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VARIATIONS IN PIGMENT PATTERNS IN *PYRRHOPAPPUS* AND RELATED TAXA OF THE CICHORIEAE

JEFFREY B. HARBORNE
Botany Department, The University, Reading, U.K.

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Abstract—The chalcone of the yellow ligules of *Pyrrhopappus* has been identified as coreopsin. Related species in the same subtribe differ in having yellow carotenoids in the ligules and in having flavonols in the leaves. These chemical results confirm the distinctiveness of *Pyrrhopappus* from other members of the Microseridinae already evident in its different geography and chromosome number. Two chalcones in flowers of *Coreopsis nuecensis*, a Texan endemic, were identified as marein and lanceolin.

INTRODUCTION

The recent report of unidentified anthochlors in *Pyrrhopappus* (Cichorieae) was of considerable interest since this is the first time that these characteristic composite pigments have been recorded in this particular tribe of the family [1]. Previously, these yellow flower pigments have been reported mainly in the Coreopsidinae of the Heliantheae (especially *Coreopsis*), with isolated occurrences in the Cynareae (*Carthamus*) and Inuleae (*Gnaphalium Helichrysum*) [2,3]. It was of interest to know the nature of the anthochlor present in *Pyrrhopappus*, since pigments previously isolated from the Compositae fall into two structural classes: those based on a resorcinol A-ring (Heliantheae): and those based on a phloroglucinol A-ring (Cynareae, Inuleae).

The present paper, therefore, records the identification of the major anthochlor as the resorcinol-based chalcone coreopsin and also reports on the results of a survey of taxa related to *Pyrrhopappus* for this and other pigments.

RESULTS AND DISCUSSION

The main anthochlor of *Pyrrhopappus* yellow ligules, isolated from fresh flowers, was identified as coreopsin (butein 4'-glucoside) by standard analyses and also by direct comparison with the authentic sample from *Coreopsis tinctoria*. Minor amounts of butein (2',4',3,4-tetrahydroxychalcone) and sulphuretin (the aurone corresponding in structure to butein) were also identified in the flowers, but they could have been formed from coreopsin by hydrolysis and oxidation during extraction and chromography and may not necessarily occur in the intact ligule. Coreopsin was readily identified as being the major anthochlor of all five known taxa of *Pyrrhopappus* (see Table 1) and it is clearly characteristic of the genus.

A search of related taxa in the Microseridinae, the same subtribe of the Cichorieae as *Pyrrhopappus*, showed that chalcones and aurones were absent, yellow flower colour being due to carotenoid (Table 1). Analysis of leaf flavonoids of these same plants showed that all contained

Table 1. Chemical and Biological variation in the subtribe Microseridinae

Taxon	Origin and basic chromosome number	Presence/absence of chalcone	carotenoid	flavone	flavonol*
Agoseris heterophylla (Nutt.) Greene	Western	−	+	−	+
A. grandiflora (Nutt.) Greene	North	−	+	+	+
Microseris linearifolia (DC.) Sch. Bip.	America	−	+	−	+
M. heterocarpa (Nutt.) Chamb.	(x = 9)	−	n.d.	−	+
Krigia virginica (L.) Willd.†	(x = 5)	−	+	+	+
Pyrrhopappus grandiflorus (Nutt.) Nutt.		+	−	+	−
P. carolinianus (Walt.) DC.	Eastern	+	−	+	−
P. rothrockii Gray	North	+	−	+	−
P. multicaulis DC.	America				
var. *geiseri* (Shinners) North.	(x = 6)	+	−	+	−
var. *multicaulis* DC.		+	−	+	−

* Flavones were luteolin mainly, with some apigenin, present as 7-glucoside and as other 7-glycosides; flavonols were quercetin 3-glycosides; † Two other species of *Krigia* were also examined, with similar results.

flavonols (sometimes accompanied by flavones) whereas *Pyrrhopappus* species only have flavones in the leaves [see 1]. There are thus two major chemical features—presence of chalcone coreopsin in ligules and absence of flavonols in leaf—which distinguish *Pyrrhopappus* from all other genera in the same subtribe. These data confirm the distinctiveness of the genus already apparent in its different geography and anomalous chromosome number (see Table 1). These combined results suggest that *Pyrrhopappus* is an isolated genus, rather unrelated to the other genera with which it is usually placed.

