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SHORT COMMUNICATION

CHEMICAL EXAMINATION OF *MILLINGTONIA HORTENSIS*

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Abstract—Isolation of a new glycoside (scutellarein-5-galactoside) and of scutellarein from *Millingtonia hortensis* is described.

Millingtonia hortensis L. (Bignoniaceae) commonly known as Akasnim, is an ornamental plant cultivated throughout India. Its leaves are used as antipyretic[1] and have also been reported to be useful in the treatment of various skin affections.

Fresh flowers of the plant were extracted with alcohol and the extract, after concentration, was worked up to give an ether-soluble and an aqueous portion. A yellow flavone, m.p. 343–345°, was obtained from the ethereal layer which formed a tetraacetate, m.p. 238–239°, and a tetramethyl ether, m.p. 162–163°. The u.v. spectrum of the compound in alcohol showed λ_{max} at 288 and 338 nm. The former band was shifted to 302 nm on addition of $AlCl_3$,[2] indicating the presence of a free 5-hydroxyl group which was also confirmed by Wilson's boric acid test[3] and appearance of a bright yellow colour with Dimroth's reagent.[4] Addition of NaOAc[5] to the alcoholic solution of the flavone resulted in the displacement of the 338 maximum to 360 nm, showing the presence of another hydroxy group at position 7. Presence of three vicinal hydroxy groups was indicated by a positive Bargellini test[6] and thus the compound was shown to be a 5,6,7-hydroxyflavone. Alkali degradation of the tetramethyl ether gave anisic acid, indicating the presence of the fourth hydroxy group at the 4′-position. Identity of the compound as scutellarein was confirmed by comparison of its tetramethyl ether with an authentic sample.

The aqueous portion of the flower extract, after purification via lead acetate, yielded a yellow solid, m.p. 254–256°, $[\alpha]_D^{20}$ −99·5°. The u.v. spectrum of this compound showed λ_{max} at 295 and 342 nm and gave no shift with $AlCl_3$, indicating absence of a free 5-hydroxy group. It formed an acetate, m.p. 197–198°. Hydrolysis of the glycoside gave scutellarein. The failure of the glycoside to give a bathochromic shift in the u.v. absorption on addition of $AlCl_3$ suggested strongly that the 5-hydroxyl was glycosylated. This was confirmed by methylation of the glycoside and its subsequent hydrolysis when scutellarein 6,7,4′-trimethyl

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ether, m.p. 189–190°, was obtained. This was identified by comparison with authentic 6,7,4′-trimethyl ether[7] prepared by partial methylation of scutellarein with diazomethane. The sugar was identified as galactose by paper chromatography. The sugar moiety in glycoside was estimated gravimetrically as cuprous oxide and its ratio to the aglycone was found to be 1:1. The only other known glycoside of scutellarein reported in the literature[8] has glucuronic acid as the sugar moiety in 5 position.

EXPERIMENTAL

Isolation of Scutellarein

Fresh flowers of the plant (3 kg) were extracted in a soxhlet and the alcohol removed under reduced pressure. The black sticky mass thus left was taken in water (500 cm^3) and was washed thoroughly with petrol. ether to remove the fatty material and extracted with ether. The ethereal extract on evaporation gave a residue which was crystallized from the methanol when a solid (1·1 g), m.p. 342–344°, was obtained. (Found: C, 62·77; H, 4·10. $C_{15}H_{10}O_6$ required: C, 62·94; H, 3·62 per cent.) The tetra-acetate crystallized from alcohol, m.p. 238–239°. (Found: C, 60·38; H, 4·00. $C_{23}H_{14}O_{10}$ required: C, 60·79; H, 3·99 per cent.) The tetramethyl ether melted at 162–163°. (Found: C, 66·59; H, 5·40. $C_{19}H_{18}O_6$ required: C, 66·66; H, 5·30 per cent). Identity of this as scutellarein tetramethyl ether was established by mixed m.p. with an authentic sample and a superimposable i.r. spectrum.

Isolation and Identification of Scutellarein 5-Galactoside

The aqueous solution after extracting with ether was treated with neutral lead acetate and then with basic lead acetate. The lead salt formed with basic lead acetate was suspended in alcohol and then decomposed with H_2S. Filtration and concentration of the alcoholic solution gave a yellow solid (1·5 g), m.p. 254–256° (acetate, from alcohol, m.p. 197–198°). The above glycoside (1 g) was refluxed with MeOH–HCl (9:1) for 3 hr and then left overnight. This was concentrated to half of its volume and then extracted with ether after the addition of an equal amount of water. The etherial extract when evaporated left a residue which when crystallized from methanol gave the aglycone, m.p. 341–344°, which formed an acetate, m.p. 238–239°, and a tetramethyl ether, m.p. 162–163°. Melting point of the aglycone and its derivatives agreed with those of scutellarein and its corresponding derivatives. Its methyl ether gave no depression in mixed m.p. with an authentic sample of scutellarein tetramethyl ether.

The glycoside (1 g) was methylated with dimethyl sulphate (1·2 cm^3) and anhydrous K_2CO_3 (8 g) in dry acetone (60 cm^3) by refluxing for 48 hr. The product was refluxed with MeOH–HCl (9:1) for 6 hr and then left overnight. After removing half of the methanol, an equal amount of water was added and the aqueous solution was extracted with ether. The residue obtained from this was crystallized from methanol when yellow leaflets of 5-hydroxy-6,7,4′-trimethoxyflavone, m.p. 189–190°, were obtained. The m.p. was undepressed on admixture with authentic trimethyl ether, m.p. 189–190°, prepared by treatment of scutellarein with CH_2N_2.

The aqueous hydrolysate of the glycoside after extraction with ether and removal of the mineral acid was concentrated in a vacuum desiccator and was put on a Whatman Paper No. 1 along with authentic samples of different sugars (using butanol–water as solvent) when the presence of galactose was revealed.

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