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2′-*O*-METHYLCAJANONE: A NEW ISOFLAVANONE FROM *CAJANUS CAJAN*

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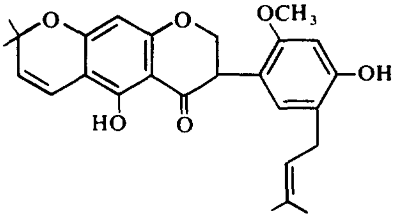
Key Word Index—*Cajanus cajan*; Papilionaceae; 2′-*O*-methylcajanone;5,4′-dihydroxy-2′-methoxy-5′-(3‴-methyl-2‴-butenyl)-2″,2″-dimethylpyrano-[5″,6″:6,7]-isoflavanone.

In continuation of our work [1, 2] on the chemical investigation of the root bark of *Cajanus cajan*, we now report the isolation and characterization of 2′-*O*-methylcajanone (1). The C_6H_6 extract of the root bark, on column chromatography over Si gel using solvents of increasing polarity, yielded a fraction on elution with C_6H_6, which on preparative TLC gave 2′-*O*-methylcajanone (1) as yellow crystalline solid from EtOAc–petrol; M^+ 436 ($C_{26}H_{28}O_6$), mp 85°; optically inactive; TLC, R_f: 0.65 (Si gel, EtOAc–C_6H_6, 1:9); olive green ferric reaction, a negative Shinoda and positive Na(Hg)/HCl tests; λ_{max}^{MeOH} nm: 225, 270, 355; +$AlCl_3$–HCl, 285, 325. The IR(KBr) showed strong absorptions at 3448 (OH) and 1648 cm^{-1} (chelated $\rangle$C=O). It formed a diacetate (Py/Ac_2O) indicating the presence of two hydroxyl groups.

The PMR (60 MHz, $CDCl_3$, δ) showed signals for one dimethylchromene group (6.58 (1H) *d*, J = 12 Hz, H_α; 5.50 (1H) *d*, J = 12 Hz, H_β; 1.42 (6H) *s*, 2Me's); one isopentenyl group (3.45 (2H) *d*, J = 7 Hz, —$C\underline{H}_2$-ϕ; 5.29 (1H) *t*, J = 7 Hz, —$\underline{C}$H=; 1.68 (6H) *s*, 2Me's); one methoxyl group (3.83 3H, *s*); three aromatic protons (7.16, *s*; 6.48, *s*; 5.95, *s*; each integrating for one proton) and one chelated hydroxyl group (12.07 1H, *s*). The isoflavanone nature [3] of 1 was indicated by the presence of one proton triplet at δ 3.95 (C-3) and a two proton complex multiplet at δ 4.70–4.85 (C-2). The complex multiplet [4] for protons at C-2 indicated that isoflavanone (1) is oxygenated at C-2′, because a simple pattern [5] of a doublet (C_2-H) and a triplet (C_3-H) for isoflavanones devoid of C-2′ oxygenation is observed.

The MS *m/e* (rel. int.) of 1 exhibited ions at 436 (M^+, 100), 421 (M-15, 97), 393 (M-43, 12), 380 (M-56, 10) and the retro-Diels–Alder fragments at 218 (18) and 203 (48) suggested that ring B must incorporate all the three isopentenyl, methoxyl and the non-chelated hydroxyl groups. Since the PMR signals for all the three aromatic protons are singlets, two of these protons occupy *para* positions in the B-ring. Treatment of 1 with HCO_2H gave a compound (TLC, R_f: 0.56; Si gel, EtOAc–C_6H_6, 1:9) which was different from 1 and responded to ferric reaction, showing thereby that the isopentenyl group is adjacent to the non-chelated hydroxyl group and hence is involved in cyclization. The signals at δ 6.48 ($C_{3'}$ or $C_{5'}$-H) and 7.16 ($C_{6'}$ or $C_{2'}$-H) in the PMR of 1 appeared at δ 6.81 and 7.02 respectively in the spectrum of 2′-*O*-methylcajanone diacetate. The downfield shift of the signal at δ 6.48 suggests that the B-ring substitution pattern is of 4′-hydroxy-5′-isopentenyl-2′-methoxy type. The presence of the weakly chelated methoxyl group at $C_{2'}$ is also favoured by the benzene shift (Δ − 0.12 δ) of the methoxyl signal [6].



1 2′-*O*-Methylcajanone

The similarity of the chemical shifts of C_6-H and C_8-H in 5-hydroxyisoflavanone [7, 8] allows two possibilities for the attachment of the dimethylchromene group in the A-ring, i.e. at 6,7 or 7,8 positions. Acetylation of 1 results in an upfield shift change (Δ − 0.22 δ) for H_α and a downfield change (Δ + 0.14 δ) for H of the dimethylchromene ethylenic protons, which agrees with the data reported for 6,7-substitution in the 5-hydroxyisoflavanones [9]. The placement of the dimethylchromene group at the 6,7-position is further supported by a positive Gibb's test, hence the structure 5,4′-dihydroxy-2′-methoxy-5′-(3‴-methyl-2‴-butenyl)-2″,2″-dimethylpyrano-[5″,6″:6,7]-isoflavanone (1) has been assigned to 2′-*O*-methylcajanone.

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