Phytochemistry, 1979, Vol. 18, p 1254. © Pergamon Press Ltd. Printed in England. 0031-9422/79/0701-1254 $02.00/0

CAJAISOFLAVONE, A NEW PRENYLATED ISOFLAVONE FROM *CAJANUS CAJAN*

S. BHANUMATI, S. C. CHHABRA and S. R. GUPTA*
Department of Chemistry, University of Delhi, Delhi-110007, India

(*Received* 4 *December* 1978)

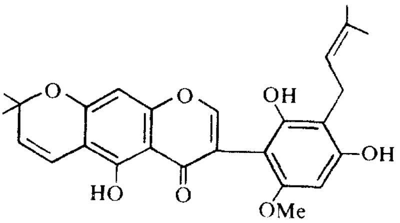
Key Word Index—*Cajanus cajan*; Leguminosae; cajaisoflavone; 5,2′,4′-trihydroxy-6′-methoxy-3′-(3‴-methyl-2‴-butenyl)-2″,2″-dimethylpyrano-[5″,6″ : 6,7]-isoflavone.

In our previous communications [1, 2] new prenylated flavonoids from *C. cajan* have been reported. We now report the isolation and characterization of cajaisoflavone (**1**). The C_6H_6 extract of the root bark, on column chromatography over Si gel using petrol, yielded a fraction which on preparative TLC (Si gel, petrol–EtOAc, 9:1) yielded **1** as an orange semi-solid, M^+ 450, $C_{26}H_{26}O_7$ (TLC R_f: 0.83 Si gel; petrol–EtOAc, 9:1; 0.66, polyamide, MeOH). It gave an olive-green ferric reaction, a negative Shinoda and a positive Na–Hg/HCl tests; λ_{max}^{MeOH} nm: 275, 295, 320, 350, 370 and 380. The IR (KBr) showed strong absorptions at 3333 (OH) and 1612 ($>$C=O). It formed a triacetate (Py/Ac_2O) showing thereby the presence of three hydroxyl groups.

The ^{1}H NMR 60 MHz ($CDCl_3$, δ) showed signals for one 2,2-dimethylchromene group (6.61 (1H), *d*, J = 11 Hz, H_α; 5.51 (1H) *d*, J = 11 Hz, H_β; 1.44 (6H), *s*, 2 Me's); one isopentenyl group (3.45 (2H, *d*, J = 7 Hz, -C$\underline{H}$ -ϕ; 5.56, *t*, J = 7 Hz, -C$\underline{H}_2$ =; 1.68 (6H), *s*, 2 Me's); one methoxyl group (3.85, 3H, *s*) and two aromatic protons (6.52, 1H, *s* and 6.01, 1H, *s*). A one-proton singlet at δ 7.80 was indicative of the isoflavone nature of **1**. The chelated hydroxyl group appeared as a singlet in the downfield region at δ 11.50 and was exchangeable with D_2O.

The MS *m/e* (rel. int.) of **1** exhibited ions at 450 (M^+, 48), 435 (M −15, 23) and 407 (M −43, 4). The retro-Diels–Alder fragments at 203 (23) and 232 (17) agree with one hydroxyl and the dimethylchromene unit in ring A and all the other substituents in ring B. Treatment of **1** with formic acid gave a mixture of two components, both of which gave a positive ferric reaction but were different from the starting compound (Si gel; 0.22 and 0.41; petrol–EtOAc, 9:1; 0.88 and 0.68 polyamide, MeOH) indicating thereby that the isopentenyl side chain is flanked by two hydroxyl groups and hence could be cyclized with either giving rise to two different products. The presence of a prominent peak at *m/e* 419 (M −31, 100) in the MS of **1** conveniently fixes the methoxyl group at the 2′- or 6′-position as the presence of this peak is a common feature in the MS of all the 2′-methoxyisoflavones [3]. The methoxyl signal shifted to δ 3.57 (Δ −0.28 ppm) when the ^{1}H NMR was recorded in C_6H_6 solution; hence the methoxyl group must be adjacent to a proton [4].

In the ^{1}H NMR of the triacetate of **1** the $C_{5'}$-H appeared at δ 6.79 against δ 6.52 in the hydroxy compound. The downfield shift (Δ +0.27 ppm) clearly shows that C-5′ proton is adjacent to a hydroxyl group. Furthermore, the upfield shift (Δ −0.21 ppm) for H_α and the downfield shift (Δ +0.20 ppm) of H_β of the dimethylchromene ethylenic protons support the attachment of the dimethylchromene group at the 6,7-positions [5]. Hence the structure 5,2′,4′-trihydroxy-6′-methoxy-3′-(3‴-methyl-2‴-butenyl)-2″,2″-dimethylpyrano[5″,6″ : 6,7]-isoflavone (**1**) has been assigned to cajaisoflavone.



1 Cajaisoflavone

REFERENCES

1. Bhanumati, S., Chhabra, S. C., Gupta, S. R. and Krishnamoorthy, V. (1978) *Phytochemistry* **17**, 2045.
2. Bhanumati, S., Chhabra, S. C., Gupta, S. R. and Krishnamoorthy, V. (1979) *Phytochemistry*, **18**, 365.
3. Campbell, R. V. M. and Tannock, J. (1973) *J. Chem. Soc. Perkin Trans. I*, 2222.
4. Fales, H. M. and Warren, K. S. (1967) *J. Org. Chem.* **32**, 501.
5. Arnone, A., Cardillo, G., Merlini, L. and Mondelli, R. (1967) *Tetrahedron Letters* 4201.

---

* To whom correspondence should be addressed.