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CAROTENOIDS OF COMPOSITAE FLOWERS

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Abstract-Flowers of twenty six species of Compositae have been investigated for their carotenoid contents. 5,6-Mono and epoxycarotenes were found in fairly large amounts and were the main pigments in a number of cases. Furanoid 5,8-mono and di-epoxides were also identified and were not artefacts due to isolation procedures. Both yellow and orange flowers had large amounts of one epoxycarotene or sometimes one epoxyxanthophyll and orange flowers did not always have a large amount of one carotene as was suggested earlier. In this survey, there was no evidence of one or more carotenoids which were specific to the Compositae although gazaniaxanthin had been shown previously to be restricted to *Gazania* flowers.

INTRODUCTION

IN AN EARLIER *survey* of eleven composites drawn from seven genera, Valadon and Mummery[1] have shown that yellow flowers tended to have more xanthophylls while orange ones had a large amount of one carotene. In the orange *Gazania rigens* which had 64·2% lycopene there was 18·9% gazaniaxanthin which was shown to be the 5′,6′ *cis* isomer of rubixanthin.[2] Rubixanthin is not common in nature, being restricted mostly to roses[3] while gazaniaxanthin has only been found in the genus *Gazania.*

Egger[4] using TLC has shown that both *cis* and *trans* forms of xanthophylls (but not furanoid 5,8 epoxides) are to be found in a number of Composite flowers. He was able to conclude that taraxanthin was *cis*-5,6 monoepoxylutein and lutein epoxide was *trans*-5,6 monoepoxy lutein and that taraxanthin was the correct trivial name. *cis*-Taraxanthin has only been identified in a few flowers (especially in composites) and this may have taxonomic implications as it has been suggested that in view of the limited distribution of certain carotenoids, they may be useful as taxonomic markers.[5] A survey of *18* genera of composites comprising 26 species was therefore undertaken and this is reported in this paper.

RESULTS AND DISCUSSION

The carotenoid pigments present in the twenty six species of flowers of Compositae studied are given in Table 1.

The total amount of carotenoids in any one flower varied from 0·25 mg/g dry weight in the dirty yellow *Santolina teretifolia* to as much as 17·09 mg/g in the yellow orange *Coreopsis grandiflora.* β-Carotene was identified in all the flowers studied in relatively small amounts, reaching 28·8% in the green yellow *Venidium decurrens.* This flower contained chlorophyll as well as carotenoids and had few individual carotenoids, lutein being the only

[1] L. R. G. VALADON and R. S. MUMMERY, *Phytochem. 6,983 (1967).*
[2] *N.* ARPIN and S. LIAAEN-JENSEN. *Phytochem.* 8. *185 (1969).*
[3] L. R. G. VALADON and R. S. MUMMERY, *Ann. Bot.* 33, 671 (1969).
[4] K. EGGER, *Planta 80, 65 (1968).*
[5] L. R. G. VALADON and R. S. MUMMERY, *Ann. Bot.* 33, 879 (1969).

TABLE 1. THE QUANTITATIVE DISTRIBUTION OF CAROTENOIDS IN SOME COMPOSITAE. THE VALUES GIVEN ARE A PERCENTAGE OF TOTAL CAROTENOIDS

