CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part X. Chemical Components of *Teloschistes flavicans*

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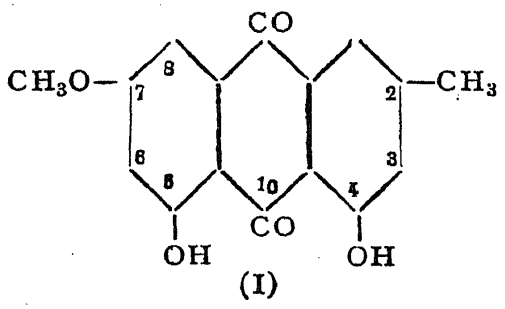
ALONG with the luxuriant growth of *Ramalina tayloriana*[1] on the sandal trees of the Simhachalam hills is found a yellow lichen (sometimes markedly orange yellow) in small quantities. Its presence in *R. tayloriana* sample is readily revealed by the isolation from the petroleum-ether extract, besides usnic acid, of a small quantity of an orange coloured substance giving the characteristic colour reactions of polyhydroxy anthraquinones. The lichen is also found on other plants of this area, though in small quantities. A sample of it was sent to Prof. Y. Asahina of Tokyo who kindly identified it as *Teloschistes flavicans* Norm.

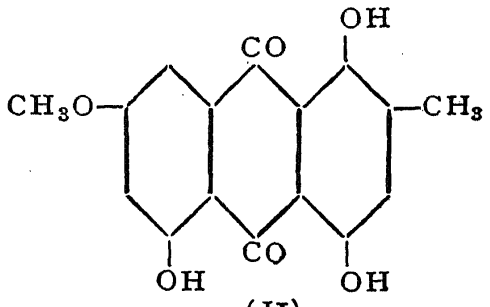
Zopf[2] was the first to study this lichen and was able to isolate from it physcion (I), m.p. 207°, and a colourless substance, m.p. 240–45°. In our experiments with this lichen we first employed ether, acetone and water in succession as solvents. The first solvent removed all crystalline products and the others yielded none. From this ether extract a colourless substance (A) could be readily separated as the alkali-insoluble portion. The alkali-soluble portion gave all the reactions for physcion, but there was difficulty in purifying it. After repeated fractional crystallisation using alcohol-chloroform mixture a fraction melting at 206–207° and agreeing with physcion in every respect could be obtained. But it was clear that a higher melting and a less soluble fraction was present in appreciable quantities and it was the cause of the difficulty in purifying physcion. This difficulty was got over subsequently by employing petroleum ether and chloroform successively for the extraction of the lichen. The petroleum ether extract contained besides the colourless substance (A) almost all the physcion and only minor quantities of the higher melting substance with the result physcion could be readily purified. In the chloroform extract only the higher melting compound was found. It is given the name ' Teloschistin ', since it does not agree with the description of any other naturally occurring compound so far isolated.

Teloschistin crystallises as dull orange plates and thin prisms melting at 229–30° and has the formula $C_{16}H_{12}O_6$ with one methoxyl group. It is

insoluble in sodium bicarbonate and carbonate solutions, but is soluble in cold dilute potassium hydroxide from which red-violet crystals separate on standing. It gives a reddish brown colour with alcoholic ferric chloride and with concentrated sulphuric acid forms a deep orange red solution which in thin layers has an eosin-like shade. In these respects it closely resembles physcion. Its composition would indicate that it has one oxygen atom more than physcion and hence it may be expected to be a hydroxy physcion and this is in accord with its higher melting point and lower solubility in organic solvents. The formation of sparingly soluble potassium salt as well as the insolubility of the substance in aqueous sodium carbonate would indicate the presence of a methoxyl group in the 7-position as in physcion (I) and erythroglaucin[3] (II). Roseopurpurin[4] (III) which has a hydroxyl in the 7-position and a methoxyl in the 4-position is soluble in aqueous sodium carbonate.



