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ISOLATION OF SCOPOLETIN, SKIMMIN AND UMBELLIFERONE FROM THE TRUNK-BARK OF *SKIMMIA LAUREOLA* HOOK

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Scopoletin, skimmin and umbelliferone have been isolated from the trunk-bark of *Skimmia laureola* Hook.

The leaves and the bark of *S. laureola* had been reported to contain a number of coumarin derivatives (Chatterjee and Bhattacharjee, this *Journal*, 1953, **30**, 33; *Curr. Sci.*, 1947, **16**, 222), but the occurrence of scopoletin in this plant had not been reported. Probably it could not be isolated because of its poor solubility in ether, which was employed by earlier workers. Scopoletin (0.035%), skimmin (0.50%) and umbelliferone (0.04%) have been isolated by the present authors in pure forms from the trunk-bark of *S. laureola*. Extraction with chloroform furnished a higher yield of scopoletin (0.025-0.035%) than that obtained by extraction with ether (0.005%).

The defatted trunk-bark after ether and chloroform extraction was percolated with ethanol from which skimmin, m.p. 204-208° (decomp.), had been obtained. On hydrolysis it yielded umbelliferone and glucose. The latter was identified as its osazone, m.p. 202°.

From the chloroform extract of the trunk-bark of the plant, another coumarin crystallised in star-shaped needles, m.p. 186-88°. It was obtained in poor yield (0.0005%) and gave identical colour reactions as scopoletin. Further work on this compound could not be done owing to paucity of the material.

The identity of coumarin, $C_{10}H_8O_4$, m.p. 202°, obtained from *S. laureola* Hook, with scopoletin has been established from mixed m.p., chemical analysis and spectral measurements of the compound and its derivatives. On methylation with diazomethane, the compound forms a dimethoxycoumarin, $C_{11}H_{10}O_4$, m.p. 144°. The latter has been shown to be identical with aesculetin dimethyl ether.

EXPERIMENTAL

Air-dried and powdered trunk-bark (1.0 kg.) was defatted with petroleum ether (b.p. 40-50°) for 24 hours and then soxhletted with ether (2 litres) for 60 hours. The ether extract (P) was kept aside. After ether extraction, the marc was extracted with chloroform for 60 hours. The chloroform extract was freed of the solvent when a pasty resinous mass (Q) separated.

Isolation of Skimmin

The defatted trunk-bark (100 g.), previously extracted with ether and chloroform, was percolated in cold with aqueous ethanol (60%). The brown extract (500 c.c.) was concentrated to 150 c.c. under vacuum at 50-60°. The insoluble resinous matter separated out and the supernatant solution was shaken with ether. The aqueous solution was removed and treated with a saturated lead acetate solution in excess. The lead precipitate was filtered off. The filtrate was treated with H_2S. The precipitated lead sulphide was removed. The light brown solution was then

concentrated under vacuum to a syrupy consistency (5 c.c.). No crystalline solid separated and the solution was subsequently evaporated to dryness in vacuum at room temperature. A sticky mass was obtained. It was taken up in methanol (50 c.c.) and treated with norite. The pale yellow solution was evaporated to dryness under vacuum when a light brown hygroscopic crystalline solid was obtained (0.5 g.). The compound decomposed above 210° with previous shrinking at 206°. (Found in a dry sample : C, 54.98 ; H, 4.82. Calc. for $C_{15}H_{16}O_8$: C, 55.55; H, 4.94%). The glucoside was hydrolysed with 5% H_2SO_4 for 6 hours on a water-bath. The solution was then cooled and shaken with ether. Umbelliferone was obtained from the ether extract which on crystallisation from ethyl acetate yielded colorless needles, m.p. 222-23°. It showed no depression in m.p. when admixed with an authentic sample of umbelliferone. The aqueous solution after removal of umbelliferone was neutralised with sodium carbonate and decolorised with norite, and treated with phenylhydrazine acetate. In about 10-15 mins. at the temperature of water-bath, yellow precipitate (sheaves of corn under a microscope) appeared. It was crystallised from dilute ethanol in yellow needles, m.p. 202-204°. Mixed m.p. with glucosazone remained undepressed.

