and some red crystalline solid separated. Acetone was filtered and the residue was treated with water when an orange-yellow solid was obtained. Some more of it was obtained when acetone was evaporated from the above filtrate and the residue treated with water. The combined solid was ground with aqueous sodium carbonate (5%) several times till a fresh extract with the carbonate was not coloured. It was washed well with water and crystallised twice from ethanol when teloschistin was obtained as orange-yellow needles, m.p. 238–40° (0·110 g.). The carbonate extract on acidification yielded a small quantity of citreorosein (25 mg.).

The above sample of teloschistin (0·1 g.) was acetylated with acetic anhydride (1 c.c.) containing a drop of concentrated sulphuric acid and the acetate crystallised from ethyl acetate, when teloschistin acetate was obtained as yellow needles, m.p. 193–94° (0·11 g.), mixed m.p. with teloschistin acetate prepared from physcion through the NBS reaction[3] was undepressed. The acetate was deacetylated using methanolic sulphuric acid. Teloschistin crystallised as orange needles from benzene, m.p. 243–44° (0·06 g.) undepressed by admixture with the sample obtained by the NBS reaction.[3]

Oxidation of teloschistin

Synthetic teloschistin (0·02 g.) was oxidised with active manganese dioxide in benzene solution as carried out in an earlier case; the oxidation product crystallised from benzene as orange-yellow needles (12 mg.), m.p. 250–51° alone or when mixed with fallacinal isolated from *T. flavicans*.

SUMMARY

A sample of *Teloschistes flavicans* collected in summer 1955 was found to contain physcion and fallacinal in the proportion of 4:1 and did not contain any appreciable amount of teloschistin. A pure sample of teloschistin has been obtained by the partial methylation of citreorosein using methyl sulphate and potassium carbonate and is found to melt at 243–44°. On oxidation with manganese dioxide it has yielded fallacinal.

ACKNOWLEDGEMENT

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