(I)



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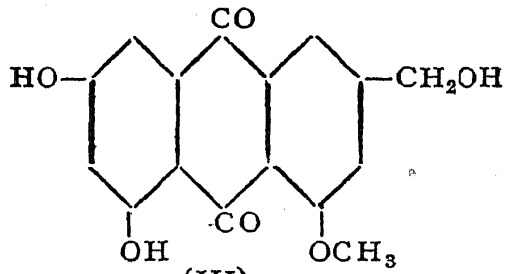

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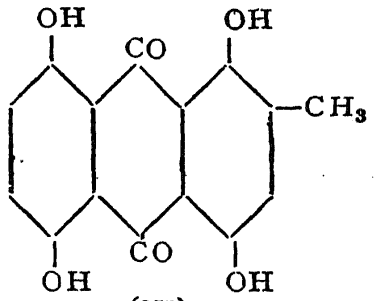
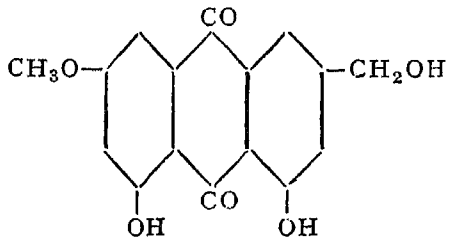


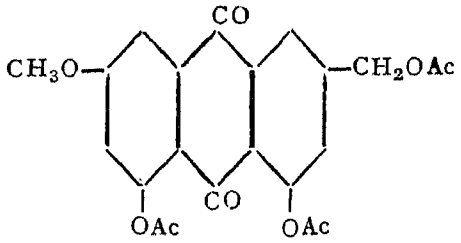
(IV)

The location of the extra hydroxyl group of teloschistin in the physcion structure could be arrived at from the following considerations. Polyhydroxy anthraquinones with hydroxyls para to one another as in 1 : 4 : 5 and 1 : 4 : 5 : 8 arrangements exhibit strong fluorescence in glacial acetic acid solution and give a brilliant blue colour with conc. sulphuric acid, *e.g.*, erythroglaucin (II) and cynodontin[5] (IV). But the new compound teloschistin, just like physcion, does not exhibit these characteristics. Hence the presence of the additional hydroxyl in the 1- or 8-position could be ruled out. A close study of the naturally occurring hydroxy anthraquinones would suggest as the next possibility the position in the side chain. Teloschistin would then be ω-hydroxy physcion (V). This constitution is supported by the observation that though it forms a triacetate (VI), m.p.

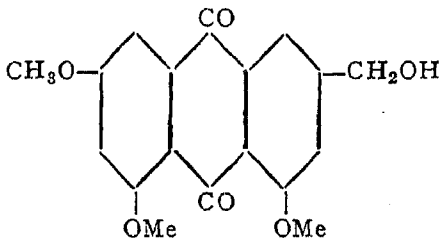
192–93°, it yields only a dimethyl ether (VII), m.p. 222–23°, one hydroxyl thus remaining unmethylated when methylation is carried out with dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium. Further on treatment with hydriodic acid and red phosphorus in acetic anhydride medium the substance undergoes demethylation and reduction, and the subsequent oxidation of the product with chromic acid yields frangula-emodin (VIII) decomposing at about 255°. This series of reactions would result not only in demethylation but reduction of the ω-hydroxy group also. [Compare conversion of ω-hydroxy emodin (IX) into frangula-emodin (VIII)[6].] The abovementioned structure for teloschistin as ω-hydroxy physcion is thus definitely established.



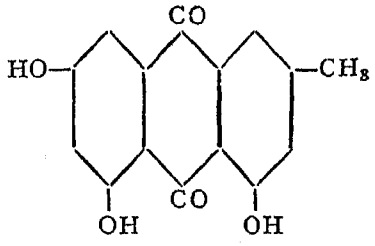
(V)



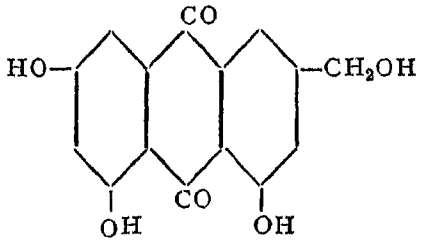
(VI)



(VII)



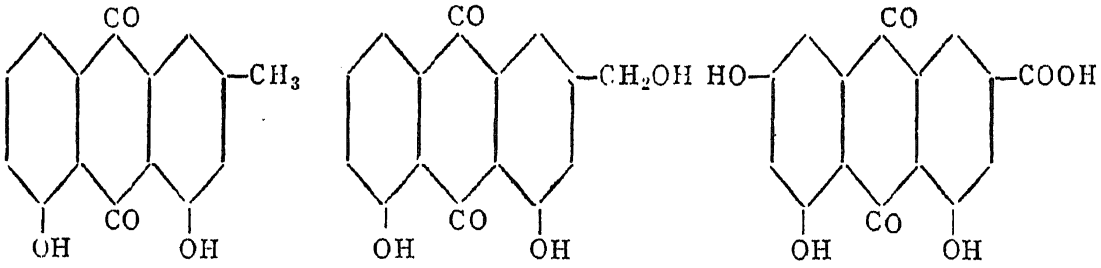
(VIII)



