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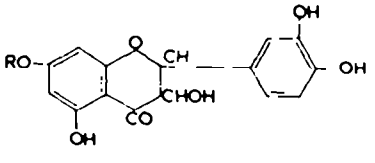
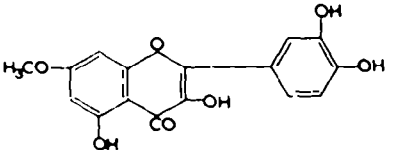
A NEW dihydroflavonol, Padmatin (Ib) has been isolated from the heartwood of *Prunus puddum*. A study of its reactions and properties indicates that it is 3:5:3′:4′-tetrahydroxy-7-methoxyflavanone and is related to taxifolin (Ia) since on methylation it gives taxifolin 5:7:3′:4′-tetramethylether. Oxidation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

month. The ether solution was separated from the sticky solid (fraction A), and concentrated to one litre, and extracted successively with 5% aqueous sodium carbonate (fraction B), 0·1% sodium hydroxide (fraction C) and 5% sodium hydroxide (fraction D). Complete evaporation of the remaining ether solution gave only a little wax.

Fraction A: (*leucocyanidin*). The sticky solid did not give a test for glycosides; after boiling with alcoholic sulphuric acid (7%), no test for sugars was obtained. Fraction A gave a test for leucocyanidin by the method already reported.[5]

Fraction B: (*taxifolin*. Ia). This fraction on acidifying with HCl deposited a dark product which solidified on cooling. It was filtered, washed with water and dried *in vacuo*. On dissolving in ethyl acetate (40 cc) and precipitating coloured impurities by adding light petroleum (b.p. 40–60°), the clear yellow solution on concentration gave a pale yellow solid (6·0 g) which on crystallisation from alcohol melted at 230–32°, and with ferric chloride in alcohol gave a brown colour, with Mg and HCl a red colour and with Zn and HCl a pink colour. Horizontal paper chromatography using phenol saturated with water gave Rf 0·78 at 33°. All these properties agreed with those of an authentic sample of ··-taxifolin and the mixed melting point was undepressed. The identity was confirmed by oxidation[6] with iodine, glacial acetic acid and potassium acetate yielding quercetin and subsequently quercetin penta-acetate.

Fraction C: [*genkwanin, sakuranetin and padmatin* (1b)]. Addition of HCl gave a sticky solid which was washed with water, filtered and dried (*in vacuo*) (3·5 g). It was dissolved in boiling methanol (50 cc), and on cooling a yellow crystalline solid (0·4 g) was deposited which when recrystallised from ethanol melted at 282–83°, undepressed by an authentic sample of genkwanin. Its acetate (acetic anhydride-pyridine) melted at 194–95°.

The methanolic mother liquor was evaporated and the residue dissolved in ether, and the solution extracted with saturated aqueous borax solution. The remaining ether solution yielded on evaporation sakuranetin, which crystallised from ethanol as colourless prismatic needles (0·2 g) m.p. 151–52°. Its acetate[7] formed small colourless prisms from ethyl acetate, m.p. 98–99°.

The solid that separated on acidifying the borax extract was filtered, dried and crystallised from ethyl acetate-petroleum ether mixture when colourless needles of padmatin (1 g), m.p. 170–71° were obtained. An alcoholic solution gave a deep brown colour with ferric chloride, red with Mg and HCl and pink with Zn and HCl acid (Found: C, 59·9; H, 4·2; OMe, 9·2; $C_{16}H_{14}O_7$ requires: C, 60·4; H, 4·4; OMe, 9·7%).

Methylation of padmatin to taxifolin-tetramethyl ether. Padmatin (1b, 0·3 g), anhydrous potassium carbonate (2·5 g), dry acetone (20 cc) and dimethyl sulphate (2 cc) were refluxed for 15 hr. The product crystallised from alcohol as colourless needles, m.p. 169–70° undepressed by an authentic sample of taxifolin tetramethyl ether.[8]

Iodine oxidation of padmatin to rhamnetin (II). Padmatin (1b, 0·5 g) was dissolved in glacial acetic acid (15 cc) and fused potassium acetate (2·5 g) added. Iodine (0·4 g) in glacial acetic acid (10 cc) was added to the boiling solution during the course of an hour and heating continued for another hour. Acetic acid was removed under reduced pressure and saturated sulphur dioxide water (150 cc) added. The solid obtained was filtered, washed with water and dried (*in vacuo*). It was first crystallised from ethylacetate-petroleum ether mixture and then from alcohol yielding yellow needles (0·2 g), m.p. 290–92° alone or when mixed with an authentic sample of rhamnetin. Circular paper chromatography using phenol saturated with water as solvent at 30° gave Rf 0·80, while butanol-acetic acid-water gave Rf 0·88. These properties and colour reaction, agreed with those of rhamnetin prepared by Jain *et al.*[9] Acetylation (acetic anhydride, pyridine) gave colourless needles of rhamnetin tetraacetate m.p. 186–87°; mixed m.p. with an authentic sample was undepressed. The infra-red spectra of the above product and an authentic sample of rhamnetin (solid in potassium bromide) showed peaks at 3·1(s), 6·2, 6·4(s), 6·7, 6·9(w), 7·5(w), 7·6(s), 8·1, 8·3, 8·6, 9·2(w), 9·7(w), 10·1, 10·5(w), 10·7(w), 11·4(w), 12·2, 12·7(w)μ.

