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C-GLYCOSYLFLAVONES FROM *RHYNCHOSIA MINIMA*

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During seed germination studies on the title plant, an unusually prominent brownish–black halo was observed around each seed sown on moist filter paper. The seed coats and pericarps were found to contain gallic acid, protocatechuic acid, prodelphinidin and hydroquinone diacetate [1, 2].

While studying the role of proanthocyanidins in seed germination and the metabolism of hydroquinone diacetate in this plant, we studied the phenolics of the leaves. This report deals with flavonoids.

The mature and air-dried leaves (250 g) were extracted with hot MeOH–H_2O (1:1). The concentrated extract was freed of chlorophyll and fatty matter and partitioned between *n*-BuOH and H_2O. The butanol-soluble portion was chromatographed on paper (Whatman 1 mm) using 5% HOAc. Three main bands B_1, B_2 and B_3 were located (UV). B_2 was subjected to PC using BAW (4:1:5). Four spots were located and the major band yielded Rm-1. B_3 similarly on PC using TBA (3:1:1) gave Rm-2 from the major band. Approx. yields: Rm-1 (1.2–1.3 g), Rm-2 (0.5 g).

The high R_f values on PC using either H_2O or aq. HOAc were consistent with Rm-1 and Rm-2 being glycosides and the UV spectral data [3] showed them to be apigenin derivatives with all three phenolic groups free. As expected for *C*-glycosides, no apigenin could be detected after acid hydrolysis.

After elimination of non-flavonoid contaminants (70%) by column chromatography on polyamide using 50% aq. MeOH, and purification by PC using BAW (4:1:5), Rm-1 was found to be identical with authentic 6-*C*-glucosyl apigenin (isovitexin) on TLC and PC in a range of solvents, including those allowing to distinguish 6-*C*-glucosyl from 6-*C*-galactosyl apigenin [4]. The 6-*C*-glucosylapigenin structure was confirmed by permethylation of Rm-1 and direct comparison of MS and R_f of the PM derivative with those of PM isovitexin [5].

TLC of Rm-2 on cellulose using *n*-BuOH–27% aq. HOAc (1:1) showed three interfering spots: R_f 0.48, 0.55 (major) and 0.60. However, TLC of permethylated Rm-2 on Si gel using $CHCl_3$–EtOAc–Me_2CO (5:4:1) showed two main bands, one of which gave the same MS and R_f as PM 6-*C*-glucosyl 8-*C*-arabinosylapigenin (PM schaftoside) [5]. The MS of the other band showed the presence of two products, a PM di-*C*-hexosylapigenin (M^+ 748) and a PM *C*-pentosyl-*C*-hexosylapigenin (M^+ 704) which was deduced to be a PM 6-*C*-hexosyl-8-*C*-pentosylapigenin from the presence and importance of the corresponding M-103 and M-175 peaks [5]. Moreover, the R_f agreed with that showed by PM 6, 8-di-*C*-glucosylapigenin (PM vicenin-2) or PM 6-*C*-glucosyl 8-*C*-xylosyl apigenin (PM vicenin-3). Finally, co-chromatography of Rm-2 with authentic samples in the aforementioned conditions confirmed the presence of schaftoside (0.55), vicenin-2 (0.48) and vicenin-3 (0.60).

Since there was no free apigenin or other flavonoid aglycones before or after hydrolysis of leaf extracts, all flavonoids of *Rynchosia minima* leaves are *C*-glycosides.

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