The finding of coreopsin in Cichorieae, a pigment otherwise characteristic of *Coreopsis* in the Heliantheae, is probably coincidental and is hardly grounds for suggesting a link between two tribes which differ in so many other characters [4]. It does, however, confirm the strong chemical link between the Cichorieae and the rest of the family [5] and argues in favour of keeping the Cichorieae within the Compositae, rather than separating it into its own family, as has often been suggested [6].

In the course of seeking an authentic source of coreopsin in *Coreopsis*, the anthochlors of *C. nuecensis* Heller, a species endemic to Texas, were examined. This recently described species is visually distinct due to the presence of red brown spots towards the base of the yellow ray flowers. Coreopsin was, in fact, absent but there were two major anthochlors, identified as marein (2′,3′4′,3,4-pentahydroxy chalcone 4′-glucoside). Although these pentahydroxychalcone 4′-glucoside) and lanceolin (2′,4′, 3,4-tetrahydroxy-3′-methoxychalcone 4′-glucoside). Although these two compounds occur separately in other *Coreopsis* species, this is the first time they have been found together in the same plant. Their co-occurrence here distinguishes this Texan endemic from all other *Coreopsis* which have been chemically analyzed [3].

EXPERIMENTAL

Plant Material. Plants were collected in the field variously in Texas, U.S.A., in Mexico (nr. Monterrey) and around Santa Barbara, California. They were identified by B. L. Turner, R. Sanders and Dale M. Smith and voucher specimens have been deposited in the herbaria at the Universities of Texas and of California at Santa Barbara.

Pigment Analyses. Chalcones and aurones were isolated, purified and characterised by standard procedures [7]. Coreopsin was identified by UV spectrum (+ shifts), R_f in 5 solvents and hydrolysis with β-glucosidase to butein, identified in turn by UV spectrum, MS (parent ion at 272, $C_{15}H_{12}O_5$ requires 272) and R_f in 5 solvents. Authentic coreopsin and butein were obtained from *Coreopsis tinctoria* flowers [see 3]. Marein was similarly identified, authentic markers being also obtained from *C. tinctoria*. Lanceolin was identified as such on the basis of comparison with lit. data. Its identity was confirmed by MS of the aglucone lanceoletin (2′,4′,3,4-tetrahydroxy-3′-methoxychalcone) which showed a strong parent iron at 302 m.u. ($C_{16}H_{14}O_6$ requires 302) and two characteristic fragmentations at 166 (A-ring fragment with two hydroxyl and one methoxyl substitution) and at 135 (B-ring fragment with two hydroxyl groups). That it was not based on the isomeric stillopsidin (2′,4′,5′,3,4-pentahydroxychalcone) skeleton, which occurs in *C. stillmanii*, was ruled out by absorptive spectral analysis. Sulphuretin was identified by spectral and R_f comparison with a synthetic sample. Carotenoids were identified variously as flower pigments in *Krigia*, *Agoseris* and *Microseris* by measuring the UV and visible spectra of direct methanolic extracts. All showed characteristic carotenoid peaks at 422, 446 and 474 nm. Measurement in the 310–400 nm region showed that none of the carotenoid-containing species had any significant pigment contribution from yellow flavonoids. Flavone and flavonol glycosides were identified on the basis of 2D-chromatographic profiles of direct extracts and of detection of luteolin, apigenin and/or quercetin after acid hydrolysis.

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REFERENCES

1. Northington, D. K. (1974) *Spec. Publ. Mus. Tex. Tech. Univ.* **6**, 1.
2. Harborne, J. B. (1977) In *Biology and Chemistry of the Compositae* (V. H. Heywood, J. B. Harborne and B. L. Turner, eds.) in press. Academic Press, London.
3. Bohm, B. A. (1975) In *The Flavonoids* (J. B. Harborne, T. J. and H. Mabry, eds.) pp. 442–504. Chapman & Hall, London.
4. Wagenitz, G. (1976) *Plant Syst. Evol.* **125**, 29.
5. Gonzalez, A. G. (1977). In *Biology and Chemistry of the Compositae* (V. H. Heywood, J. B. Harborne and B. L. Turner, eds.) in press. Academic Press, London.
6. Stebbins, G. C. (1953) *Madrono* **12**, 65.
7. Harborne, J. B. (1967) *Comparative Biochemistry of the Flavonoids*. pp. 78–86. Academic Press, London.