(IX)

In further confirmation of the above conclusion could be mentioned the following:—Raistrick, *et al.*,[6] subjected ω-hydroxy-emodin (IX) to partial methylation and obtained the corresponding 7-monomethyl ether. Its melting point (229–31°) recorded by them agrees with that of teloschistin isolated from *T. flavicans*. Posternak[4] subjected roseopurpurin (III) to energetic methylation and obtained 4:5:7-trimethoxy-2-hydroxymethyl anthraquinone (VII) as a minor product. Its crystal structure and melting point (222–24°) agree with those of the dimethyl derivative of teloschistin.

The association of teloschistin with physcion is rather interesting; the difference is an ω-hydroxyl group. Similar pairs are found in chrysophanol (X) and aloe-emodin (XI) occurring in *Cascara sagrada*.[7] A different type of association involving an additional nuclear hydroxyl is found in a number of *Aspergillus glaucus* species[3] which contain physcion (I) and erythroglaucin (II).



(X) (XI) (XII)

Physcion (I) is fairly widely distributed in lichens especially in the species of Xanthoria and Placodium. Its isolation from a number of moulds by Raistrick and co-workers[3] supports the view that it owes its origin to the fungal half of the fungus-alga symbiont. This view is supported further by the present isolation of teloschistin from *T. flavicans*, because the closely related ω-hydroxy emodin (IX) having a hydroxyl in the 7-position instead of the methoxyl of teloschistin has been found along with emodic acid (XII) in the mould, *Penicillum cyclopium*.[6]

Experimental

Petroleum ether extract

[*Physcion (I), Teloschistin (V) and colourless substance A*].—250 g. of the air-dried lichen in coarse powder form was extracted in a Soxhlet extractor with light petroleum (b.p. 60–80°) till the extract syphoning over was almost colourless. The solvent was distilled off from the extract and the residue was crystallised from chloroform–alcohol mixture (1 : 1) when fraction I melting above 215° was collected; yield 0·3 g. From the mother-liquor after addition of excess of alcohol was obtained fraction II melting at 190–95°; yield, 2·1 g.

Fraction I [*Teloschistin (V)*].—Fraction I was recrystallised twice from hot benzene when it was obtained in the form of dull orange rectangular plates and thin prisms melting at 229–30°; yield, 0·2 g. (Found: C, 64·2; H, 4·0; OCH_3, 10·6; $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0; and OCH_3, 10·3%.) It was sparingly soluble in petroleum ether, alcohol and acetone, moderately in benzene and more easily in hot chloroform and glacial acetic acid. It was not soluble in aqueous sodium bicarbonate and carbonate, but soluble in 2N potassium hydroxide giving a deep purple red solution

from which separated red-violet crystals after standing for some time. With conc. sulphuric acid it gave a deep orange red solution which in thin layers had an eosin-like shade. With alcoholic ferric chloride it gave a reddish-brown colour. It did not exhibit fluorescence in glacial acetic acid solution.

Fraction II [*Physcion (I), and colourless substance A*].—Fraction II was treated with sodium hydroxide solution (5%) and immediately filtered. The residue (R) was washed with plenty of water and the filtrate and washings were acidified when an orange coloured crystalline substance separated. This was filtered off, washed with water till free from acid and twice recrystallised from alcohol-chloroform mixture when it came out as long reddish-orange needles melting at 206–07°; yield, 1·6 g. (Found: C, 67·3; H, 4·5; OCH_3, 11·3; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2 and OCH_3, 10·9%.) It was sparingly soluble in cold petroleum ether, methanol and acetone but quite soluble in benzene, chloroform and glacial acetic acid. Its solubility in all the solvents was more than in the case of teloschistin. It gave a beautiful magenta colour in dilute solution with conc. sulphuric acid and a rose-pink solution with 2N potassium hydroxide from which a rose-pink precipitate slowly separated. With alcoholic ferric chloride it gave a reddish brown colour. From these it was identified as physcion and this was confirmed by preparing the diacetyl derivative melting at 186–87°.

The alkali-insoluble residue (R), after washing with plenty of water, was dried and dissolved in chloroform-methanol mixture and the solution allowed to stand when a colourless crystalline solid (A), melting at 245–50°, was obtained; yield, 0·2 g.

