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THE STRUCTURE AND SYNTHESIS OF CORYMBOSIN, A FLAVONE FROM WEBERA CORYMBOSA Willd.*

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From the hexane extract of the leaves of Webera Corymbosa Willd. (Rubiaceae) a hitherto unreported natural flavone, corymbosin has been isolated. It has m.p. 188–189° and analyses for $C_{19}H_{18}O_7$ (mol. wt. by mass spec. 358) (Found : C, 63.6; H, 5.0; $C_{19}H_{18}O_7$ requires C, 63.7; H, 5.1%). The brown ferric colour and a red magnesium-hydrochloric acid colour in ethanolic solution indicated that the compound is a flavone derivative with a phenolic hydroxyl group. It formed a monoacetate m.p. 178° (Found : C, 63.1; H, 5.0; $C_{21}H_{20}O_8$ requires C, 63.0; H, 5.0%) on acetylation with pyridine-acetic anhydride. Corymbosin did not show any IR bands in the hydroxyl region and the carbonyl absorptions were at 1670 and 1630 cm^{-1}. The UV spectrum was characteristic of flavones with λ_{max}^{EtOH} 211, 240 (infl.), 272 and 332 mμ (log ∈ 4.44, 4.12, 4.04 and 4.08) unaltered by the addition of sodium acetate. Addition of aluminium chloride to the ethanolic solution showed bathochromic shifts of bands I and II with λ_{max} 211, 280, 304 and 385 mμ indicative of a 5-hydroxy flavone[1]. The NMR data (Table I) showed the presence of four methoxyl groups and the one proton singlet at 12.7 δ indicated a strongly hydrogen bonded hydroxyl group which could be placed in the 5-position[2]. In the aromatic region the two proton singlet at 7.12 δ could be ascribed to the 2', 6' protons of ring C, a singlet at 6.6 δ to the 3 proton of

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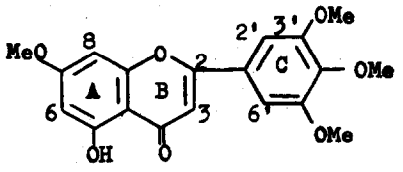
ring B and the AB quartet centered at 6.44 (J = 2 c/s) to the 6,8-meta protons of ring A. This evidence pointed to structure (I) for corymbosin.



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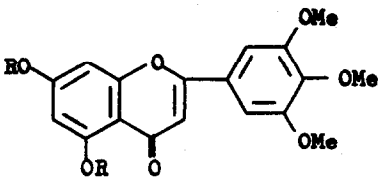

II

TABLE I

NMR Spectral Data

Compound	Type of protons	(No. of protons)	Shape of peaks (J)
Corymbosin I (in $CDCl_3$)	3', 5', 7 - OMe	3.97 (9)	Singlet
	4'- OMe	3.9 (3)	Singlet
	5 - OH	12.7 (1)	Singlet
	2', 6'- H	7.12 (2)	Singlet (unresolved)
	3 - H	6.6 (1)	Singlet
	6, 8 - H	6.38 (1), 6.5 (1)	AB quartet (2 c/s)
II; R = H (in DMSO + $CDCl_3$)	3', 5'- OMe	3.98 (6)	Singlet
	4'- OMe	3.83 (3)	Singlet
	2', 6'- H	7.21 (2)	Singlet
	3 - H	6.85 (1)	Singlet
	6, 8 - H	6.25 (1), 6.5 (1)	AB quartet (J = 2 c/s)
II; R = Ac (in $CDCl_3$)	5 - COMe	2.35 (3)	Singlet
	7 - COMe	2.43 (3)	Singlet
	3', 4', 5'- OMe	3.95 (9)	Singlet
	3 - H	6.59 (1)	Singlet
	2', 6'- H	7.1 (2)	Singlet
	6, 8 - H	6.85 (1), 7.38 (1)	AB quartet (J = 2 c/s)

A final proof of the constitution was provided by synthesis of (I). The dihydroxy flavone (II: R=H) was prepared by the Allan-Robinson method[3] and also by the condensation of phloroglucinol with ethyl-3,4,5-trimethoxybenzoyl acetate[4]. It formed a diacetate (II; R = Ac) m.p. 155°C (Found : C, 61.8; H, 4.7; $C_{22}H_{20}O_9$ requires C, 61.7; H, 4.7%). Methylation of II with diazomethane afforded (I) identical in all respects with corymbosin.

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