Phytochemistry, 1968, Vol. 7, pp. 505 to 506. Pergamon Press. Printed in England

SHORT COMMUNICATION

LUTEOLIN 7-GLUCOSIDE, THE FLAVONOID PIGMENT OF *HELIOTROPIUM TENELLUM*

JACQUES KAGAN

Departments of Chemistry and of Biological Sciences,
University of Illinois at Chicago Circle, Chicago, Illinois 60680, U.S.A.

(*Received* 13 *September* 1967)

Abstract—The flavonoid pigment of *Heliotropium tenellum* has been isolated and shown to be luteolin 7-β-glucoside.

THE SLENDER heliotrope, *Heliotropium tenellum* (family Boraginaceae), is a very common plant in central Texas, flowering from May to October.[1] A collection made near Austin, Texas, in September 1966 was examined for flavonoid pigments.

The air dried plant material (360 g) was extracted with methanol at room temperature. The extract was taken to dryness under vacuum in presence of nylon powder, which was then washed successively with chloroform, water and methanol. All the flavonoids were in the methanol wash, from which yellow crystals (4 g) precipitated upon standing. The product was pure from two-dimensional paper chromatography. A sample recrystallized from methanol melted at 252–255°. Its NMR spectrum in dimethylsulfoxide-d_6 indicated that it was a mono-glycoside with ring protons at the 3- (singlet at 6·73), 6- (doublet at 6·46, J = 2), 8- (doublet at 6·80, J = 2), 2′- (singlet at 7·4), 5′- (doublet at 6·92, J = 7) and 6′-position (doublet near 7·42, J = 7, obscured by the 2′-proton signal). The glycoside was therefore a luteolin derivative.

The nature of the sugar moiety was established gas chromatographically after hydrolysis for 2 hr with 2 *N* HCl.[2] The trimethylsilyl ether gave two peaks with retention times matching separately and in mixture those from an authentic sample of glucose equilibrated in pyridine prior to trimethylsilylation.

The position of attachment of glucose to the flavonoid nucleus was determined spectroscopically.[3] The u.v. spectrum of the glycoside showed maxima at 256 and 267 nm (Band II) and 350 nm (Band I). The presence of free hydroxyls at the 3′- and 4′-positions was demonstrated by the shift of Band I to 405 nm in presence of sodium acetate, which was only partially reduced (to 374 nm) in presence of added boric acid. Band II did not shift in presence of sodium acetate indicating that the 7-hydroxyl was not free and that the single glucose was therefore attached to that position. This was confirmed by measuring the absorption spectrum of the aglucone, obtained with difficulty by acid hydrolysis, which gave a shift of Band II in presence of sodium acetate. That the glucose had the β-configuration was inferred from the

[1] M. M. WILLS and H. S. IRWIN, *Roadside Flowers of Texas*, p. 188, University of Texas Press (1961).
[2] J. KAGAN and T. J. MABRY, *Anal. Chem.* 37, 288 (1965).
[3] L. JURD, In *The Chemistry of Flavonoid Compounds* (edited by T. A. Geissman), p. 107, Macmillan, New York (1962).

NMR spectrum of the glycoside, in which the H-1 sugar proton showed the characteristic broad signal near 5·1 ppm, and from the facile hydrolysis with β-glucosidase.

Our compound was compared to an authentic sample of luteolin 7-β-glucoside. They had identical spectral and chromatographic properties, and likewise the acetates, m.p. 134°, were identical.

No other flavonoid was found in this plant, an unusually rich source of luteolin 7-glucoside. To our knowledge this represents the first report of flavonoid analysis in *Heliotropium*.

EXPERIMENTAL

The NMR spectra were recorded on a Varian A-60A spectrometer and are expressed on the δ-scale in ppm downfield from an internal standard of tetramethylsilane. The coupling constants are expressed in c/s. The u.v. spectra were recorded on a Beckman DB-G spectrophotometer and the gas chromatographic analysis was performed on a 3 per cent SE-52 column in a F & M 402 apparatus.

Acknowledgement—We wish to thank Professor M. C. Johnston (Dept. of Botany, University of Texas) for identifying the plants,[4] and the Research Board of the University of Illinois for financial support.

[4] A specimen (No. 250379) has been deposited at the Herbarium of the University of Texas, Austin, Texas.