Chloroform extract

[*Teloschistin (V)*].—The lichen powder left after extraction with petroleum ether was extracted in the same apparatus with chloroform and the extract on evaporation left a dull orange coloured solid melting above 200°. It was first crystallised from alcohol-chloroform mixture and the product melting above 220° was recrystallised twice from hot benzene when dull orange-coloured rectangular plates and thin prisms melting at 229-30° were obtained; yield, 1·3 g. Mixed melting point with the product obtained from fraction I was undepressed. The colour reactions were identical.

Triacetate (VI).—Teloschistin (0·3 g.) was dissolved in acetic anhydride (15 c.c.) and boiled for ten minutes under reflux with a few drops of conc. sulphuric acid. The greenish yellow solid that separated when the solution was poured into water, was crystallised from glacial acetic acid when lemon yellow large rectangular plates melting at 192–93° were obtained. The

product did not give any colour with alcoholic ferric chloride. (Found: C, 61·8; H, 4·0; $C_{22}H_{18}O_9$ requires C, 61·9 and H, 4·3%.)

Dimethyl ether (*VII*).—The substance (0·4 g.) was dissolved in dry acetone (150 c.c.) and dimethyl sulphate (0·8 c.c.) and anhydrous potassium carbonate (10 g.) were added. The mixture was refluxed for 20 hours, the solvent was evaporated and the residue treated with a little water. The yellow solid that separated was crystallised from a large volume of alcohol when it was obtained as fine long yellow needles melting at 222–23°; yield, 0·3 g. It did not give any colour with alcoholic ferric chloride. (Found C, 66·3; H, 4·6; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·8%.) Posternak[4] reported the melting point of 4: 5: 7-trimethoxy-2-(hydroxy-methyl) anthraquinone as 222–24°.

Demethylation and reduction to frangula-emodin [(4: 5: 7-*trihydroxy* 2-*methyl-anthraquinone* (*VIII*)].—A mixture of teloschistin (0·5 g.), acetic anhydride (10 c.c.), hydriodic acid (3 c.c., sp. gr. 1·7) and red phosphorus (0·6 g.) was boiled under gentle reflux for three hours. The reaction mixture was cooled and poured into water. The pale brown solid that separated was filtered off, washed and dried. The dry solid was extracted with boiling glacial acetic acid (40 c.c.) and the solution allowed to cool overnight when a granular pale brown powder was obtained which appeared as almost colourless tiny plates under the microscope. When heated it began to darken at 250° and finally decomposed. (Decomposition point of 4: 5: 7-trihydroxy-2-methyl anthranol, 250–58°[6].)

The anthranol (0·3 g.) was dissolved in boiling glacial acetic acid (40 c.c.) and chromium trioxide (0·5 g.), dissolved in acetic acid (10 c.c. glacial acetic acid and 2 c.c. water), was added quickly. The mixture was kept at 60° (water-bath) for 30 minutes and then poured into water (250 c.c.). It was ether-extracted and the ether extract washed with water till free from acid and the residue (0·2 g.) left after evaporation of the ether was crystallised from glacial acetic acid when orange yellow needles melting at 250–55° (decomp.) separated. The product was identified as frangula-emodin (VIII) by means of its colour reactions and analysis. (Found: C, 66·5; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·7 and H, 3·7%.)

Our thanks are due to Prof. Y. Asahina for the identification of the lichen.

Summary

A yellow lichen accompanying *Ramalina tayloriana* has been identified as *Teloschistes flavicans*. Besides physcion and a colourless substance, another orange coloured compound melting at 229–30° and having the

formula $C_{16}H_{12}O_6$ is now isolated. It is designated 'Teloschistin'. It resembles physcion closely and its constitution is established as 4:5-dihydroxy-7-methoxy-2-hydroxymethyl anthraquinone (ω-hydroxy physcion).

References

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2. Zopf .. *Ann.*, 1905, **340**, 300.
3. Ashley, *et al.* .. *Biochem. J.*, 1939, **33**, 1291.
4. Posternak .. *Helv. Chim. Acta.*, 1940, **23**, 1046.
5. Anslow and Raistrick .. *Biochem. J.*, 1940, **34**, 1546.
6. Anslow, *et al.* .. *Ibid.*, 1940, **34**, 159.
7. Lidder, *et al.* .. *J. Amer. Pharm. Ass.*, 1942, **31**, 1616.