

derived, lends further support to the proposed structure of genuine bacogenin [2].

EXPERIMENTAL

All mp's are uncorrected. NMR spectra were recorded on a 60MHz machine in CDCl₃ unless otherwise stated.

Bacogenin A₃ (1a). M.p. 190°. $\nu_{\text{max}}^{\text{KBr}}$: 3344, 2907, 2825, 1630, 1450, 1380, 1276, 1221, 1027, 1000, 940, 905, 835 cm⁻¹. $\lambda_{\text{max}}^{\text{EtOH}}$: 230 nm (ϵ 9630), NMR (ppm): 0.78, 0.84, 0.98, 1.03 (H each, s, 4 C—Me), 1.53 (6H, d, J 1.5 Hz, 2 C=C—Me), 1.76 (3H, d, J 1.5 Hz, C=C—Me), 3.21 (1H, m, —CH—O—), 4.1 (4H, broad s, 2 —CH₂—O—), 5.43 (1H, m, C=C—H). MS: m/e 454 (M⁺), 439 (M-15), 436 (M-18), 411, 334, 318, 316, 301, 274, 257, 241, 207, 189, 175, 173, 161, 149, 135, 121. (Found: C, 79.13; H, 10.45, C₃₀H₄₆O₃ requires C, 79.27; H, 10.20%).

Acetyl bacogenin A₃ (1b): A mixture of bacogenin A₃ (250 mg), C₅H₅N (2.5 ml) and Ac₂O (2.5 ml) was allowed to stand overnight. After usual work up, the product was crystallized from MeOH, mp 220°. $\lambda_{\text{max}}^{\text{EtOH}}$: 235 nm NMR (ppm): 0.86 (9H, s, 3 C—Me), 1.05 (3H, s, C—Me), 1.53 (6H, d, J 1.5 Hz, 2 C=C—Me), 1.78 (3H, d, J 1.5 Hz, C=C—Me), 2.05 (3H, s, OCO Me), 4.1 (4H, broad s, 2 —CH₂—O—), 4.48 (1H, m, —CHOAc), 5.45 (1H, m, —C=C—H). MS: m/e (M⁺ absent), 316, 301, 273, 257, 241, 203, 189, 175, 173, 161, 149, 147, 135, 121.

Ozonolysis of 1b: A soln of 1b (100 mg) in CH₂Cl₂ (10 ml) containing C₅H₅N (0.02 ml) was saturated with ozonized oxygen at -80° for 45 min. The solvent was evap. off and the product (3) crystallized from MeOH as colourless needles, mp 246°. $\nu_{\text{max}}^{\text{KBr}}$: 1730, 1670, 1635, 1265, 775 cm⁻¹. $\lambda_{\text{max}}^{\text{EtOH}}$: 243 nm (ϵ 1150). NMR (ppm): 0.86 (9H, s, 3 C—Me), 1.05 (3H, s, C—Me), 2.05 (3H, s, OCOMe), 2.15 (3H, broad s, C=C—Me), 4.15 (2H, s, —CH₂O—), 4.5 (2H, ABq J 14 Hz, —CH₂O— and 1H, m, CHOAc), 9.96 (1H, s, —CHO). MS: m/e 470 (M⁺), 189, 175, 161, 149, 135, 121, 107, 93, 81, 69.

Hydrogenation of 1b. Acetylbacogenin A₃ (1b), 125 mg, was hydrogenated over Adam's catalyst in CHCl₃-EtOAc (1:1, 10 ml) for 4 hr. The product was purified by PLC on Si gel with C₆H₆ - MeOH (96:4) and crystallized from C₆H₆: petrol as colourless needles (4a), mp 145° (100 mg), $\nu_{\text{max}}^{\text{KBr}}$: 3350, 1725, 1250

