SHORT COMMUNICATIONS

BIFLAVONES FROM THE LEAVES OF FITZROYA PATAGONICA HOOK F.

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Previous work on Fitzroya patagonica has revealed the presence of amentoflavone, cupressus flavone and hinokiflavone, and partial identification of mono-O-methylated flavone and apigenin. In the present investigation, we report the isolation and characterization of podocarpus flavone (Ia) and isocryptomer (IIa) in addition to the other reported biflavones. The isolation of isocryptomerin from the first time from genus Fitzroya is of chemotaxonomic significance and shows chemical affinity of the genus with other comifers.

The acetone extract of the air-dried and powdered leaves of F. patagonica (1.0 kg) procured from Sims park, Coonoor, India, was concentrated and treated with petrol (60–80), benzene and chloroform, successively, till the solvent in each case was almost colourless. The residue was treated with boiling water and the insoluble gummy mass was dried and extracted with ethyl acetate. The ethyl acetate extract was evaporated to dryness to yield a dark brown solid (2.5 g) which responded to the colour test with Zn-HCl (pink).

TLC examination [silica gel (BDH), benzene-pyridine-formic acid (BPF), 36:9:5] showed three compact spots. The crude product was separated by preparative TLC (silica gel, BPF, 36:9:5) into three components which were labelled as FP-I (300 mg, Rf 0.18), FP-II (100 mg, Rf 0.34), and FP-III (80 mg, Rf 0.52).

FP-I: FP-I was found identical with the constituents reported earlier.

FP-II: FP-II was comparable with podocarpus flavone-A on TLC. But on methylation it gave a mixture of hinokiflavone pentamethyl ether (minor) and amentoflavone hexamethyl ether (major). FP-II was acetylated with pyridine and acetic anhydride. The acetate, on crystallization from CHCl3-MeOH, gave colourless needles of the major constituent, m.p. 255–56°. It was characterized as 4', 5, 5', 7, 7'-pentaacetoy-4'-O-methylamino flavone (Ib). 1H NMR (CDCl3, 100 MHz, δ-scale) of Ib: 7.25 (1H, d, J = 3 Hz, H-8), 6.84 (1H, d, J = 3 Hz, H-6), 6.98 (1H, s, H-6'), 7.40 (1H, d, J = 9 Hz, H-5'), 7.99–8.03 (2H, m, H-2', 6'), 7.49 (2H, d, J = 9 Hz, H-2'', 6''), 6.78 (2H, d, J = 9 Hz, H-3'', 5''), 6.60, 6.68 (1H each, s, H-3, 3'), 2.05 (3H, s, OAc-4'), 3.76 (3H, s, OMe-4''), 2.44, 2.48 (6H, singlets, OAc-5,5') and 2.08, 2.31 (6H, singlets, OAc-7, 7').

FP-III: FP-III was comparable with isocryptomerin and its permethylated derivative was identical with hinokiflavone pentamethyl ether. FP-III was acetylated with pyridine and acetic anhydride and crystallized from CHCl3-MeOH to yield colourless needles of isocryptomerin tetraacetate (Ib), m.p. 213–14°.

1H NMR (100 MHz, CDCl3, δ-scale): 6.84 (1H, d, J = 3 Hz, H-6), 7.31 (1H, d, J = 3 Hz, H-8), 7.24 (1H, s, H-8'), 6.62 (1H, s, H-3), 6.58 (1H, s, H-3'), 7.79 (2H, d, J = 9 Hz, H-2', 6'), 7.91 (2H, d, J = 9 Hz, H-2'', 6''), 7.03 (2H, d, J = 9 Hz, H-3', 5'), 7.24 (2H, d, J = 9 Hz, H-3'', 5''), 3.92 (3H, s, OMe-7''), 2.44 (3H, s, OAc-5'), 2.35 (6H, s, OAc-5,7) and 2.31 (3H, s, OAc-4'').

29 December 1986; Revised 20 March 1987