

FLAVONOL 3,7-DIGLYCOSIDES OF *VERBESINA ENCELIoidES*

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During a survey for flavonoids in Indian plants of possible medicinal value, *Verbesina encelioides* (Cav.) Benth **8** Hooker fil ex A. Gray was examined. Only one species of *Verbesina* has been examined previously, *V. myricephala*, in which rhamnocitrin 3-O-glucuronide [1] was found.

Two diglycosides and one monoglycoside of quercetin were detected on 2-D Whatman No. 1 paper chromatograms of 70% ethanolic flower extracts of *V. encelioides*. All these glycosides were subsequently isolated from leaf extracts and their R_f data are presented in Table 1. On acid hydrolysis the diglycosides yielded quercetin and equimolar mixtures of glucose and xylose and glucose and galactose, respectively. On mild acid hydrolysis in N HCl for 10 or 20 min, both diglycosides yielded some quercetin 7-glucoside which agreed with an authentic standard by chromatography, UV spectra and colour reactions when viewed under UV light. The detection of the 7-glucoside as an intermediate of acid hydrolysis indicates that the original compound had this sugar in the 7-position [2].

Table 1 shows the UV-spectral data for the quercetin glycosides. The diglycosides showed no shift of band II with NaOAc suggesting a substitution at the 7-position. Also, the spectral maximum at band I for each of the two diglycosides indicates a substitution at

the 3-position. This agrees with the spectral shifts for substitution at the 3-position [3]. The isolated quercetin 3-galactoside gave a typical UV spectrum and shifts for a 3-substituted quercetin. The colour reactions of the isolated diglycosides when the chromatograms were viewed under UV light suggested substitution in the 3- and 7-positions. The diglycosides appeared as dull brown spots on paper but gave the characteristic fluorescent yellow of quercetin 3,7-diglucoside when fumed with ammonia [4]. The quercetin 3-galactoside changed from a dull brown to yellow when exposed to ammonia under UV. Reaction of the two different diglycosides with β -glucosidase yielded the 3-galactoside or 3-xyloside of quercetin, respectively which suggested that the glucose was attached at the 7-position in both cases.

From these results, the three flavonoid glycosides found in *V. encelioides* are identified as: quercetin 3-galactoside, quercetin-3-galactoside-7-glucoside and quercetin 3-xyloside-7-glucoside. Quercetin 3-xyloside was not found. This is the first report of quercetin 3-galactoside-7-glucoside in nature.

EXPERIMENTAL

Plant material was collected from the fields of the Botanical Garden of the Department of Botany, University of Rajasthan, Jaipur, India and a voucher specimen is deposited in the Herbarium of that Institution. After collection, both flower and leaf material was dried, ground and extracted with

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Table 1. R_f and spectral characteristics of the quercetin glycosides of *V. encelioides*

Glycoside	$R_f(\times 100)$ in				$\Delta\lambda_{\max}(\text{nm})$ in			
	BAW	15% HOAc	H ₂ O	Phenol*	80% MeOH	NaOAc	AlCl ₃	H ₃ BO ₃
	Band II	Band I	Band II	Band I	Band I	Band I	Band I	Band I
3-O-Galactoside 7-o-glucoside	32	68	36	45				
3-O-Xyloside 7-o-glucoside	39	65	41	65				
3-O-Galactoside	65	42	13	56				
3-O-Xyloside	76	45	15	75				
3-O-Rutinoside	51	56	29	46				
7-O-Glucoside	37	9	3	38				
3-O-Galactoside 7-o-glucoside	256 (265)†	358	0	62	42	22		
3-O-Xyloside 7-o-glucoside	256 (265)	358	0	62	42	22		
3-O-Galactoside	256 (265)	358	18	62	42	22		
3-O-Xyloside	256 (265)	358	16	62	42	20		

* For solvent composition see ref. [5].

† Infection.

aq. EtOH. The conc extracts were examined by 2D-PC on Whatman No. 1. The three flavonoids that could be detected were isolated and identified by standard procedures [5]. Acid hydrolysis using 2 M HCl for 1 hr yielded galactose as the only sugar in one sample, but the other two glycosides yielded mixtures of galactose and glucose or xylose and glucose, respectively, in *ca* equimolar amounts. Quercetin was the only aglycone isolated from all three glycosides and it agreed with authentic material (UV, co-chromatography and colour reactions in UV light). When fresh, aq. samples of the diglycosides were treated with β -glucosidase they yielded either the 3-galactoside or 3-xyloside of quercetin, which agreed with authentic standards in all respects.

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