Isolation of Umbelliferone and Scopoletin from Ether Extract (P)

The deep wine-red ether extract (P) was concentrated to half its bulk and shaken with 2*N*-HCl (3 × 200 c.c.). The brown ether solution (A) was kept aside. The wine-red aqueous acid layer was cooled and made alkaline with sodium bicarbonate and shaken with chloroform. The chloroform layer was separated from the alkaline solution (B). It was washed with water. The washings were added to (B) which was made feebly acidic (*p*H 2-3) and shaken with ether (4×250 c.c.). The ether extract was washed with a small quantity of saturated ammonium sulphate solution. It was dried over anhydrous sodium sulphate and the solvent was completely removed. The white solid was crystallised from ethyl acetate when scopoletin (0.05 g.) was obtained in colorless needles, m.p. 202°. It showed no depression in melting point with an authentic sample of scopoletin when admixed. [Found in a dry sample: C, 62.48; H, 4.13; OMe, 16.2; M.W., 196 (by Rast). Calc. for $C_{10}H_8O_4$: C, 62.5; H, 4.17; OMe, 16.14%; M.W., 192]. The compound showed the following peak absorptions : λ_{max} at 230mμ (log ε 4.18), 255mμ (log ε 3.79) and 347mμ (log ε 4.09); λ_{max} at 2.97 μ (— OH), 5.85 μ (conjugated lactone), 6.10 μ (unsaturation), 6.2 μ (phenyl nucleus), characteristic of scopoletin.

Methylation of scopoletin was performed by treating a methanolic solution of the substance with diazomethane in ether. The monomethylscopoletin was crystallised from methanol in colorless needles, m.p. 118°. (Found in a dry sample : C, 64.29; H, 5.48; OMe, 30.56. Calc. for $C_{11}H_{10}O_4$: C, 64.07; H, 5.34; OMe, 30.09%).

Isolation of Umbelliferone from 'A' (vide supra)

The brown ether solution was washed with water and then shaken carefully with 2% sodium bicarbonate solution (500 c.c.). The alkaline layer with a violet fluorescence was acidified (*p*H 2-3) when umbelliferone separated. It was taken up in ether and the solution was washed with water and dried over anhydrous sodium sulphate. The solvent was then removed to a small bulk and kept in a refrigerator overnight, when crude umbelliferone (0.5 g.), m.p. 220-27°, was obtained. It was crystallised from ethyl acetate in colorless needles (0.4 g.), m.p. 222-24°. (Found in a dry sample : C, 66.71; H, 3.72. Calc. for $C_9H_6O_3$: C, 66.66; H, 3.68%). The compound did not depress the m.p. of an authentic sample of umbelliferone when admixed. Its methyl ether, $C_9H_5O_2.OCH_3$, melted at 118-19°. (Found in a dry sample : C, 68.20; H, 4.61; OMe, 17.7. Calc. for $C_{10}H_8O_3$: C, 68.18; H, 4.54; OMe, 17.61%).

Isolation of Scopoletin from Fraction (Q) (vide supra)

The fraction (Q) was refluxed with dry benzene (500 c.c.) for 2 hours when most of the resin dissolved. The benzene solution was cooled and decanted. The clear benzene solution was carefully shaken with 2*N*-HCl (3×200 c.c.). The yellow aqueous acid layer was separated and treated with sodium bicarbonate till the *p*H of the solution was 2 to 3. It was then vigorously shaken with a litre of ether (4×250 c.c.). The ether solution was washed with a saturated ammonium sulphate solution, dried over anhydrous sodium sulphate and concentrated on a water-bath to about 20 c.c., when scopoletin (0.35 g.), m.p. 185-92°, separated as a granular solid. On repeated crystallisations from ethyl acetate, it yielded colorless needles (0.30 g.), m.p. 202°. From the mother-liquor coumarin, m.p. 186-88° (0.005 g.), was obtained.

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