Phytochemistry, 1980, Vol. 19, pp. 483–484. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0301-0483 $02.00/0

RHYNCHOSIN, A NEW 5-DEOXYFLAVONOL FROM *RHYNCHOSIA BEDDOMEI*

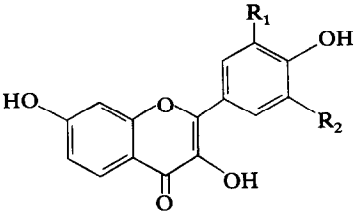
DAMA ADINARAYANA*, DUVVURU GUNASEKAR*, OTTO SELIGMANN† and HILDEBERT WAGNER†

* Department of Chemistry, Sri Venkateswara Univeristy, Tirupati-517502, India;
† Institut für pharmazeutische Arzneimittellehre der Universität Müchen, Karlstraße 29, D-8000 München 2, W. Germany

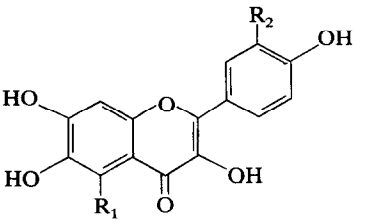
(*Received* 2 *July* 1977)

Key Word Index—*Rhynchosia beddomei*; Leguminosae; 6,7,3',4'-tetrahydroxyflavonol; 5-deoxyquercetagetin; rhynchosin.

Flavonols lacking a 5-hydroxyl group have been encountered in plants of all the three subfamilies of Leguminosae. It is interesting that 5-deoxy compounds of kaempferol, quercetin and myricetin, viz. 7,4'-dihydroxyflavonol (**1**), fisetin (**2**) and robinetin (**3**), occur in several plants [1]. In contrast, the 5-deoxy compounds corresponding to the 6-hydroxylated flavonols, galetin (**4**) and quercetagetin (**5**), have not been reported so far (Fig. 1).



1 $R_1 = R_2 = H$
2 $R_1 = OH$, $R_2 = H$
3 $R_1 = R_2 = OH$

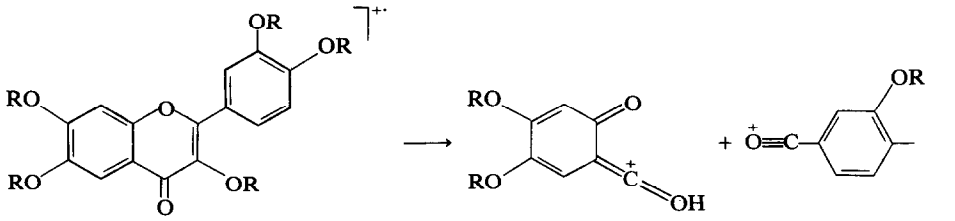


4 $R_1 = OH$, $R_2 = H$
5 $R_1 = R_2 = OH$
6 $R_1 = H$, $R_2 = OH$

Fig. 1.

This note reports the identification of 5-deoxyquercetagetin (rhynchosin) from the leaves of *Rhynchosia beddomei* (Bak.). Rhynchosin, obtained as yellow crystals from ethanol, did not melt below 320° but only darkened between 315 and 320°. UV spectral data showed the compound to be a flavonol with a free hydroxyl at 7-position with an *ortho* dihydroxy system in the A-ring [2]. The NMR spectrum of the compound indicated the ABX pattern for the B-ring protons indicating substitution at the 3',4'-positions. Two singlets at δ 7.0 and 7.38 were assigned to H-8 and H-5, respectively. All the five hydroxyl protons appeared as a broad peak at δ 9.51. The pentaacetate formed by Py–Ac_2O showed agreement with a 3,6,7,3',4' pentahydroxy substitution pattern.

Mass spectrum of the compound gave the molecular ion peak at *m/e* 302 and the retro-Diels–Alder fragments at *m/e* 153 $(A_1+H)^+$ and 137 (B_2^+), and for the permethylated derivative the corresponding values were 372, 181 and 165, respectively (Fig. 2). Rhynchosin was readily distinguishable from the isomeric compound 7,8,3',4'-tetrahydroxyflavonol [3] by observing an alcoholic solution of the compound under UV. The former exhibited a bright green fluorescence while the latter showed a golden yellow fluorescence.



