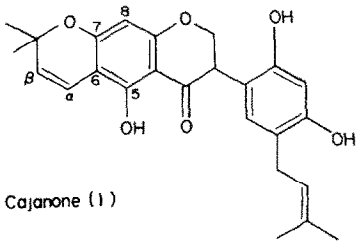
group with which it cyclises when cajanone is refluxed in methanolic HCl. The derivative thus formed is isomeric with cajanone (M^+422), but has no isopentenyl group (NMR). The chemical shift of the B-ring protons in the NMR spectrum of cajanone (7.10 and 6.44δ) assigns them to C-2′ or C-6′ and C-3′ or C-5′ respectively. The signal at 6.44δ appears at 6.95δ in the spectrum of cajanone triacetate, while the 7.10δ cajanone signal is found at 7.00δ. 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.



Cajanone (1)

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 0.26δ for H_α and a downfield shift change of 0.12δ for H_β, 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; flavonol 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 flavonol 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 flavonol. 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 7.16δ (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 3.03δ was clearly due to a C-4 methylene function while the shape of the signal at 5.32δ was similar to those observed for the 3-position of (–)-epicatechin gallate and (–)-epigallocatechin gallate. The aromatic signals at 7.12, 6.76 and 6.04δ were undoubtedly due to the gallate group, a pyrogallyl moiety, and phloroglucinol

protons, respectively. The remaining aromatic signals at 6.72. 6.96 and 7.16δ appeared very similar to those of the catechol ring of (−)-epicatechin gallate. The fact that the non-aromatic signals showed only small coupling constants indicates that both flavanol moieties possess the epi configuration. This appears to be the first report of the occurrence of a gallyl proanthocyanidin. Further material must be isolated before a final structure is presented, however.

EXPERIMENTAL

Air-dried leaves of *D. pruriens* F. Muell were kindly supplied by B. P. M. Hyland, Forestry and Timber Bureau, Australian Department of Agriculture, Atherton, Queensland. Plant material was extracted and the neutral flavonoid clycosides isolated by methods described elsewhere [6]. The sulfate derivatives, after normal chromatography on Sephadex LH-20 and cellulose partition columns [6], were purified by preparative TLC on cellulose with BAW (4:1:5). The three compounds showed the same electrophoretic mobility on Eastman cellulose chromagrams: 3.8 cm at 400 V, 8 mA for 1 hr. After the normal sugar analysis [6] the aqueous portion of the hydrolysate was evaporated to dryness, taken up in a few drops of 0.1 M nitric acid and tested with $BaCl_2$. A white precipitate confirmed the presence of sulfate ion. R_f values in BAW and 20% acetic acid for the kaempferol, quercetin and myricetin compounds were 86, 74; 83, 69; and 81, 65, respectively. R_f values (× 100) for the flavanols on polyamide 6.6 in Me_2CO–MeOH–HOAc (5:5:1) were: (−)-epicatechin gallate, 50; (−)-epigallocatechin gallate, 37; compound C, 26; and compound D, 10.

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TWO NEW SULPHATED FLAVONOL GLUCOSIDES FROM LEAVES OF *MALVA SYLVESTRIS*

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Fresh leaves were extracted with 25%EtOH, followed by column chromatography (cellulose). Two successive fractions, eluted with H_2O, were found to contain two new anionic flavonol glycosides (G, mp 320° decomp.) and (H, mp 332° decomp.), respectively. Both G and H showed chromatographic properties of highly glycosylated flavonols and migrated towards the anode on electrophorograms (Table 1).

Compound G on acid hydrolysis (N HCl) gave glucose and gossypetin (mmp, colour reactions[1], co-chromatography and UV data [2] Table 1); The hydrolysate gave also a white ppt. with $BaCl_2$.

On treatment with β-glucosidase, G gave a single positively charged product (G_1, dark brown on PC under UV, Table 1) which on acidification (0.05N HCl) gave gossypetin and a white ppt. with $BaCl_2$, but no sugar. Controlled acid hydrolysis of G with 0.05N HCl gave rise to only one intermediate G_{II} beside gossypetin. G_{II} (yellow spot on chromatograms under UV) which started to appear immediately after acidification of G was identified as gossypetin-8-*O*-β-D-glucoside (gossypin) through enzymic hydrolysis, co-chromatography and UV data (Table 1).

The above data prove that G (dark brown spot changing to brownish–yellow with NH_3 on chromatograms under UV) is a gossypin-mono-sulphate ester with its sulphate group (presented as $KHSO_3$) most probably at C-3 (Found: S: 5.4%, Calc. for $C_{21}H_{20}O_{16}SK$, S: 5.34%). K was detected by flame spectrophotometer and by a ppt. obtained with Na cobaltinitrite. Esterification at position 3 was confirmed through the hypsochromic shift observed on comparing the UV spectra of both G and gossypin (Table 1).

Compound H, on acid hydrolysis gave glucose and 8-hydroxyluteolin (hypolaetin, mp 295°–296°, lit. [3] 296°) the hydrolysate gave a white ppt. with $BaCl_2$. R_f-values, colour reactions and UV spectral analysis (Table 1) confirmed hypolaetin [3]; this was confirmed through the prolonged heating of the aglycone with N HCl–EtOH (1:1), whereby the corresponding 6-OH isomer was formed and by alkali fusion which yielded pyrogallol and protocatechuic acid. Glycoside H on treatment with β-glucosidase gave a positively charged product H_1 (bluish–black colour on PC and electrophorograms under UV, Table 1) which on acidification with 0.05N HCl gave hypolaetin and a white ppt. with