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SHORT COMMUNICATION

SULPHURETIN GLYCOSIDES OF *COREOPSIS MUTICA*

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Abstract—The anthochlor complement of *Coreopsis mutica* has been determined. The compounds observed were all glycosidic derivatives of sulphuretin, being the mono- and di-glucosides and two new glucosidic derivatives acylated with caffeic acid.

INTRODUCTION

THE ANTHOCHLOR pigments (chalcones and aurones) are of restricted occurrence in plants. The compounds are found in the subtribe Coreopsidinae of the Compositae, and also occur sporadically in a number of other families.[1,2] Geissman and co-workers have elucidated the anthochlor components of a number of species of *Coreopsis*.[3–5] Shimokoriyama and Hattori[6] and Shimokoriyama[7] have also been concerned with these pigments in *Coreopsis*. In spite of the work which has been done, fewer than 10% of the species in the genus have been investigated for chalcones and aurones. In a recent taxonomic study of the Mexican species *Coreopsis mutica*,[8] tentative identifications were given for several anthochlors found in the flowers and leaves of the plants. The purpose of this paper is to report the structures of the aurone compounds which include two new acylated derivatives.

RESULTS AND DISCUSSION

Two dimensional paper chromatographic separation of the petal extracts of all varieites of *Coreopsis mutica* yielded four aurone glycosides and the parent aglycone, sulphuretin. All analytical chromatographic data on these compounds were obtained by means of standard TLC techniques (Table 1). The compounds were further characterized by spectral methods using standard shift reagents (Table 2). The small amounts of chalcone compounds found in some of the mixtures were not characterized, however, these compounds, residues of the oxidation to aurones, were separated from the corresponding aurone by paper chromatographic methods.

Spectral data (Table 2) showed that these compounds, all derivatives of the aurone aglycone sulphuretin (I), had only the functional group (—OH) at C_6 substituted. Evidence for the above assignment was obtained by spectral shifts.[9,10]

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TABLE 1. R_f VALUES OF AURONE GLYCOSIDES FROM PETALS OF *Coreopsis mutica*

Compound	$R_f \times 100$ in*				
	BAW	30% HAc	15% HAc	TBA	AHW
A	37	22	9	27	16
B	55	58	24	48	42
C	38	68	33	19	54
D	23	32	15	11	22
Sulphuretin	74	8	3	69	6

* Determined by TLC on Avicel micro-crystalline cellulose plates (250 μ) as listed in the Experimental.

Acid hydrolysis in all cases produced the parent aglycone, sulphuretin and glucose; thus, compounds *D* and *A* were characterized by TLC as the di- and mono-6-*O*-β-D-glucosides of sulphuretin respectively. Partial hydrolysis[11] of the acylated compound *B* produced in order of appearance; caffeic acid and compound *D*; then, compound *A* and finally the aglycone. Acylated compound *C* hydrolyzed first to caffeic acid and a triglucoside, then, compound *D*, compound *A* and sulphuretin in that order.

TABLE 2. SPECTRAL PROPERTIES OF AURONES FROM *Coreopsis mutica* PETALS

Compound	λ_{max} (nm) in MeOH						
	Band I					Band II	
	Alone	NaOMe	$AlCl_3$	$AlCl_3$–HCl	NaOAc–H_3BO_3	Alone	NaOAC
A	403	491	450	405	432	275	278
B	397,323*	490	450	405	430	284	280
C	400,323*	495	445	405	429	285	287
D	402	500	450	402	431	275	275
Sulphuretin	395	467	450	400	424	270	270

* Indicates acylation.

Alkaline hydrolysis of acylated compounds *B* and *C*[12] produced caffeic acid, as shown by TLC, plus the partially hydrolyzed glycosides, compounds *D* and *A*. This information confirmed the interpretation arrived at by spectral methods.

Alkaline degradation[13] of mixtures of the chalcone–aurone pairs, which were found together in the petal extracts, was carried out under nitrogen in 15% barium hydroxide. The

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degradation products of this reaction were examined by TLC and thin layer electrophoretic (TLE) methods. In each case, the degradation showed the expected products; resorcinol, protocatechuic acid and 2,4-dihydroxyacetophenone. These data, then, confirmed the preceding observations that there were no substitutions in the 'A' ring other than at C_6.

This appears to represent the first report of acylation in anthochlor compounds. Because so few species of *Coreopsis* have been surveyed for chalcones and aurones, it is impossible to draw any meaningful taxonomic or phylogenetic conclusions from the data at hand. It is of interest to note, however, that the other two species in the same section as *Coreopsis mutica* (sect. Electra), i.e. *C. cuneifolia* and *C. parvifolia*, also appear to contain the same acylated compounds. In addition, the three taxa in the closely related section Anathysana contain acylated anthochlors.[14] The plants in these two sections display a number of morphological features which are considered to be primitive. In other words, these species are probably the most primitive members of *Coreopsis* which have as yet been analysed for anthochlors.

EXPERIMENTAL

Plant material and extraction. Ray florets of *Coreopsis mutica* were obtained from plants in Mexico and also from the progeny of the same plants grown from seed in the greenhouse. Extractions were carried out in cold MeOH for 24 hr and subsequently were separated on Whatman 3 MM papers developed downwards with *TBA* t-butyl alcohol–acetic acid–water (3:1:1) followed by 15% HOAc. The individual spots were cut out, and extracted with cold MeOH.

Chromatography. Two dimensional TLC was performed on Avicel micro-crystalline cellulose plates (250 μ) using *BAW*, *n*-BuOH–HOAc–H_2O (4:1:2) in the first direction and 30% HOAc in water for the second direction development. Other analytical procedures were performed on Avicel plates as above in the following solvent systems: *BAW* (as above); *TBA* (as above); 15% and 30% HOAc; *AHW*, HOAc–HCl (12 N)–H_2O (25:3:72); *CAW*, $CHCl_3$–HOAc–H_2O (50:45:5); *BzAW*, benzene–HOAc– H_2O (6:7:3 upper phase); 2% HOAc. Sugars were developed on Whatman No. 1 with *BAW*; and, on buffered (0·3 M KH_2PO_4) silica gel plates (250 μ) which were developed in *n*-BuOH–Me_2CO–H_2O (4:5:1)[15] and visualized by means of the Partridge reagent.[16]

Thin layer electrophoresis. TL electrophoresis[17,18] was carried out on Avicel microcrystalline cellulose plates (500 μ) which were carefully sprayed with 0·05 M borate buffer (pH 10). The compounds were developed for 2 hr using 250 V. The plate was removed and sprayed with the DSA reagent[19] for visualization.

Spectral analyses. UV spectra (Table 2) were determined in MeOH and with addition of reagents as described.[9,10]

Acid hydrolysis. Hydrolysis was in 2*N*–HCl in 50% MeOH for 1 hr at boiling. Aglycones and sugars were separated and identified using standard techniques.[20] Partial acid hydrolysis of the respective pigments (*B* or *C*) was performed by the method of Abe and Hayashi.[11]

Alkaline degradation. A concentrate of the respective (chalcone–aurone) mixture in methanol was refluxed for 1 hr in 1–2 ml of 15% $Ba(OH)_2$ in N_2.[13] The phenolic acids and other degradative compounds were extracted with Et_2O and identified with TLC in *CAW*, *BzAW* and 2% HOAc.

Alkaline hydrolysis. Mild alkaline hydrolyses of the pigments (*B* or *C*) was carried out in N_2 according to the method of Albach, *et al.*[12]

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Key Word Index—Coreopsis mutica; Compositae; aurones; suphuretin; acylated glycosides.