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A NATURAL FLAVAN.

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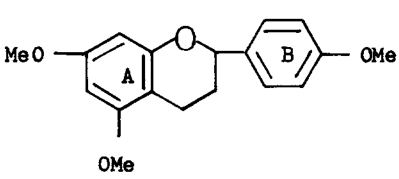
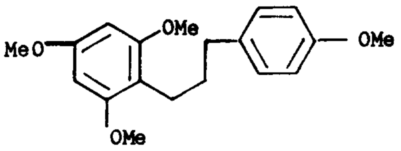
The resinous exudates of Australian Xanthorrhoea (Liliaceae) ("blackboys") contain a complex mixture of aromatic compounds[1]. The pure substances so far isolated in small proportion are chiefly related to flavonoids[2] although some naphthalene[3] and probably anthracene[2] derivatives are sometimes present. The fresh exudate is chemically simpler than the aged resin, that of X.hastile consisting largely of cinnamyl p-coumarate[4]. From the commercial resin of X.preissii, kindly supplied by Mr. A.R.Penfold, we have extracted naringenin and what is probably its 5-methyl ether, both soluble in carbonate solution[5]. The caustic-soluble main fraction, after methylation with methyl sulphate and potassium carbonate in acetone, gave by chromatography on alumina small proportions of crystalline compounds. These included 6'-hydroxy-2',4,4'-trimethoxychalcone, m.p. 112-114°, 5,7-dimethoxyflavanone, m.p. 168-170°, and a substance $C_{18}H_{20}O_4$ m.p. 109-111°, shown to be (I) on the basis of the information below.

The ultra-violet spectrum, λ_{max} 235(sh.), 274, 280(sh.) mμ log ε, 4.42, 3.36, 3.26 indicates an unconjugated aromatic system. The infra-red spectrum indicates the absence of carbonyl and hydroxyl. The p.m.r. spectrum showed resonances at τ 6.2 (6H) and 6.27 (3H) corresponding to 3 OMe; the aromatic protons appear as a symmetrical multiplet characteristic of an A_2B_2 system, τ 2.89 (4H) and an AB quartet (J 3 c.p.s.) τ 3.92 (2H). The aliphatic CH appears at τ 5.1 as a quartet and the remaining aliphatic protons appear as methylene multiplets at τ 7.36 (2H) and 7.9 (2H). All the protons of (I) are thus accounted for. The authentic (I) is recorded[6] to have m.p. 107-108°. Reduction of (I) with sodium and ethanol in liquid ammonia[7] and methylation gave (II), m.p. 64.5 - 65.5°, shown by mixed m.p. to be identical with the authentic substance kindly supplied by Professor J.W.Clark-Lewis.

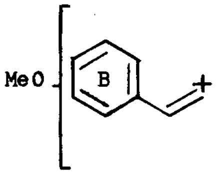
Before this comparison was made (I) was submitted to mass spectrometry by Dr.M.Barber (A.E.I.) and Dr.A.Pelter, the results when taken in conjunction with their other work on related compounds[8], support the structure (I). A peak at m/e 300 confirms the parent formula $C_{18}H_{20}O_4$, and one at 134 corresponds to a mono-methoxy ring-B (fragment (III). A peak at m/e 166 corresponds to (IV), confirming two OMe in ring-A. The flavan structure is also supported by a peak at m/e 179 corresponding to (V)[8].



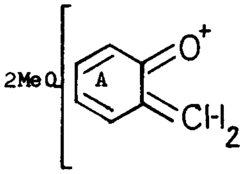
I



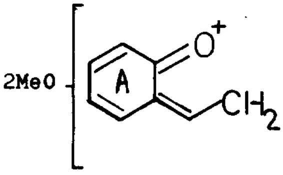
II



III



IV



V

The flavan (I) must be present in the original resin as a phenolic precursor of an unknown degree of methylation (if any). Since (I) is unstable to light and air, darkening to a red resin, the phenol is probably more unstable and some at least of the red plant resin may arise from it. (I) is optically inactive, although the flavanones present are laevorotatory, but seems unlikely to be an artifact apart from the Me groups. It is the first flavan derivative to be obtained from natural sources not containing an oxygen attached to the heterocyclic ring, and completes the series, those already known having oxygen at the 3 or 4 or the 3,4-positions. The pigments dracorubin and dracorhodin[9] probably arise by oxidation of a similar flavan; possibly the red Xanthorrhoea resins contain similar oxidation products.

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