

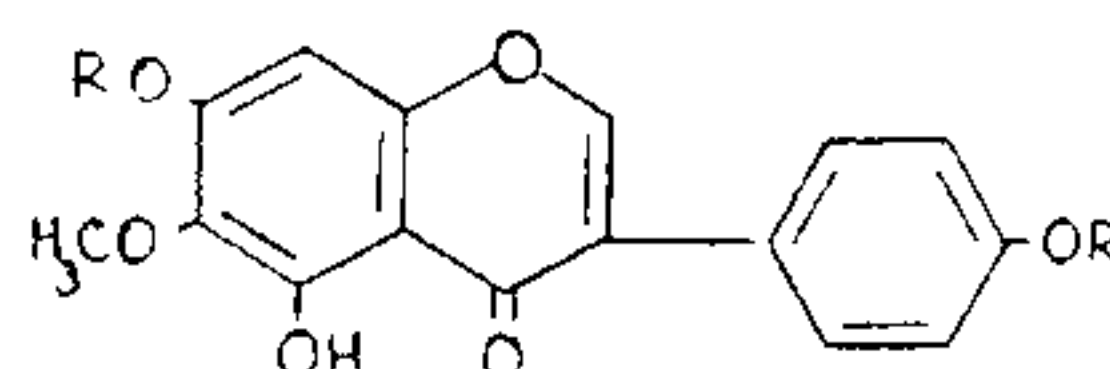
OCCURRENCE OF 7, 4'-DIMETHYL- TECTORIGENIN IN THE FLOWERS OF *DALBERGIA SISSOO*

THE occurrence of three isoflavones, biochanin-A, tectorigenin and 7-methyltectorigenin, in the flowers of *Dalbergia sissoo* has been reported earlier.¹ The identification of another isoflavone, 7, 4'-dimethyltectorigenin, in the same source is described in the present communication.

The air-dried flowers were extracted by cold percolation with petroleum ether and then ether; the ether extract, on concentration, deposited a white solid which was found to be a mixture of three substances by thin-layer chromatography [chloroform: methanol (9:1), silica gel G, alcoholic ferric chloride spray]. The two slower moving components were identified as tectorigenin and 7-methyltectorigenin by cochromatography with authentic specimens but the fastest moving substance did not correspond to any of the compounds isolated earlier from the flowers. This was obtained in a pure condition by refluxing the above crude solid with petroleum ether followed by repeated fractional crystallisation from methanol (yield, 31 mg. from 800 g. of flowers). The methanol mother liquors contained 7-methyl tectorigenin and the ethereal solution, after removal of these two compounds, contained tectorigenin.

The sparingly soluble compound mentioned above had m.p. 184° and was homogeneous when examined by TLC. Analysis agreed with the molecular formula $C_{18}H_{16}O_6$ and the presence of three methoxyl groups. It did not give a red colour on reduction with magnesium and hydrochloric acid in alcoholic solution; however, a pink colour was obtained on reduction with sodium amalgam in alcoholic solution followed by acidification. This test indicated the isoflavone nature of the substance. The U.V. spectrum of the compound [$\lambda_{\text{max}}^{\text{EtOH}}$ 267 m μ (log ϵ , 4.50); inflexion at 325 m μ (log ϵ , 3.60)] supported this inference and resembled those of tectorigenin and its derivatives. The compound gave a purple ferric reaction (becoming green with excess of the reagent) showing the presence of a chelated phenolic hydroxyl group; this was supported by the insolubility of the compound in aqueous sodium carbonate solution. On acetylation (acetic anhydride-pyridine) a monoacetate of the formula $C_{20}H_{18}O_7$ (m.p. 211°) was obtained suggesting the presence of one hydroxyl group in the molecule.

Complete methylation of the substance (methyl sulphate-potassium carbonate in acetone) gave a monomethyl ether (m.p. 178°) which was identified as 5, 6, 7, 4'-tetramethoxy isoflavone by m.m.p. determination with an authentic sample. It was, therefore, concluded that the compound m.p. 184° is, most probably, 5-hydroxy-6, 7, 4'-trimethoxy isoflavone (7, 4'-dimethyltectorigenin). A comparison of its U.V. spectrum ($\lambda_{\text{max}}^{\text{EtOH}}$ 267 m μ) with those in the presence of sodium acetate (λ_{max} 267 m μ) and of aluminium chloride (λ_{max} 275 m μ) supported this structure. A direct comparison (m.p. and m.m.p.) of the compound and its acetate with synthetic 5-hydroxy-6, 7, 4'-trimethoxy isoflavone and its acetate^{2,3} established their identities.



- I $R = R' = H$
 II $R = CH_3$; $R' = H$
 III $R = R' = CH_3$

The occurrence of so many partial methyl ethers of 5, 6, 7, 4'-tetrahydroxy isoflavone in *Dalbergia sissoo* flowers may be of significance. The simplest of these is tectorigenin (I); the biogenesis of this compound is probably similar to that of the 6-methyl ethers of flavonoids which has been discussed earlier.^{4,5} It seems to undergo stepwise methylation, first in the most active 7-position to yield 7-methyltectorigenin (II) and next in the 4'-position to form 7, 4'-dimethyltectorigenin (III). In these flowers the resistant 5-hydroxyl group is left unmethylated.

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