(R = H, *m/e* 302)
(R = Me, *m/e* 372)

(R = H, *m/e* 153)
(R = Me, *m/e* 181)

(R = H, *m/e* 137)
(R = Me, *m/e* 165)

Fig. 2.

Thus rhynchosin is identified as 6,7,3′,4′-tetrahydroxyflavonol or 5-deoxyquercetagetin.

EXPERIMENTAL

The Me_2CO extract of shade-dried leaves of *R. beddomei* (3.2 kg) [4] yielded after TLC separation and recrystallization from EtOH yellow crystals of rhynchosin (30 mg) which did not melt below 320° but darkened between 315 and 320°. PC: R_f 0.41 in BAW (*n*-BuOH–HOAc–H_2O, 4:1:5), 0.33 in Forestal and 0.03 in 15% HOAc. Dark olive green colour with alc. $FeCl_3$ and a red colour with Mg/HCl. Under UV light an alcoholic soln exhibited bright green fluorescence. Substance in conc H_2SO_4 was bright yellow with green fluorescence under UV light. UV λ_{max}MeOH nm: 237, 257 sh, 357; $AlCl_3$: 212, 235 sh, 282, 436; + $AlCl_3$–HCl 267, 365 sh, 422; NaOAc 260, 371; H_3BO_3–NaOAc 292, 362. IR $\tilde{\nu}_{max}^{KBr}$ cm^{-1}: 3410, 1600, 1575, 1520, 1495, 1410, 1330, 1295, 1220, 1112, 1080, 1013, 940, 860, 848, 802, 775, 750, 670. ^{1}H NMR (60 MHz, DMSO-d_6 TMS int. standard): δ 6.92 ppm (1H, *d*, J = 8.5 Hz, H-5′), 7.00 (1H, *s*, H-8), 7.38 (1H, *s*, H-5), 7.61 (1H, *dd*, J = 2.5, 9 Hz, H-6′), 7.72 (1H, *d*, J = 2.5 Hz, H-2′) and 9.51 (5H, *br* OH). Its MS showed the following ions (EI 70 eV, 4 kV, 100 μA 200°; DI 180°): *m/e* 302 (M^+, 100%), 301 (27), 286 (2.5), 285 (2), 274 (6), 273 (7), 229 (6), 153 (13), 152 (2), 137 (14), 128 (11), 109 (4), 69 (3). The MS of the permethyl ether showed the following ions: *m/e* 372 (M^+, 100%), 371 (95), 358 (38), 357 (76), 344 (5), 343 (10), 341 (14), 329 (24), 181 (90), 180 (5), 173 (5), 165 (14), 137 (5).

3,6,7,3′,4′-*Pentaacetoxyflavone.* ^{1}H NMR (DMSO-d_6, TMS int. standard): δ 2.35 ppm (15H, *s*, OAc); 7.57 (1H, *d*, J = 9 Hz, H-5′); 7.82 (2H, *m*, H-2′, 6′); 7.90 (1H, *s*, H-8); 7.99 (1H, *s*, H-5); MS *m/e* 512 (M^+, 2%), 470 (37), 428 (50), 386 (72), 344 (85), 302 (100), 273 (18), 153 (11), 137 (14), 43 (86).

Acknowledgements—We thank Prof. J. B. Clark-Lewis, Flinders University, South Australia, for a sample of 7,8,3′,4′-tetrahydroxyflavonol and one of the authors (D. G.) is grateful to CSIR, New Delhi, India, for financial assistance.

REFERENCES

1. Gottlieb, O. R. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.) pp. 346–348. Chapman & Hall, London.
2. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids* pp. 50, 51. Springer, New York.
3. Clark-Lewis, J. W. and Dainis, I. (1967) *Aust. J. Chem.* **20,** 2191.
4. Adinarayana, D., Gunasekar, D., Seligmann, O. and Wagner, H. (1980) *Phytochemistry* **19,** 480.