	Phytofluene	α-Carotene	cis-Epoxy-α-carotene	*trans*-Epoxy-α-carotene	β-Carotene	*cis*-Monoepoxy-β-carotene	*trans*-Monoepoxy-β-carotene	*cis*-Diepoxy-β-carotene	*trans*-Diepoxy-β-carotene	β-Zeacarotene	δ-Carotene	Cryptoxanthin isomer	Cryptoxanthin	Flavochrome	Mutatochrome	Aurochrome	*cis*-Taraxanthin	*trans*-Taraxanthin	Lutein	Zeaxanthin	Antheraxanthin	Chrysanthemaxanthin	Flavoxanthin	Auroxanthin	Total carotenoids (mg/g)
Acnuea ageratum	3·0	1·4		12·4	7·7		52·8												5·4				16·8	0·5	0·45
A. filipendulina					2·8	1·4	76·3		4·5										8·6				6·4		1·35
Bidens ferulaefolia		0·1		0·8	5·5		52·5												28·3				6·7	6·1	5·76
Chrysanthemum carinatum		0·3		0·3	0·6		7·2	8·8	26·3		0·1	1·1			14·2	0·3			0·1					40·7	10·53
C. coronarium					1·3	0·7	83·9												1·9				12·0	0·2	2·61
C. segetum		0·2		9·2	0·4		40·7							1·7	40·1								3·3	4·4	6·97
Coreopsis grandiflora		0·1		26·5	1·9		35·2		22·2				3·8		6·2				1·6		2·5				17·09
C. tinctoria	0·1	0·7		8·6	5·1		63·3											1·2	8·3				8·7	4·0	6·59
C. verticillata		0·5			0·8	7·2	63·2		2·3				4·1		14·0				3·9				4·0		4·94
Cosmidium brunette		0·3		2·5	11·3		63·4		4·7										14·5				3·3		3·68
Crepis capillaris				35·8	0·8				23·8						11·4								28·2		8·94
Gaillardia aristata					3·7	6·3	36·5					29·1								9·0		2·0	9·3	4·1	1·34
Helianthus decapitatis var. Loddon Gold	0·1	0·1		1·2	0·7	12·7	13·3		13·5					0·3	7·5	2·7	29·6	8·2				1·7	8·2	0·2	9·60
Helichrysum bracteatum	1·2	0·5		10·3	5·9		35·7		15·1										3·6				77·3	0·4	0·65
Layia elegans		0·6		3·3	1·3		27·1	34·0	5·6				15·5										11·9	0·7	5·16
L. platyglossa		0·4		37·5	1·3		39·9					11·0											9·8	0·1	4·47
Rudbeckia speciosum	0·8				2·0	0·7	4·0						73·8						2·0			0·6	10·7	0·4	3·77
Santolina teretifolia	0·8				7·0		9·8		34·7										9·1				38·6		0·27
S. viridis		0·6		11·5	5·6		48·6		10·8										12·4				9·3	1·2	0·54
Solidago canadensis				0·5	3·3				34·6		0·2		17·4					8·2	4·7				23·3	7·8	1·47
Solidago sp var. Tom Thumb	0·7	0·3		3·7	1·1		46·1						5·8					4·0	5·0			0·9	32·4		1·39
Tanacetum vulgare				10·2	2·7			22·9	29·1	0·8					9·7				3·2				21·4		0·69
Taraxacum kok-saghyz		0·2		7·2	0·9				46·1					6·2	23·5		4·1	7·1					4·7		3·31
Tragopogon pratensis		0·1		4·2	1·7			13·4	13·1									34·6	9·2				20·6	3·1	1·51
Ursinia calendulifiora		0·8			13·9		3·6	8·0	8·5				1·7		3·6								38·6	21·3	1·86
Venidium decurrens		1·2			28·8				19·3						48·3				2·4						1·08

xanthophyll present. Lutein, the principal xanthophyll of green leaves, was not universally identified in the flowers studied.

A feature of this survey was undoubtedly the presence of large amounts of 5,6 and 5,6:5′,6′ epoxides of carotenes making up more than 50 % of total carotenoids in most cases. While both the *cis* and *trans* forms of 5,6 monoepoxy-β- and 5,6:5′,6′ diepoxy-p-carotenes were found in a number of cases, only *trans*-5,6 monoepoxy-a-carotene was identified and this in 18 of the 26 species. *trans*-Taraxanthin (5,6 Monoepoxylutein) however, was rather uncommon and found in 4 species alone and together with cis-taraxanthin in 2 species only : ***Helianthus decapitatis*** and ***Taraxacum kok-saghyz***. Taraxanthin seems therefore to be rather restricted in distribution but not the 5,6 and 5,6,5′,6′ epoxides of carotenes. The presence of large amounts of these epoxycarotenoids in flowers is rather puzzling and three suggestions have been put forward as to their functions. Firstly, they may be intermediates in the transfer of oxygen and formation of xanthophylls[6] but as very little xanthophyll (excluding the compounds themselves) is found in these flowers, this suggestion is unlikely to be the correct one here. Secondly, they may play some part in the reproduction of plants. [7] Again this is not likely as these expoxycarotenoids are not restricted to floral parts and have been identified in green leaves[8] as well. Thirdly, as the epoxides revert to carotenes by loss of oxygen,[9] they may act as oxygen carriers in plants which seems more likely.

