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3′, 4′, 7-Trihydroxyflavone in *Albizzia julibrissin*

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Abstract□ From the stembark of *Albizzia julibrissin*, 3′, 4′, 7-trihydroxyflavone and α-spinasteryl-D-glucoside were isolated.

Keywords□ *Albizzia julibrissin*; Leguminosae 3′, 4′, 7-trihydroxyflavone; α-spinasteryl-D-glucoside.

Previous workers have demonstrated that *Albizzia julibrissin* contains quercetin 3-O-galactoside and quercetin 3-O-rhamnoside[1]. We now report the isolation and identification of a rare 5-deoxyflavone, 3′,4′,7-trihydroxyflavone, from the stembark of the plant.

Column chromatography of the ethylacetate soluble fraction of the stem bark methanol extract on silica gel using a solvent ($CHCl_3$-MeOH-7%HAc=25:8:5) to give the flavonoid together with α-spinasteryl-D-glucoside.

3′,4′,7-*Trihydroxyflavone*, mp 314-316°, yellow needles crystallized from MeOH, showed M^+ at *m/e* 270 (100%) and other peaks at *m/e* 242 (M-CO, 29), 137 (RDA fragment with A ring +H, 73) and 134 (RDA fragment with B ring, 31). The UV (in MeOH) showed absorption peaks characteristic of a flavone at 239 and 345 nm, which were shifted by addition of NaOMe (259, 408 nm), NaOAc (255, 375 nm), NaOAc $+H_3BO_3$(259, 372 nm) and $AlCl_3$ (239, 377 nm). Addition of HCl resulted in the decomposition of $AlCl_3$ complex, returning to original spectrum.

The ^1H NMR (60 MHz, DMSO-d_6, TMS) exhibited signals at δ 7.90 (1H, d, J=9Hz, H-5), 7.43(1H, d, J=2Hz, H-2′), 7.40(1H, dd, J=2 and 6.5 Hz, H-6′) 6.96(1H, d, J=2Hz, H-8), 6.93(1H, dd, J=2 and 9 Hz, H-6), 6.89(1H, d, J=6.5Hz, H-5′) and 6.62 (1H, s, H-3). These spectral data were in agreement with those for the structure of 3′,4′,7-trihydroxyflavone.

It was confirmed by the following ^{13}C NMR data (22.50 MHz, DMSO-d_6, TMS)δ 176.6 (C-4) 163.0 (C-2) 162.8 (C-7) 157.6 (C-9) 149.1 (C-4′) 145.8 (C-3′) 126.2 (C-5), 122.2 (C-1′) 118.2 (C-6′) 116.2 (C-5′) 116.0 (C-10) 114.6 (C-6) 113.2 (C-2′) 104.8 (C-3) 102.5 (C-8).

The presence of this compound in the plants has previously been reported in *Trifolium* spp.[2,3] *Medicago sativa*[4] *Baptisia* spp[5,6]., *Juncus trifidus, Luzula purpurea*[7], *Salvertia convallariodora* and *Vochysia* spp[8].

This is the first report of its occurrence

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in *Albizzia* genus.

α-Spinasteryl-D-glucoside, mp 278–281°, white needles crystallized from MeOH, is a well-known natural product; the aglycone, mp 167–169°, obtained by acid hydrolysis was identified by direct comparison with authentic sample (TLC, GLC and MS[9]);the sugar was shown to be D-glucose (TLC and GLC as TMSi ether).

EXPERIMENTAL

Isolation of α-Spinasterol-D-glucoside.

The commercially available stem bark of *Albizzia julibrissin* reduced to a coarse powder was extracted with methanol to exhaustion and the extract was concentrated *in vacuo* to a drak brown viscous residue which was partitioned between equal volumes of n-hexane and water. The aqueous layer was partitioned with an equal volume of chloroform and subsequently partitioned with ethylacetate to effect an ethylacetate soluble fraction.

Every partition was complete when the organic solvent layer from the last partition was nearly colorless.

The ethylacetate phases were combined and concentrated *in vacuo* to dryness and dissolved in small amount of methanol and then stood at room temperature to yield colorless needles, mp 278–281°, IR ν_{max}^{KBr} cm^{-1}: 3330 (OH) 1100–1000 (glycoside) 965 (*trans* disubstituted double bond) 840−790(trisubstituted double bond) MS *m/e*: 574 (M^+), 395 ($M-C_6H_{11}O_6$). Acetate obtained by treatment with acetic anhydride in pyridine, mp 174−175°, NMR ($CDCl_3$, TMS) δ : 0.55, 0.79 (3H, each, all s), 2.00, 2.02, 2.04 and 2.09 (3H each, all s), 4.60 (1H, d, J=7Hz).

Hydrolysis of α-Spinasteryl-D-glucoside.

The sample was dissolved in 5%HCl-MeOH and refluxed for 2 hr.

After cooling the reaction mixture was poured in water to give solids which were collected by filtration, when crystallized from MeOH, separated in colorless needles melting at mp 167–169°, identified by the direct comparison with an authentic sample of α-spinasterol.[9]

The co-existance of trace amounts of Δ^7-stigmastenol in the sample was shown by MS data (a small peak at *m/e* 414 besides the parent peak at *m/e* 412) and GC data (column, OVI, 60–80 mesh, 1.5m×4mm; column temp., 170°; inj. temp. 190°; detector temp. 200°; N_2 45ml/min; tr for α-spinasterol 5,8, for Δ^7-stigmastenol, 6.5).

The filterate was concentrated *in vacuo* and refluxed with acid to hydrolyze methyl glucoside.

After neutralizing with Ag_2CO_3, the aqueous solution was concentrated, in which only D-glucose was detected by TLC (MeOH-$CHCl_3$-Acetone-NH_4OH=5:2:2:3, Rf=0.23; $CHCl_3$-MeOH-H_2O=52:25:8, Rf=0.15) and GC of the TMS derivative (conditions, same as above; tr, 6.5, 7.2).

Isolation of 3',4',7-trihydroxyflavone.

The methanol solution, from which α-spinasteryl-D-glucoside had been separated by filtration, was evaporated to dryness, the residue subjected to column chromatography over silica gel using $CHCl_3$-MeOH-

7%HOAc=25:8:5 to yield the flavonoid, crystallized from MeOH as yellow needles, mp 314–316°, UV λ_{max}^{MeOH} nm (logε): 239 (4.32), 312 (4.21), 345 (4.36); with NaOMe, 259 (4.46), 318 (3.58), 340 (3.90), 408 (4.47); with NaOAc, 255 (4.13), 375 (4.25); with NaOAc+H_3BO_3, 259 (4.16), 308 (4.03), 372 (4.33); with $AlCl_3$, 239 (4.32), 305 (4.01), 377 (4.19); with $AlCl_3$+HCl 239 (4.25), 256 (4.11), 309(4.03), 347 (4.16).

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