Phytochemical Investigation on the Leaves of *Callicarpa macrophylla* Vahl.

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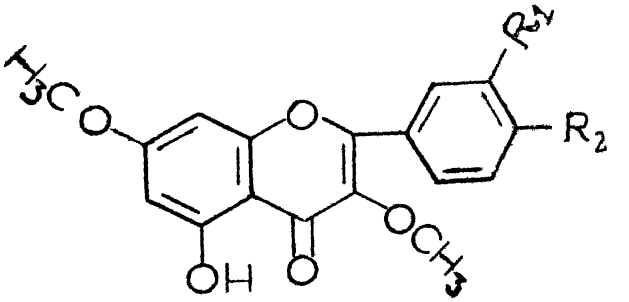
PHYTOCHEMICAL investigation on the leaves of *Callicarpa macrophylla* Vahl. (Fam. Verbenaceae), led to the isolation of a number of terpenoids, sterols and some known flavonoids[1,2,3a,3b,3c]. The medicinal and piscicidal properties of this plant are well known[4,5,6a,6b,6c]. As a part of our programme on plants possessing antifeeding principles we became interested to reinvestigate the leaves of *Callicarpa macrophylla*. A flavone provisionally designated as CMF-1 has been isolated from the petrol ether extract of this plant along with ursolic acid and β-sitosterol. The characterisation of the flavone, CMF-1 is described in this communication.

The concentrated petroleum ether extract of the leaves of *C. macrophylla* on chromatographic resolution over silica gel and elution with benzene-ethylacetate (9.5 : 0.5) afforded a yellow solid which crystallised from petrol-benzene as pale yellow needles, m.p. 165-66°, $C_{18}H_{16}O_7$ (M^+ 344). A positive Shinoda test indicated it to be a flavone. Functional group analysis revealed the presence of three-OMe (one 6*H* singlet at 3.95δ and one 3*H* singlet at 4.0δ), an α, β-unsaturated ketone (ν_{max}^{KBr} 1660, 1600 cm^{-1}), a chelated phenolic -OH (ν_{max}^{KBr} 3460 cm^{-1}, 1*H* singlet at 13.4δ, exchangeable with D_2O, brown colour wiih $FeCl_3$), a phenolic -OH group (1*H* singlet at 6.0δ, exchangeable with D_2O) and a complex aromatic substitution pattern (ν_{max}^{KBr} 1490, 1350, 1210, 1155, 810, 710 cm^{-1}). The presence of five aromatic protons is also discernible in the NMR spectrum. The substitution pattern of this compound is assignable from the NMR spectrum. In the NMR spectrum the-quartet at 6.42δ (J=3Hz) for 2*H* is due to the C_6 and C_8 protons[7]. The doublet at 7.04δ (J=9 Hz) is assigned to the $C_{2'}$ and $C_{6'}$-protons[8]. An 1*H*-multiplet at 7.68δ (J=6 Hz) suggests the presence of $C_{5'}$-H in the compound. It appears, therefore, that the compound has got two substitutions in both A and B-rings respectively. No bathochromic shift of the longest wave length with $AlCl_3$ is a clear indication that there is one methoxyl group at C_3-position[9] [λ_{max}^{EtOH} 255, 357 nm, $\lambda_{max}^{EtOH+AlCl_3}$ 268, 360 nm] which is also in agreement with the mass spectral data[10] [m/e 329 ($M-CH_3$) and m/e 301 ($M-COCH_3$)]. The UV spectrum remained, however, unaffected in the presence of sodium acetate, indicating thereby that there is a $-OCH_3$ group[9] at C_7. Based on these evidence, the structure of the flavone may be written as (I) or (II), which is also consistent with the mass spectral fragmentation pattern. [m/e (M^+) 344, m/e 329 (M^+-15), m/e 301 (M^+-43), m/e 258, m/e 243, m/e 215, m/e 267 and m/e 105 (RDA fragments)].



I. $R_1=OH$, $R_2=OCH_3$
II. $R_1=OCH_3$, $R_2=OH$

A flavone having structure (II) has already been isolated from the plant *Larrea cauneifolia*[7] Cav. The UV and mass spectral data of (II) show close resemblance with the flavone, CMF-1 isolated by us. But we have observed certain differences in respect of the NMR signals of some protons and the UV shifts with $AlCl_3$ and NaOAc. However, a direct comparison of the properties (m.p., m.m.p., Co-TLC) of CMF-1 with those of the flavone (II)[7] was found to be similar, thereby proving the identity of CMF-1 as 5, 4'-dihydroxy 3. 7, 3'-trimethoxy flavone.

Experimental

M. p. is uncorrected, UV spectra were recorded in EtOH. For column chromatography silica gel (Gouri Chemicals, Calcutta, 60-100 mesh) was used. NMR spectrum was recorded in $CDCl_3$ with TMS as internal standard. The leaves of *C. macrophylla* were collected during the month of January, 1976.

Isolation

Air dried powdered leaves of *C. macrophylla* (1.5 kg) were exhaustively extracted (24 hr) with petroleum ether (60-80°) and the resulting extract was concentrated and chromatographed over silica gel (300 g). The chromatogram was eluted with solvents of increasing polarity. Benzene-ethyl acetate (1 : 1) eluates afforded a yellow oily residue which was further purified by rechromatography over silica gel. Elution of this chromatogram with benzeneethylacetate (9.5 : 0.5) furnished a yellow solid which crystallised from benzene-petrol as yellow needles, m.p. 165-66° (yield 0.002%) TLC: Rf. 0.7. (benzene-ethyl acetate-1 : 1), +ve Shinoda Test, +Ve $FeCl_3$ color reactions.

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