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## SCROPHULARIACEAE

# ISOLATION OF ANTIRRINOSIDE FROM *LINARIA VULGARIS*

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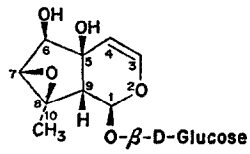
**Abstract**—Antirrinoside (I) has been isolated from dried leaves of *Linaria vulgaris* Mill. The occurrence of aucubin reported by Valdés[1] for the flowers and leaves of various *Linaria* species was not confirmed.

**Zusammenfassung**—Aus getrockneten Blättern von *Linaria vulgaris* Mill. wurde Antirrinosid (I) isoliert. Das Vorkommen von Aucubin, welches von Valdés[1] für Blüten und Blatter verschiedener *Linaria*-Species beschrieben wurde, kann nicht bestätigt werden.

RECENTLY, Valdés[1] has studied the flower and leaf pigments present in the genus *Linaria* and in several species he also detected aucubin. The near relationship of the genus *Linaria* to *Antirrhinum* led us to doubt the presence of aucubin in the former. The iridoid glucosides so far isolated from *Antirrhinum* species are antirrinoside (I),[2] 5-*O*-*β*-glucosyl-antirrinoside[3] and antirride.[4]

Our investigation of *Linaria vulgaris* Mill. showed, that aucubin is not present either in the leaves or in the flowers. Using TLC, the principle iridoid constituent was shown to have similar properties to (I) and to occur both in flowers and in leaves. The NMR spectrum of the isolated compound shows all the typical peaks for antirrinoside (I) (see Experimental).




I

## EXPERIMENTAL

50 g of dried leaves of *Linaria vulgaris* (collected in June 1970 near Ligerz, Switzerland) were extracted for 30 min with hot 95% EtOH. The suspension was filtered and the residue re-extracted. The EtOH was removed under vacuum and the residue, after addition of $H_2O$, was extracted several times with $Et_2O$. Phenols, tannins and flavonoids were removed from the aqueous solution by filtration using $Al_2O_3$.[5] The filtrate was evaporated to dryness. The iridoids were separated by column chromatography using silica gel (*n*-BuOH–MeOH–$H_2O$, 70:5·20) The crude antirrinoside was purified by column chromatography using silica gel (acetone).[2] After filtration (MF-Millipore GSWP 0·22 $\mu$m) and lyophilization, 2·15 g (4·3%) of pure, amorphous antirrinoside (I) were obtained ($[\alpha]_D^{22}$ −78·3° (c = 4·21; dioxane)) The IR and NMR spectra of the isolated antirrinoside have been found to be identical with the spectra of an authentic sample of J.* NMR spectrum of antirrinoside (see also[2]) ($D_2O$, TMS as external standard; 100 MHz): $\delta$ (ppm) 6·91 d

* Isolated from *Antirrhinum majus* L. (Scrophulariaceae).

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[4] M. L. SCARPATI and M. GUISO, *Gazz. Chim. Ital.* **99**, 807 (1969).
[5] O. STICHER, *Pharm. Acta Helv.* **44**, 453 (1969) and references cited therein.

($J$(c/s) = 6·2), for H at C-3; 5·95 d ($J$ = 6·2), for H at C-1; 5·41 d ($J$ = 6·2), for H at C-4; 4·53 d ($J$ = 2·0), for H at C-6; 4·05 d ($J$ = 2·0), for H at C-7; 2·95 d ($J$ = 6·2), for H at C-9; 1·95 s, for 3 H at C-10.

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# MONOCOTYLEDONAE

## ORCHIDACEAE

## ISOQUERCITRIN FROM *ORCHIS SAMBUCINA*

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**Abstract**—A flavonoid pigment of *Orchis sambucina* is isolated and identified as 3-*O*-β-D glucoside of quercetin (isoquercitrin).

*Plant. Orchis sambucina* L. (syn.: *Dactylorchis sambucina* L., *Dactylorhiza sambucina* (L.) Soò).[1]

*Material.* Air-dried flowers of yellow *O. sambucina*, collected at Colle di Tenda (Piemonte, Italy), about 1700 m above sea level, Summer 1969.

*Previous works.* No information on chemical constituents of this species. The congenerial *O. mascula* is referred as containing cyanidin 3,5-diglucoside.[2]

*Uses.* The roots of several Orchidaceae, probably including *O. sambucina*, furnish Tubera Salep, forming a water-jelly highly nutritious and also used as an industrial starch.[3]

*Isolated flavonoid.* Isoquercitrin (3,3′,4′,5,7-pentahydroxyflavone 3-*O*-β-D glucoside), from the 20% MeOH extract of the defatted flowers by polyamide column[4] and preparative paper chromatography. Identified by UV spectra,[5–7] $R_f$ values,[8] and hydrolysis. The PMR spectrum of the compound acetate (pyridine, acetic anhydride; 24 hr) agree with the

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