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AURONE GLYCOSIDES OF *ANTIRRHINUM ORONTIUM*

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Plant. Antirrhinum orontium L. (*Misopates orontium* (L.) Raf.) has been placed in the unclassified section of the Antirrhinae as it lacks aurones. *Source.* Seeds of two types, the (rarer) pale form of the British Isles and the magenta form, collected in Belgium, both obtained from Kew. *Previous work.* Dayton [1] and Harborne [2] both recorded the absence of aurones from this plant.

Present work. The presence of aureusidin-6-glucoside (aureusin) was confirmed and of bracteatin-6-glucoside inferred, both being present in, and along the base of, the corolla tube hairs. *Extraction.* Flowers of both types were extracted in 1% HCl in MeOH, this being used as the stock solution which was streaked onto Whatman 3MM chromatography paper. Purification and identification then proceeded according to standard methods [3, 4]. *Identification.* The faster of the two aurones co-chromatographed with aureusin-6-glucoside in six solvents (TBA, BAW, CAW, PhOH, 15% HOAc and 30% HOAc) and yielded aureusidin and glucose on acid hydrolysis. Spectrometry: faster aurone: λ_{max} 272, 321, 404 $\Delta\lambda$(alk) = +84, $\Delta\lambda(AlCl_3)$ = +63 faster aurone (hydrolysed) λ_{max} 253, 269, 400. The slower of the aurones cochromatographed with bracteatin-6-glucoside (aureusin and bracteatin-6-glucoside were both extracted from *sulf/sulf inc/inc* genotypes of *Antirrhinum majus*) in all six solvents, but there was too little of it to ascertain a precise structure. However, there seems little doubt as to its identity.

Discussion. Hitherto, the absence of aurones in *Antirrhinum orontium* has been used to separate it from the section Antirrhinum. This may no longer be employed as a criterion.

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COUMARIN GLYCOSIDES FROM *PEUCEDANUM OSTRUTHIUM*

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Key Word Index—*Peucedanum ostruthium*; Umbelliferae; scopolin; marmesinin; glycoside of oxypeucedanin hydrate.

Plant. Peucedanum ostruthium L. (Koch), syn. *Imperatoria ostruthium* L. - Umbelliferae, collected in South-Tyrol.* *Previous work.* Several coumarins, furocoumarins, a chromone, and hesperidin were previously isolated from the roots [1].

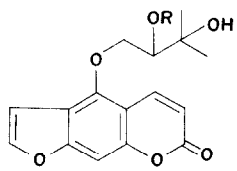
Present work. Dried roots (440 g) were extracted with C_6H_6. The residue of the benzene extract yielded osthol, ostruthin, ostruthol, isoimpera-

* The plant was kindly collected by F. Augscheller, St. Martin, South-Tyrol, Italy.

torin, imperatorin, oxypeucedanin, oxypeucedanin hydrate, peucenin, and a sterol mixture (MP, TLC, UV, IR, NMR, MS).

The concentrated methanolic extract was kept in a refrigerator. The precipitated hesperidin was filtered off and the fluorescing components of the mother liquor were separated on a polyamide column. Elution began with H_2O followed by H_2O–MeOH mixtures. TLC control of the fractions eluted with 20% MeOH showed the presence of several fluorescing polar compounds. They were separated by preparative TLC (silica gel) in $CHCl_3$–MeOH 9:1. The most polar zones yielded a yellow (R_f: 0·22; system: $CHCl_3$–MeOH 85:15), and three violet fluorescing compounds. One of the latter (R_f: 0·19) was identified (TLC, hydrolysis) as scopolin, the second (R_f: 0·25) as marmesinin. The third glycoside (R_f: 0·10) afforded on acidic hydrolysis the same aglycon as marmesinin. Its R_f-value suggests to be a diglycoside of marmesin.

The yellow fluorescing glycoside crystallized from MeOH in white needles, turning slowly yellow by heating (m. 210–220°, dec.). Its UV spectrum is typical of the 5-alkoxy-furocoumarin nucleus [2]; λ_{max}: 240 sh, 249, 259, 266, 308 nm; λ_{min}: 235, 255, 263, 275 nm. The glycoside was hydrolysed with N H_2SO_4, the aglycon extracted with EtOAc and identified as oxypeucedanin hydrate (**1**). The sugar moiety was identified by PC as D-glucose. Thus, the probable structure of the glycoside is **2.**



(**1**) R = H

(**2**) R = Glc

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ISOLATION OF IPOLAMIIDE FROM *STACHYTARPHETA INDICA*

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Key Word Index— *Stachytarpheta indica*; Verbenaceae; iridoids; ipolamiide; hebenstreitia glycoside B.

Plant. Stachytarpheta indica VAHL. (Voucher specimen deposited at Faculty of Pharmaceutical Sciences, Chulalongkorn University, Department of Pharmacognosy). *Local name.* Ya Phannguu-Khieo, Pra-in-proei. *Source.* Ayudhaya, Thailand. *Previous work.* Occurrence of hebenstreitia glycoside B in *Stachytarpheta*-species [1].

Present work. Aerial parts (dry, 1200 g) of *Stachytarpheta* were macerated overnight with 80% EtOH. After decantation the residue was remacerated. The EtOH was removed under vacuum and the residual aqueous solution treated by standard procedures (lead acetate and charcoal method) [2]. Crystallization and recrystallization from EtOH afforded 14 g needles (1·17%). The properties of this compound and of its tetra- and penta-acetates are identical with those reported for ipolamiide [3] and its acetates respectively (analysis, m.p., optical rotation, UV, IR, NMR). M^+ of the penta-acetate *m/e* 616.

The compound is also identical (m.p., TLC, IR) with the hebenstreitia glycoside B isolated by Kooiman [1].

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