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NOTE

Further Works on *Limnophila rugosa* (Roth.) Merill and *Hoppea fastigiata* Clarke (Gentianaceae)

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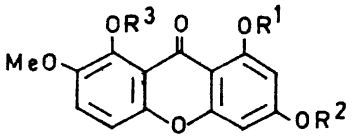
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In continuation of our previous studies on *Limnophila rugosa*[1,2] and *Hoppea fastigiata*[3], we now report the isolation and characterisation of one more flavone from petroleum ether extract of *L. rugosa* and a new xanthone from methanolic extract of *H. fastigiata.*

The concentrated petroleum ether (b.p. 60–80°) extract of the aerial parts and roots of *L. rugosa* on chromatographic analysis over silica gel (60–120 mesh) afforded a yellow solid crystallised from benzene as needles, $C_{16}H_{12}O_6$, m.p. 206–08°, [M^+] *m/z* 300, in petroleum ether-benzene (1 : 1) elute. It responded positively to flavonoid test with magnesium and hydrochloric acid and exhibited λ_{max} (EtOH) 220 (log ε 4.30), 280 (4.10), 325 (4.20) nm; ν_{max} (KBr) 3 350 (bonded OH), 1 640, 1 600 and 1 570 cm^{-1} (chelated α,β-unsaturated carbonyl). The ^1H nmr spectrum (90 MHz; $CDCl_3$) of the parent flavone showed resonance for one methoxyl attached to aromatic ring at δ 4.25 (3H, s), one proton singlet at 7.10 assignable to C_3-proton, two A-ring protons at C_6 and C_8 appearing respectively at 7.25 (1H, d, *J* 2.5 Hz), 7.45 (1H, d *J* 2.5 Hz) and three aromatic proton signals at 8.00 (1H, d, *J* 10 Hz), 6.80 (1H, d, *J* 10 Hz) and 7.45 (1H, d, *J* 2.5 Hz) suggestive of the presence of a 2′,4′-disubstituted B-ring[4] in the compounds. On methylation with diazomethane, the flavone formed a dimethyl derivative, $C_{18}H_{16}O_6$, m.p. 186–88°, which was found to be identical with 5-hydroxy-7,2′,4′-trimethoxyflavone[2] in all respects (m.m.p., co-ir and co-tlc). Thus the bonded hydroxyl group in the compound must be at C_5 position. The parent flavone does not exhibit any significant change of short wavelength band at 280 nm on addition of NaOAc solution locating thereby the presence of the only methoxyl group at C_7 position[5]. Further, on methylation with dimethyl sulphate and potassium carbonate, the flavone forms a trimethyl derivative, $C_{19}H_{18}O_5$, m.p. 178–79°, which was found to be identical with 7,5,2′,4′- tetramethoxyflavone[4] by comparison of physical and spectral data. The above spectral and chemical evidence led us to identify this flavone as 7-methoxy-5,2′,4′-trihydroxyflavone (artocarpetin)[6].

The methanolic extract of *H. fastigiata* on usual chromatography over silica gel yielded a light yellow solid, $C_{14}H_{10}O_6$, m.p. 258–59°, [M^+] *m/z* 274; λ_{max} (EtOH) 240, 261, 320 and 370 nm (characteristic of 1,3,7,8-tetraoxygenated xanthone)[7]; ν_{max} (KBr) 3 390 (br, chelated hydroxyl), 1 660, 1 625, 1 615 and 1 590 cm^{-1} (chelated α,β-unsaturated carbonyl). The spectral evidence suggests the presence of a 1,3,7,8-tetraoxygenated xanthone nucleus in the compound. The ^1H nmr spectrum (90 MHz; $CDCl_3$) of the compound showed two *meta*-coupled proton signals at δ 6.40 (1H, d, *J* 3 Hz), 6.65 (1H, d, *J* 3 Hz) and two *ortho*-coupled signals at δ 7.12 (1H, d, *J* 9 Hz) and 7.40 (1H, d, *J* 9 Hz) in addition to a singlet of three protons at

δ 3.92 due to three protons of methoxy group attached to aromatic ring. On complete methylation with dimethyl sulphate and potassium carbonate, the xanthone afforded a trimethyl derivative, $C_{17}H_{16}O_6$, m.p. 162–65° [M^+] *m/z* 316. Further, this trimethyl derivative was identified as 1,3,7,8-tetramethoxyxanthone (**2**)[8] by comparison of physical constants and spectral data. This confirms that four oxygen substituents (three hydroxy and one methoxy) in the compound are present at 1, 3, 7 and 8 positions. Again, on methylation with diazomethane the parent xanthone forms only a monomethyl derivative, $C_{15}H_{12}O_6$, m.p. 190°, (M^+ 288) (**3**), indicating the presence of two bonded hydroxyl groups in the molecule. The presence of two bonded hydroxyls along with the absence of any peak at *m/z* (*M*-18)[9] ruled out the possibility of locating the only methoxyl group of the compound either at C_1 or at C-8. In the uv absorption spectrum of the xanthone in ethanolic sodium acetate solution, there was a bathochromic shift of longer wavelength maximum by 20 nm (370 → 390 nm). This suggests the absence of methoxy group at C_3 position[10]. Consequently, the only methoxy group in the xanthone must be at C_7. Therefore, this new xanthone was characterised as 1,3,8-trihydroxy-7-methoxyxanthone (**1**).



1 ; $R^1 = R^2 = R^3 = H$
2 ; $R^1 = R^2 = R^3 = CH_3$
3 ; $R^1 = R^3 = H$, $R^2 = CH_3$

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