

ISOLATION OF XANTHYLETIN FROM THE BARK OF *CITRUS ACIDA*, ROXB.

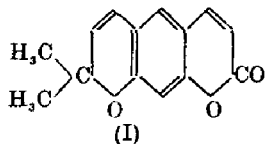
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Xanthyletin, a 2:2-dimethylchromeno-coumarin, m.p. 131.5°, has been isolated from the bark of *Citrus acida*, Roxb.

Citrus acida, Roxb. is a variety of *Citrus medica* (*Iconum Botanicarum, Index Londinensis*, 1930, 2, 224, 225) and it belongs to the family *Rutaceae*. The plant is highly valued in therapeutics for its antiscorbutic properties and it is very rich in essential oils which are strongly carminative and stomachic.

From the bark of *Citrus acida*, Roxb. which was collected from Darjeeling, a neutral crystalline compound, m.p. 131.5° has been isolated in a yield of 0.25 per cent. The compound is neutral towards litmus and indifferent towards ferric chloride. It shows no optical activity and dissolves in concentrated sulphuric acid with an orange solution. It is insoluble in 1% aqueous potassium hydroxide, but dissolves in alcoholic alkali, which turns yellow. The solution on dilution remains clear but on acidification precipitates the original substance. These properties indicate that the substance is a coumarin. The C-H values of the compound are found to agree with the formula $C_{14}H_{12}O_3$. The compound does not contain any methoxy group and does not produce acetyl derivative with acetic anhydride, nor does it form a semicarbazone or phenylhydrazone thus showing the absence of —OH and —CO— groups. These properties of the compound as also the analyses of the substance indicate close agreement with those of xanthyletin (I) which has been isolated so far only from two different *Rutaceous* plants, namely, *Xanthoxylum americanum*, Mill (Robertson and Subramaniam, *J. Chem. Soc.*, 1937, 286; Bell and Robertson, *ibid.*, 1936, 1828; Dieterle and Kruta, *Arch. Pharm.*, 1937, 275, 45) and *Luvanga scandens*, Ham (Bose and Mookerjee, *J. Indian Chem. Soc.*, 1944, 21, 281; Späth, Bose, Dobrovolny and Mookerjee, *Ber.*, 1939, 72, 1450; 1940, 73, 1361). A direct comparison of the substance with xanthyletin isolated from *L. scandens* (*vide supra*) has been made. It is found that the physical properties of the two compounds are identical and a mixture of the two melts also at 131.5° and gives similar colour reactions with concentrated sulphuric acid.

The tetrahydro derivative of the substance has the same m.p. (158.5°) as tetrahydro-xanthyletin, and both of them show no depression in their mixed melting point. Thus the coumarin of *Citrus acida* is identical with xanthyletin (I).



EXPERIMENTAL

Isolation of Xanthyletin.—Sun-dried bark (800 g.) of *C. acida* was crushed in a mortar and sieved. The fine powder, thus prepared, was soxhletted with ether (1.5 litres) during

4 hours. The green ethereal extract was concentrated to 30 c.c. and kept in a frigidairc or about a month. The crystals (1.00 g.), m.p. 129.5°, were collected and rapidly washed with ether and the filtrate was further worked up for coumarins by the method of Späth and Socias (*Ber.*, 1934, 67, 59).

The filtrate was freed from the solvent and the oil obtained (50 g.) was cooled to about 20° and to it was added 50 c.c. of 20% methyl alcoholic potassium hydroxide with constant shaking. The mixture was allowed to stand for 45 minutes at the same temperature and then poured into 250 c.c. of ice-water. The mixture was extracted 5 times with ether. The reddish brown aqueous solution was acidified with hydrochloric acid (Congo-red) and allowed to stand overnight. Next morning, the greater portion of methyl alcohol was removed under reduced pressure, then cooled and thrice extracted with ether (100 c.c.). The reddish brown ethereal extract was twice washed with 20 c.c. of 25% potassium carbonate solution and then with water. The ethereal digest was dried over anhydrous sodium sulphate and distilled. The residue solidified on keeping in an ice-chest for a few days. This was washed with a little ether and dried over a porous tile to remove adhering oil. This had m.p. 129.5° (1 g.).

The two crude fractions (*vide supra*) were mixed together and crystallised from alcohol, when colourless plates, m.p. 131.5°, were obtained. On further crystallisation from alcohol, acetone and benzene there was no change in m.p. Further distillation *in vacuo* at 140-45°/0.1 mm. the melting point could not be raised. (Found in a sample dried *in vacuo* over P_2O_5 for 3 hours at 90° : C, 74.12; H, 5.4. $C_{14}H_{12}O_3$ requires C, 3.7; H, 5.3 per cent).

Action of Dilute Alkali on Xanthyletin.—The substance (0.1 g.) in pure methyl alcohol (5 c.c.) was mixed with aqueous potassium hydroxide (40 c.c.) and the solution was refluxed on the water-bath for 1 hour. The yellow solution gradually turned brown. It was acidified with hydrochloric acid (congo-red), kept overnight and extracted with ether next morning. The residue obtained from the ethereal extract crystallised from alcohol in plates, m.p. 131.5° and no change in m.p. was noticed when mixed with the starting compound.

Catalytic Hydrogenation of Xanthyletin.—The substance (0.2 g.) was dissolved in glacial acetic acid (5 c.c.) and was shaken in an atmosphere of hydrogen with platinum oxide catalyst (0.1 g.). Hydrogen absorbed was found to be 42.9 c.c. at 27° and 762 mm. $C_{14}H_{12}O_3$ requires 42.74 c.c. at 27° and 762 mm.

The solution was filtered off from the catalyst, freed from the solvent and the residue was crystallised from alcohol. Colourless rhombic plates separated, which melted at 58.5° and showed no depression in m.p. when mixed with tetrahydroxanthyletin which melted alone at 158.5°.

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