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VERBENACEAE

5,6,7-TRIMETHOXY FLAVONE FROM CALLICARPA JAPONICA

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Kutney and Hall¹ recently reported 5,6,7-trimethoxy flavone for the first time in Zeyhera tuberculosa. The same compound has now been isolated from Callicarpa japonica Thunb., and found to show piscicidal activity against Oryzias latipes.

The piscicidal principal (I) was obtained by column chromatography of the benzene extract of air-dried leaves over alumina and silica gel. (I) recrystallized from ethyl acetate gave a colorless prism crystal which yielded about 0.2% from dry wt, m.p. $167-167.5^{\circ}$; $C_{18}H_{16}O_5$; ν_{max} (KBr) 1630 cm⁻¹; λ_{max} (EtOH) 265 (log ϵ 4.37), 305 (log ϵ 4.34) nm; NMR, δ 3.89, 3.95, 3.97 (5,6,7-OMe), 6.62 and 6.81 (3 or 8-H), 7.48 (3',4',5',-H), 7.84 (2',6'-H) ppm in CDCl₃.

Demethylation of (I) with AlCl₃ afforded a trihydroxy derivative (II), m.p. 263-264°; ν_{max} (KBr) 1655 cm⁻¹; NMR, δ 12.66 (5–OH) ppm in DMSO- d_6 . (II) was methylated with diazomethane to give a 5-hydroxy-6,7-dimethoxy derivative (III), m.p. 162–163°; ν_{max} (KBr) 1665 cm⁻¹; NMR, δ 12.70 (5–OH) ppm in CDCl₃.

Anker et al.² found that the signals of the flavones shifted to the downfield by adding CF_3COOH to the $CDCl_3$ solution. We applied this technique to (I), and its values were in good agreement with those of 5,6,7-trimethoxy flavone. Since, furthermore, the melting points of (I), (II), and (III) approximated to the reported values, (I) was not 5,6,8- or 5,7,8- trimethoxy flavone but 5,6,7-trimethoxy flavone.

The UV spectrum of (II) showed λ_{max} (MeOH) 274 and 323 nm, and the spectra which added AlCl₃ (247, 272, and 375 nm). AlCl₃-HCl (282 and 346 nm), NaOAc (252 and 360 nm), NaOAc-H₃BO₃ (277 and 333 nm), and sodium methoxide (257 and 366 nm), showed a good agreement with those of baicalein.³

The alkaline degradation of (I) gave benzoic acid and 2-hydroxy-4,5,6-trimethoxyacetophenone which was identified with the synthetic material using IR and NMR spectra.

A piscicidal activities of (I), (II), and (III) were tested, and their TLM were at 5, 2 and 2 ppm, respectively.

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