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THE GLYCOFLAVONE VICENIN-2 AND ITS DISTRIBUTION IN RELATED GENERA WITHIN THE LABIATAE

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Key Word Index—*Origanum*; Labiatae; vicenin-2; glycoflavone; chemotaxonomy.

Abstract—In a leaf flavonoid survey of *Origanum* the flavone *C*-glycoside, vicenin-2, was found to be restricted to the section *Majorana*. This is the first report of a glycoflavone in the Labiatae.

The genus *Origanum* L. is a taxonomically confused genus containing approximately 22–26 species whose geographical distribution extends from North Africa and western Europe to central Asia, although most species occur in the Mediterranean basin. The genus has been variously treated in the past, some authors recognizing a number of distinct genera (e.g. [1]), others recognizing only sections (e.g. [2]); both treatments are still in current use [3, 4].

In the course of a phytochemical survey of *Origanum* and other genera, in which at least 75% of the species within each group was examined, it was observed that while flavone *O*-glycosides occurred ubiquitously, the biosynthetically distinct flavone *C*-glycoside, vicenin-2 (V-2), occurred sporadically. However, closer examination of the distribution of V-2 revealed that it occurred only in certain taxonomic groups (see Table 1). Thus, section *Majorana* of the genus *Origanum*, sections *Pseudothymbra* and *Thymus* of the genus *Thymus* and the genus *Hyssopus* are characterized by the accumulation of V-2 (together with flavone *O*-glycosides), whereas the other two sections of the genus *Origanum* (e.g. *Origanum*, *Amaracus*) and other genera (e.g. *Lycopus*, *Rosmarinus*, *Calamintha* and *Melissa*) contain only the flavone *O*-glycosides.

This is the first reported occurrence of a flavone *C*-glycoside in the genus *Origanum* and probably also in the Labiatae [5]. Further, its occurrence appears to be taxonomically significant since it does not reflect any geographic pattern and so is probably independent of environmental influence. It is noteworthy that all the genera except *Origanum* have proven in this survey to be homogeneous with regard to V-2 distribution. Within *Origanum*, the section *Majorana* is alone in accumulating V-2. Morphologically it is distinguished from the other two sections on the basis of calyx shape. There are problems in delimiting section *Majorana* morphologically and the presence of V-2 appears to provide a useful character for this purpose.

EXPERIMENTAL

Samples of each specimen studied are deposited in the University of Reading herbarium (RNG).

Phytochemical procedures. Dry leaf material was ground and extracted 2× with MeOH–H_2O (1:1). 2D-PCs (Whatman 3 MM, 46 × 57 cm) were spotted with the extract from *ca* 50 mg of plant material (dry wt) and run in *n*-BuOH–HOAc–H_2O (4:1:5, BAW) and 15% HOAc. UV-absorbing spots in the region of V-2 (R_f 0.30, BAW; 0.56, HOAc; 0.57, phenol) were eluted and treated with 2 N HCl at 100° for 1.5 hr. Compounds unaffected by this treatment were chromatographed against V-2 ex *Conocephalum conicum* [6] and schaftoside/isoschaftoside ex. *Philodendron evansii* in the solvents; BAW, 15% HOAc and phenol–H_2O (4:1). An MS run on the permethyl ether of V-2 from *Origanum majorana* showed the following major ions (*m/z*): 717 (72.7%, M − 31), 645 (8.1%, M − 103), 585 (19.8%, M − 163), 573 (32.9%, M − 175 hexose fragment), 559 (5%, M − 189), 543 (5.2%, M − 205) and 541 (5.7%, M − 207).

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Table 1. Distribution of apigenin 6,8-di-*C*-glucoside (vicenin-2) in *Origanum* species and selected species from related genera. Family Labiatae (subtribe Thyminae, tribe Saturejeae)

Genera	Section	Species	Geographical location of the investigated plants	Presence/ absence of V-2
Origanum L.	*Majorana* (Miller) T. Vogel	*O. majorana* L.	Spain, Italy	+
		O. microphyllum (Benth.) Boiss.	Crete	+
		O. onites L.	Greece, Spain	+
		O. syriacum L.	Libya, Jordan	+
		O. majoricum Camb.	Spain	+
	Amaracus Benth.	*O. dictamnus* L.	Crete	–
		O. scabrum Boiss. & Heldr.	Greece	–
		O. rotundifolium Boiss.	Turkey	–
		O. leptocladum Boiss.	Turkey	–
		O. sipyleum L.	Turkey	–
		O. tournefortii Aiton.	Greece, Crete	–
		O. ciliatum Boiss. et Kotschy	Turkey	–
		O. libanoticum Boiss.	Syria, Lebanon	–
		O. vetteri Briq. & W. Barbey	Crete	–
	Origanum Benth.	*O. vulgare* L.	U.K., U.S.S.R., Germany	–
		O. virens Hoffmanns. & Link	Spain, Teneriffe	–
		O. compactum Benth.	Spain, Portugal	–
		O. heracleoticum L.	Greece	–
		O. akdarense Ietswaart & Baulus	Libya	–
		O. isthmicum Danin	Israel	–
		O. ramonense Danin	Israel	–
Thymus L.*	*Pseudothymbra* Benth.	*T. longiflorus* Boiss.	Spain	+
		T. membranaceus Boiss.	Spain	+
		T. villosus L.	Spain, Portugal	+
		T. antoninae Rouy & Coincy	Spain	+
		T. mastigophorus Lacaita	Spain	+

		T. leucotribcus Halácsy	Crete	+
		T. cherlerioides Vis.	Albania, Bulgaria	+
		T. cephalotos L.	Portugal, Spain	+
		†*T. dolopicus* Form.	Greece	−
	Thymus (section *Vulgares* Velen., section *Zygis* Willk.)	*T. vulgaris* L.	Spain	+
		T. capitellatus Hoffmanns.	Portugal	+
		T. zygis L.	Spain	+
		T. camphoratus Hoffmanns.	Portugal	+
		T. hyemalis Lange	Spain	+
		T. baeticus Boiss. ex Lacaita	Spain	+
		T. hirtus Willd.	Spain	+
Lycopus L.		*L. europaeus* L.	U.K., Spain	−
		L. exaltatus L. fil.	U.S.S.R., Roumania	−
		L. americanus Muhl.	U.S.A., Canada	−
		L. laurentianus Rolland-Germain	U.S.A., Canada	−
Rosmarinus L.		*R. officinalis* L.	Spain, Malta	−
		R. eriocalix Jordan & Fourr.	Spain, Libya	−
		R. tournifortii de Noé	Algeria	−
		R. laxiflorus Noé ex Lange var. *reptans*	Algeria	−
Hyssopus L.		*H. officinalis* L.	Spain, France	+
		H. officinalis subsp. *montanus* (Jordan & Fourr.) Briq.	C.C.C.P.	+
		H. officinalis subsp. *canescens* (DC.) Briq.	Spain	+
Melissa L.		*M. officinalis* L. subsp. *officinalis*	Spain, U.K., France U.K., Italy, Spain	− −
Calamintha Miller		*C. grandiflora* (L.) Moench	Spain, Yugoslavia, U.K., Italy	−
		C. nepeta (L.) Savi	U.K., Greece	−
		C. sylvatica Bromf.	Canary Islands	−
		C. ascendens Jordan	U.K., Greece	−
		C. cretica (L.) Lam.	Crete	−

* A few species of other sections of *Thymus* were examined. These do show the presence of V-2 but the sample studied was not large enough to include in this survey.

† Result unconfirmed due to small amount of material available.