A number of carotenoids identified were found in very few cases, e.g. I-carotene, β-zeacarotene, cryptoxanthin, lutein, antheraxanthin and zeaxanthin and then only in small amounts. The 5,8 and 5,8,5′,8′ furanoid epoxides of carotenes, namely aurochrome, mutatochrome and flavochrome were found in only ten species, while the 5,8 and 5,8,5′,8′ furanoid epoxides of xanthophylls, auroxanthin, chrysanthemaxanthin and flavoxanthin were rather more common and were found in fairly large amounts. Egger[4] did not detect any 5,8 and 5,8,5′,8′ furanoid epoxides of xanthophylls in the Compositae he studied, namely, ***Taraxacum officinale***, ***Helianthus annuus*** and ***Tussilago farfara*** and suggested that the furanoid 5,8 and 5,8,5′,8′ epoxides found by other workers may be regarded as artefacts due to the isolation procedures. Our results are not in agreement with this observation. It is true that as Egger[4] was more interested in the carotenoids of the hypophasic fraction, he did not identify those of the epiphasic fraction and therefore he may or may not have obtained the 5,8 and 5,8,5′,8′ furanoid oxides of carotenes. Even so, the epoxy compounds we obtained were not found in all cases studied which would have been the case had they been artefacts. Furthermore, there is a difference between epoxides of carotenes and those of xanthophylls; whereas 5,6 and 5,6,5′,6′ epoxides of xanthophylls take a few minutes to be converted to the corresponding 5,8 and 5,8,5′,8′ compounds ***in vitro,*** the epoxides of carotenes take a matter of hours. Therefore, one would have expected to find all the epoxides of xanthophylls as the 5,8 and 5,8,5′,8′ furanoid oxides and no, or very little, 5,8 and 5,8,5′,8′ epoxides of carotenes as these would not have been formed in the few minutes it takes to extract the carotenoids.

As far as we are aware, the pigment composition of the flowers of ***Tragopogon pratensis, Senecio nemorensis*** and ***Solidago canadensis*** were the only ones that had been reported previously. Karrer and Notthafft[10] showed that ***T. pratensis*** contained lutein and violaxanthin, whereas in the present study no violaxanthin was obtained but 34·6% of ***trans***-

[6] L. Cholnoky, C. Gyorgyfy, E. Nagy and M. Panczel, *Acta Chim. Acad. Sci. Hung. 6, 143 (1955).*
[7] F. B. Jungalwala and H. R. Cama, *Biochem. J. 85,* 1 (1962).
[8] L. R. G. Valadon and R. S. Mummery, *J. Exptl. Bot. 20,132 (1969).*
[9] P. Karrer, E. Jucker, J. Rutschmann and K. Steinlein, *Helv. Chim. Acta* 28, 1146 *(1945).*
[10] P. Karrer and A. Notthafft, *Helv. Chim. Acta* 15, 1195 (1932).

taraxanthin, as well as a-carotene, monoepoxy-a-carotene, p-carotene, diepoxy-p-carotene, lutein, flavoxanthin and auroxanthin. Karrer and Notthafft[10] based their identification on absorption spectra and did not use the conc. HCl-ether test and therefore might have wrongly identified their violaxanthin. The possibility exists, however, that flowers grown in Switzerland may have a different pigment composition to those grown in Britain (vide Valadon and Mummery'). Nitsche and Egger[11] studying the c&isomers of xanthophylls in plants showed that *Solidago canadensis* contained all *trans* and Neo U taraxanthin while *Senecio nentorensis* only had the all *trans* form. We found trans-taraxanthin in the two flowers but were unable to detect the *cis* form in S. *canadensis*. A number of other carotenoids were found as well and these compare very closely with the pigments identified in a horticultural variety of *Solidago* var. Tom Thnmb. The two *Solidago* species are bright yellow flowers and have been shown to have the same amount of total carotenoids.

In the present study, apart from *Solidago* the genera with two or more species are *Achillea*, *Chrysanthemum*, *Coreopsis*, *Layia* and *Santolina*. The two species of *Achillea* are mustard yellow and contain *trans*-5,6 monoepoxy-p-carotene as the main pigment with *A. filipendulina* having three times as much carotenoid as *A. ageratum*, and having slight differences in their carotenoid composition. The three species of *Chrysanthemum* are lemon yellow, white yellow and yellow and one would expect appreciable differences between them. The lemon yellow C. *carinatum* has the most pigments with a large proportion of auroxanthin followed by the yellow C. *segetum* and then the white yellow C. *coronarium;* *trans*-5,6 monoepoxy-p-carotene making up 7, 40 and 84% total carotenoids respectively. These yellowish flowers do not have more xanthophylls than carotenes.