cm⁻¹. NMR (ppm): 0.85 (9H, s, 3 C—Me), 1.08 (3H, s, C—Me), 0.85 (12H, d, J 7Hz, 4 —CHMe), 2.03 (3H, s, OCOMe), 2.18 (2H, ABq, J 16 Hz, —CH₂CO—), 3.96 (2H, ABq, J 12 Hz, —CH₂OH), 4.48 (1H, q, J 5 and 9 Hz, —CHOAc), MS: m/e 502 (M⁺), 472, 443, 428, 412, 399, 390 (M-side chain + H), 372, (390-H₂O), 357, 339, 333, 330, 315, 312, 297, 262, 205, 203, 189, 135, 121, 109, 107, 95, 93. The product (4a, 50 mg) was acetylated with Ac₂O-C₅H₅N to furnish a diacetate (4b, 38 mg) $\nu_{\text{max}}^{\text{KBr}}$: 1727, 1244 cm⁻¹; NMR (ppm): 1.96, 2.03, (3H each, s, 2 OCOMe), 4.43 (2H, ABq, J 12 Hz, —CH₂OAc), 4.55 (1H, m, —CHOAc). The diacetate (4b, 60 mg) was saponified with 2M ethanolic KOH at room temp. for 16 hr. The deacetylated product (4c, 45 mg) was obtained as a colourless powder. $\nu_{\text{max}}^{\text{KBr}}$: 3344, 1727 cm⁻¹. NMR 0.80, 0.90, 1.00, 1.10 (3H each, s, 4 C—Me), 0.85 (12H, d, J 7 Hz, 4 CH—Me), 2.18 (2H, ABq, J 16 Hz, —CH₂CO—), 3.24 (1H, m, CHOH), 4.0 (2H, ABq, J 12 Hz, —CH₂OH). MS: m/e 460 (M⁺), 442 (M-18), 429 (M-CH₂OH), 411, 375, 348 (M-side chain + H), 330, 315, 297, 284, 279, 256, 213, 207, 189, 185, 149, 141, 113 (side chain), 99, 97, 85. (Found: C, 78.32; H, 11.60. C₃₀H₅₂O₃ requires C, 78.20; H, 11.37%).

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CAJANONE: AN ANTIFUNGAL ISOFLAVANONE FROM *CAJANUS CAJAN*

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Key Word Index *Cajanus cajan*; Leguminosae; pigeon pea; isoflavanone; antifungal

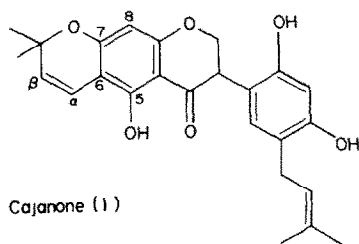
Plant. Pigeon pea, *Cajanus cajan* (Millsp.). **Source:** International Institute of Tropical Agriculture, Ibadan, Nigeria.

Present work. Cajanone (M⁺ 422, C₂₅H₂₆O₆) is the major phenolic compound of the roots of pigeon pea, of which it comprises ca 0.14% dry weight. Its 60 MHz NMR spectrum shows signals for one dimethylchromene group (6.61 δ , d, J 12 Hz, H_{α} , 5.49 δ , d, J 12 Hz, H_{β} , 1.42 δ , s, 2 Me's), one isopentenyl group (3.27 δ , bd, —CH₂—, ca 5.4 δ , t, —CH=, 1.73, 1.74 δ , s, s, Me's), a chelated hydroxyl group (12.10 δ , s) and three aromatic protons (7.10 δ , s, 6.44 δ , s, 5.95 δ , s). These data, together with the UV spectrum, $\lambda_{\text{max}}^{\text{EtOH}}$ 225 sh (log ϵ 4.11), 273 (4.30), 293 (4.05), 306 sh (3.87), suggest a flavanone or isoflavanone structure; absence from the NMR spectrum of the signal

near 2.8 δ characteristic of the C-3 proton of flavanones [1] and the presence of a one-proton triplet (J 6 Hz) for H-3 at 3.95 δ show that cajanone is an isoflavanone. The C-2 protons appear as a complex multiplet at 4.6-4.8 δ .

