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NOTES

Synthesis of fraxidin

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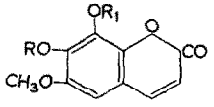
THE application[1] of Dakin's reaction to 7-methoxy-8-acetyl coumarin gives a satisfactory yield of 7-methoxy-8-hydroxy coumarin.

This method has been applied to the synthesis of fraxidin, a naturally occurring compound isolated by Späth and co-workers[2] from the bark of German ash wood and its constitution established as 6:7-dimethoxy-8-hydroxy coumarin (I). It was prepared by Wessley and Demmer[4] from fraxin, 6-methoxy-7-hydroxy-8-glucosidoxy coumarin by methylation and subsequent hydrolysis. Späth *et al.*[5] attempted the partial methylation of fraxetin (II) and obtained a mixture of the two monomethyl ethers (I) and (III) which was separated with difficulty. A satisfactory synthesis of fraxidin (I) has now been carried out using 6:7-dimethoxy-8-acetyl coumarin prepared by the method of Aghoramurty and Seshadri.[6] The identity of the final product was confirmed by the preparation of its methyl and ethyl ethers.



I $R=CH_3$; $R_1=H$
II $R=R_1=H$
III $R=H$; $R_1=CH_3$

EXPERIMENTAL

7-Methoxy-8-hydroxy coumarin. 7-Methoxy-8-acetyl coumarin[2] (2 g) was heated on a boiling water bath with aqueous sodium hydroxide (17 cc, 4%) for 15 min. The clear solution was cooled to 0° and hydrogen peroxide (1 cc, 30%) added during the course of 15 min. The mixture was left at 0° for 2 hr, acidified with dilute hydrochloric acid, extracted with ether and the ether evaporated. The residue was crystallised first from dilute methanol and finally from ethyl acetate as colourless rectangular prisms and needles, m.p. 172–73°, agreeing with the earlier record.[7] (Found: C, 62·2; H, 4·5; calc. for $C_{10}H_8O_4$: C, 62·5; H, 4·2%). On methylation with dimethyl sulphate and potassium carbonate in acetone solution it yielded 7:8-dimethoxy coumarin, m.p. 119–20°. Mixed m.p. with an authentic sample prepared by methylation of 7:8-dihydroxy coumarin[8] was undepressed. The same melting point was also recorded earlier.[9]

6:7-Dimethoxy-8-hydroxy coumarin (fraxidin) (I). 6:7-Dimethoxy-8-acetyl coumarin[6] (1 g) was dissolved in hot aqueous sodium hydroxide (10 cc, 4%), the solution cooled to 0° and treated slowly

[1] V. D. N. Sastri, N. Narasimhachari, P. Rajagopalan, T. R. Seshadri and T. R. Thiruvengadam, *Proc. Indian Acad. Sci.* **A37**, 681 (1953).
[2] D. B. Limaye and M. C. Joshi, *Rasayanam* 226 (1941).
[3] E. Späth and Z. Jerzmanowska Scienkiewiczowa, *Ber.* **B70**, 1019 (1937).
[4] F. Wessley and E. Demmer, *Ber.* **B62**, 120 (1929).
[5] E. Späth and Z. Jerzmanowska Scienkiewiczowa, *Ber.* **B70**, 1672 (1937).
[6] K. Aghoramurty and T. R. Seshadri, *J. Chem. Soc.* 3065 (1954).
[7] A. Gandini, *Gazz. Chim. Ital.* **70**, 611 (1940).
[8] V. Pechmann, *Ber.* **17**, 929 (1884).
[9] G. Bargellini, *Gazz. Chim. Ital.* **46**, 249 (1916).

with hydrogen peroxide (0·5 cc, 30%). After 2 hr at 0° it was acidified with dilute hydrochloric acid; the solid product (0·8 g) crystallised from methanol as colourless stout rectangular prisms, m.p. 196-97°. (Found: C, 59·5; H, 4·9; calc. for $C_{11}H_{10}O_6$: C, 59·5; H, 4·5%). Späth *et al.*[9] reported the same m.p.

Methylation with dimethyl sulphate and potassium carbonate in acetone solution gave 6:7:8-trimethoxy coumarin, m.p. 104-5°. Mixed m.p. with an authentic sample prepared by the methylation of 6-hydroxy-7:8-dimethoxy-coumarin with dimethyl sulphate and potassium carbonate in acetone medium was undepressed. Wessley and Demmer[10] reported same m.p. for this product.

The ethyl ether prepared by the ethylation of the above fraxidin sample crystallised from methanol as colourless fine needles, m.p. 108-9°, agreeing with fraxidin ethyl ether.[4]

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[10] F. Wessley and E. Demmer, *Ber.* **61**, 1279 (1928).

Padmatin,* a new component of the heartwood of *Prunus puddum*

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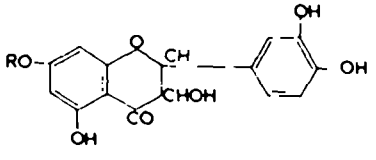
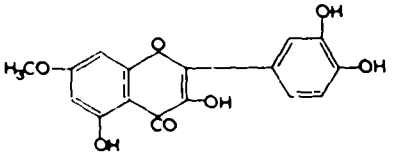
A NEW dihydroflavonol, Padmatin (Ib) has been isolated from the heartwood of *Prunus puddum*. A study of its reactions and properties indicates that it is 3:5:3′:4′-tetrahydroxy-7-methoxyflavanone and is related to taxifolin (Ia) since on methylation it gives taxifolin 5:7:3′:4′-tetramethylether. Oxidation of padmatin gives rhamnetin (II) which confirms the methoxy group in position 7.



Ia; R=H
Ib; R=CH_3



II

It has been recorded[1,2,3,4] that the components of the bark of *Prunus puddum* are 7-methyl ethers which resulted from the selective methylation of the corresponding hydroxy compounds which did not occur in the bark. The investigation of the heartwood has provided significant evidence in support of the suggestion because padmatin and its precursor taxifolin occur together in it. Another significant feature is the co-occurrence of taxifolin and its reduction product leucocyanidin in the wood.

EXPERIMENTAL

Extraction. Dry heartwood shavings (2 kg) were extracted (3 × 1 day) with cold light petroleum (b.p. 60–80°), the extract yielding on concentration a small amount of a wax, which gave no colour with alcoholic ferric chloride and with Mg and HCl. The residual heartwood was exhaustively extracted (6 × 12 hr) with boiling alcohol and the alcoholic solution concentrated to 300 cc under reduced pressure and excess of ether (3 l.) added. The mixture was kept in a refrigerator for one

* From the Indian plant Padmakashta. The investigation is Part VII of the series "Special components of commercial woods and related plant materia.l"

[1] N. Narasimhachari and T. R. Seshadri, *Proc. Indian Acad. Sci.* **30A**, 271 (1949).
[2] N. Narasimhachari and T. R. Seshadri, *Proc. Indian Acad. Sci.* **35A**, 202 (1952).
[3] B. Puri and T. R. Seshadri, *J. Sci. Industr. Res.* **13B**, 698 (1954).
[4] T. R. Seshadri, *Ann. Rev. Biochem.* **20**, 507 (1951).