The three species of *Coreopsis* (yellow, orange or orange red) have different amounts of total carotenoids and large amounts of the xanthophylls 5,6 and 5,6,5′,6′ epoxides of carotenes. The red colour is due to anthocyanins and these may also be present in the yellow orange *Coreopsis* which were not investigated for their anthocyanin contents. Once again 5,6 monoepoxy-p-carotene was the major pigment. The two species of *Layia* are white yellow and had fairly similar pigment composition and total except that the cis-form of 5,6:5′,6′ diepoxy-p-carotene was the major pigment in *L. elegans* and the *trans-form* of 5,6 monoepoxy-p-carotene in *L. platyglossa.* It is rather unusual to have the cis-form as a major pigment but this seems to occur occasionally e.g. cis-taraxanthin in *Taraxacum* and in *Helianthus*. The two species of *Santolina* show once more fairly similar pigment composition with the yellow S. *viridis* having twice as much carotenoids as the dirty yellow S. *teretifolia*; flavoxanthin making up 38 % of total carotenoids in the latter and *trans*-5,6 monoepoxy-p-carotene 48% in the former. It is to be noted that yellow flowers have large amounts of one xanthophyll and this is in agreement with the suggestion put forward by Goodwin[12] that yellow flowers contained large amounts of xanthophylls and only traces of carotenes. However, the orange flowers studied were not characterized by the presence of large amounts of carotene.

Finally, the survey of the twenty six species failed to demonstrate any carotenoid that may have been used as a taxonomic marker. Gazaniaxanthin was not detected and seems to be restricted to *Gazania* species while the other 'rare' xanthophyll cis-taraxanthin was only found in two fairly separate genera *Helianthus* and *Taraxacum*. Perhaps a study of a greater number of species might have given a better taxonomic picture but as it stands, the carotenoids of those Compositae studied did not indicate any taxonomic affinities in that

[11] **H. NITSCHE and K. EGGER, *Phytochem.* 8, 1577 (1969).**
[12] **T. W. GOODWIN, *The Chemistry and Biochemistry of Plant Pigments,* Academic Press, New York (1965).**

most of the flowers showed an abundance of 5,6 and 5,6,5′,6′ epoxides of carotenes. Flavonoids seem to be better implicated as taxonomic markers as was shown by Harborne, *et al.*[13] among certain Compositae.

EXPERIMENTAL

Achillae ageratum L. (mustard yellow), ***A. filipendulina*** Lam. (mustard yellow), ***Bidens ferulaefolia*** D.C. (orange), ***Chrysanthemum carinatum*** Schousb. (lemon yellow), C. ***coronarium*** L. (white yellow), C. ***segetum*** L. (yellow), ***Coreopsis grandiflora*** Nutt. ex Chapm. (yellow orange), C. ***tinctoria*** Nutt. (orange red), C. ***verticillata*** L. (yellow orange), ***Cosmidium brunette*** Hort. (orange red), ***Crepis capillaris*** Wallr. (yellow), ***Gaillardia aristata*** Pursch. (yellow-red brown), ***Helianthus decapitatis var. Loddon Gold*** Hort. (yellow), ***Helichrysum bracteatum*** Andr. (yellow red), ***Layia elegans*** Torr. & Gray (white yellow), ***L. platyglossa*** A. Gray (white yellow), ***Rudbeckta speciosum*** Hort. ex Link (orange dark red), ***Santolina teretifolia*** Sennen & Elias (dirty yellow); S. ***viridis*** H&t. (yellow), ***Sofidago canadensis*** L. (yellow), S. var. Tom Thumb Hort. (yellow), ***Tanacetum vulgare*** L. (dull yellow), ***Taraxacum kok-saghyz*** Rodin (yellow), ***Tragopogonpratensis*** L. (dull yellow), ***Ursinia calenduliflora*** Benth & Hooker (orange) and ***Venidium decurrens*** Less. (green yellow) were obtained from the Botanical Supply Unit of the University of London.

Extraction ofpigments. Fully opened flowers were extracted as previously described.[1,14] The structural identity of individual carotenoids was established by comparison with authentic samples by column chromatography, TLC, circular paper chromatography, visible spectroscopy and in a few cases by IR spectroscopy. Column and TLC were carried out as already described[1,14] and circular chromatography on Silica Gel-paper Whatman SG 81 with n-hexane or increasing amounts of acetone in n-hexane as solvent.

The ***cis–trans*** isomers, chrysanthemaxanthin and flavoxanthin were extremely difficult to separate and the values for these two compounds are only approximate. The ***cis–trans*** configuration of the carotenoids was established by the iodine-isomerization test.[7] Carotenoids having 5,6 and 5′,6′ epoxy groups were characterized by their conversion into the corresponding 5,8 and 5′,8′ furanoid epoxides as described by Jungalwala and Cama,[7] using a modified conc. HCl-ether test.

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[13] J. B. HARBORNE, V. H. HEYWOOD and N. A. M. SALEH, ***Phytochem. 9, 2011*** (1970).
[14] L. R. G. VALADON and R. S. MUMMERY, ***Biochem. J.*** 106,479 (1968).