Since the NMR signals for all three aromatic protons are singlets, two of these protons occupy *para* positions in ring B. The MS shows retro-Diels-Alder fragmentation giving rise to m/e 218 (8.9%), 219 (100%) and 204 (9.2%). In view of the NMR data, the fragment at m/e 204 must incorporate ring B. This fragment loses C₄H₇ to yield m/e 149 (metastable ion at m/e 108.8) and therefore contains the isopentenyl group. The ring B substituents are now seen to be the isopentenyl group and two hydroxyl groups, one of these being adjacent to the isopentenyl

group with which it cyclises when cajanone is refluxed in methanolic HCl. The derivative thus formed is isomeric with cajanone ($M^+ 422$), but has no isopentenyl group (NMR). The chemical shift of the B-ring protons in the NMR spectrum of cajanone (7.10 and 6.44 δ) assigns them to C-2' or C-6' and C-3' or C-5' respectively. The signal at 6.44 δ appears at 6.95 δ in the spectrum of cajanone triacetate, while the 7.10 δ cajanone signal is found at 7.00 δ . The downfield shift of only one signal on acetylation indicates that only one of the B-ring protons is *ortho* to an hydroxyl group. The B-ring substitution pattern is thus uniquely defined as 2',4'-dihydroxy-5'-isopentenyl.



The similarity of the chemical shifts of H-6 and H-8 in 5-hydroxyisoflavanones [2,3] allows two possibilities for the attachment of the dimethylchromene group in ring A, i.e. at the 6,7 or 7,8 positions. Arnone *et al.* [4] have distinguished between these alternatives on the basis of

chemical shift changes observed in the NMR spectra of dimethylchromene ethylenic protons on acetylation of neighbouring hydroxyl groups. Acetylation of cajanone results in an upfield shift change of 0.26 δ for H_a, and a downfield shift change of 0.12 δ for H_b, which agree with data reported for 6,7 substitution [4]. Cajanone is therefore assigned the structure (1), although it gives a negative Gibbs test.

Cajanone, isolated by TLC from a methanolic extract of dried, milled pigeon pea roots, totally inhibited germ tube growth of *Fusarium oxysporum* f. sp. *udum*, a pigeon pea wilt pathogen, at 50 ppm *in vitro*.

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FLAVONOIDS OF *DAVIDSONIA PRURIENS*

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Key Word Index—*Davidsonia pruriens*; Davidsoniaceae; flavanol 3-*O*-rhamnosides and rhamnoside sulfates; luteolin 7-*O*-xyloside; (–)-epicatechin gallate; (–)-epigallocatechin gallate; gallyl proanthocyanidin.

Davidsonia pruriens F. Muell is a northeastern Australian tree considered to be the sole member of the Davidsoniaceae by both Takhtajan [1] and Cronquist [2]. It is thought to be closely related to members of the Cunoniaceae [1, 2] from which family it is distinguished by its alternative leaves and absence of endosperm [2]. Engler and Prantl [3] treated *Davidsonia* as a doubtful member of the Cunoniaceae. Rosenthaler [4] recorded a positive test for HCN but Gibbs [5] was unable to detect this substance using fresh leaf material.

The commonly occurring flavanol glycosides kaempferol, quercetin and myricetin 3-*O*-rhamnosides and quercetin and myricetin 3-*O*-glucosides were isolated from the monoglycoside fraction [6]. A small quantity of luteolin 7-*O*-xyloside was seen and traces of a compound were detected which has the colour reactions and R_f of larycitrin 3-*O*-rhamnoside. Three compounds were isolated from the "diglycoside" fraction [6]. All were immobile on polyamide TLC but were electrophoretically mobile at pH 2.3 strongly suggestive of sulfate derivatives [7]. Hydrolysis showed the presence of kaempferol,

quercetin and myricetin with rhamnose and sulfate in each case. UV spectra showed that substitution was in position-3 of each flavanol. The position of sulfation on the rhamnose was not determined.

Four flavanols were also observed. NMR and CD measurements identified two of them as (–)-epicatechin gallate and (–)-epigallocatechin gallate. The other two gave an anthocyanidin, gallic acid, and other fragments on acid hydrolysis. One of these flavanols (compound C) gave NMR signals at 3.03, 4.07, 4.87, 5.24, 5.82, 6.04, 6.72, 6.76, 6.96, 7.12 and 7.16 δ (deuteroacetone). While complete assignment of the peaks was not possible the presence of five non-aromatic signals suggests that the compound may be of the proanthocyanidin A type described by Haslam and coworkers [8]. The signal at 3.03 δ was clearly due to a C-4 methylene function while the shape of the signal at 5.32 δ was similar to those observed for the 3-position of (–)-epicatechin gallate and (–)-epigallocatechin gallate. The aromatic signals at 7.12, 6.76 and 6.04 δ were undoubtedly due to the gallate group, a pyrogallyl moiety, and phloroglucinol