Fraction D: (*sakuranetin and prunetin*). The extract was acidified with HCl and the precipitate was dried, refluxed with benzene (100 cc) and the solution filtered and concentrated to (40 cc). On cooling it deposited a colourless crystalline solid which on recrystallisation from ethanol gave

[5] R. Robinson and G. M. Robinson, *Biochem. J.* **27**, 206 (1933).
[6] V. B. Mahesh and T. R. Seshadri, *Proc. Indian Acad. Sci.* **41A**, 220 (1955).
[7] N. Narasimhachari and T. R. Seshadri, *Proc. Indian Acad. Sci.* **30A**, 274 (1949).
[8] A. C. Jain, K. S. Pankajamani and T. R. Seshadri, *J. Sci. Industr.* **12B**, 127 (1953).
[9] F. E. Kurth, *J. Org. Chem.* **21**, 304 (1956).

colourless prismatic needles (2·0 g) m.p. 151–52°. The product agreed in all its properties and colour reaction with sakuranetin. Its acetate prepared by the procedure of Narasimhachari *et al.*[7] gave small colourless prisms, m.p. 98–99°.

The benzene insoluble portion gave on crystallisation from alcohol pale yellow needles (1 g) m.p. 236–38°, undepressed by prunetin and acetylation yielded colourless needles, m.p. 222–24° undepressed by prunetinacetate.

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The preparation of nitroanthraquinones by the peracetic acid oxidation of aminoanthraquinones

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SOME time ago, in connection with other work, the need arose for quantities of 1-chloro-2-nitroanthraquinone. This compound had been prepared previously in 36 per cent crude yield[1] from 2-amino-1-chloroanthraquinone via the diazonium sulfate, and in unspecified yield[2] by persulfuric acid oxidation of the amine. However, we were induced to consider the use of peracetic acid for this oxidation by a report[3] of the simple conversion, in this manner, of 1:2-diaminoanthraquinone into 1-amino-2-nitroanthraquinone.

The reaction proved to be so convenient and efficient that the preparation of other nitroanthraquinones was examined. Nine amino-anthraquinones were thus converted into their nitro homologs in yields ranging from 35–82 per cent. The best yields (61–82 per cent) were encountered in the oxidation of simple aminohaloanthraquinones. The presence of negative groups adjacent to the amino group appears beneficial, since 2:6-diamino-1:5-dichloroanthraquinone and 1:4-diamino-2:3-dichloroanthraquinone were successfully oxidized, while the corresponding unchlorinated diamines gave only mixtures of unidentified products.

Kopetschni reported[2] 1-amino-4-chloroanthraquinone to be oxidized only to the nitroso homolog by the action of persulfuric acid. Peracetic acid oxidation, however, readily produced 1-chloro-4-nitro-anthraquinone. Oxidation of 1:2-diaminoanthraquinone produced, as reported,[3] some 1-amino-2-nitroanthraquinone provided the reaction mixture was heated only briefly. Continued heating, however, gave mixtures of unidentified products, in which, to judge from the yellow color, the 1-amino group was no longer present.

The reaction of 1:4-diamino-2:3-dichloroanthraquinone was unique in that only one of the amino groups suffered oxidation. Heating the product with fresh peracetic acid produced no further oxidation. On the other hand, the introduction of two nitro groups into the same ring appears to be no obstacle, since 2:3-dinitroanthraquinone was obtained from 2-amino-3-nitroanthraquinone.

Recently, Emmons described[4] his careful work upon the peracetic acid oxidation of simple amines to nitro homologs, and indicated that inferior results were obtained in the case of weakly basic or negatively substituted amines. Our results appear to contradict this generalization (as amines of the anthraquinone series are very weakly basic), and are more in agreement with the results obtained[4] by using peroxytrifluoro-acetic acid as the oxidant. It is possible that the use of the latter reagent would give superior yields in the oxidation of aminoanthraquinones, but this was not investigated.

EXPERIMENTAL

General procedure. Commercial 40% peracetic acid and a product of similar strength prepared[5] by admixture of 30% hydrogen peroxide, acetic anhydride and acetic acid, were used interchangeably.

[1] W. Bradley and E. Leete, *J. Chem. Soc.* 2129 (1951).
[2] E. Kopetschni, *Ger. Pat.* 363,930; *Frdl.* **14**, 850 (1926).
[3] I. G. Farbenindustrie, A. G., *P.B. Report No.* 70341, frames 14040-2.
[4] W. D. Emmons, *J. Amer. Chem. Soc.* **79**, 5528 (1957).
[5] W. D. Emmons, *J. Amer. Chem. Soc.* **76**, 3470 (1954).

All melting points were taken in Pyrex capillaries using a Hershberg melting point apparatus and Anschütz thermometers.