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NEOXANTHIN FROM *HELIANTHUS*, *TARAXACUM* AND *IMPATIENS*

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Dedicated to Professor Dr. KURT EGGER

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Abstract—Neoxanthin has been isolated from petals of *Helianthus annuus*, *Taraxacum officinale* and *Impatiens nolitangere*. It is identical with authentic neoxanthin from *Euglena gracilis*. MS and IR spectra were recorded, showing typical fragmentation patterns of neoxanthin, and an allene group. A pigment with the properties of deepoxineoxanthin and polar xanthophylls, which absorbed at very short wavelengths, were also isolated.

INTRODUCTION

SINCE its first isolation from *Taraxacum officinale*,[1] taraxanthin has attracted the attention of many investigators.[2–4] Its identity with lutein epoxide has been discussed in detail.[5] Other workers have been unsuccessful in reisolating a carotenoid with four oxygen functions and the properties of taraxanthin from the original sources.[6–8] Only Curl[9] has suggested that taraxanthin may be identical with *trans*-neoxanthin. In their study of neoxanthin, Cholnoky *et al.*[10] mention that an original sample of taraxanthin, isolated by Kuhn, had a molecular ion of 600 in the MS consistent with $C_{40}H_{56}O_4$ proposed both by Kuhn and Lederer[1] and by Eugster and Karrer.[11] In this paper we describe the identification of this xanthophyll as neoxanthin.

RESULTS AND DISCUSSION

The free and esterified xanthophylls of *Taraxacum*, *Helianthus* and *Impatiens* are described in detail elsewhere.[5,6,12,13] In all three plants *trans*-lutein epoxide is the main pigment together with lutein (zeaxanthin) and violaxanthin isomers. We collected and

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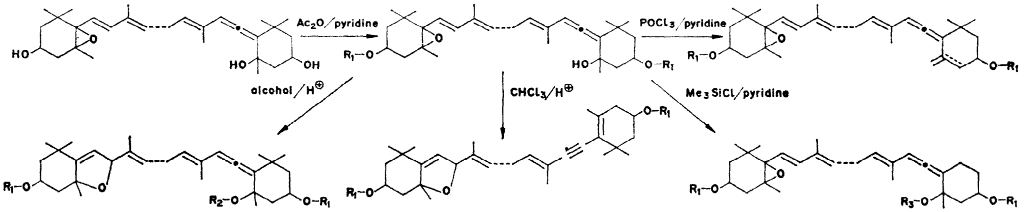
extracted very large quantities of petals from *Helianthus* (10 kg), *Taraxacum* (10 kg) and *Impatiens* (800 g). The extracts of the three species were separately fractionated on columns of basic $ZnCO_3$ and compared by TLC on basic $MgCO_3$ (see Experimental). The polar pigments were finally obtained as three column fractions A (bottom), B (middle) and C (top).

Fraction A. This pigment migrated just behind violaxanthin-neo V[14] and on co-chromatography did not separate from deepoxineoxanthin, recently isolated from the petals of *Mimulus guttatus.*[15] It gave $m/e = 584$ and a fragmentation pattern similar to neoxanthin. An allene peak was detected in the IR (1927 cm^{-1}, KBr). The diacetate, diacetate monosilanate, diacetate monoether and diatoxanthin (with acidic $CHCl_3$) were obtained. With monoperphthalic acid, deepoxineoxanthin yielded neoxanthin (a reaction not yet described).

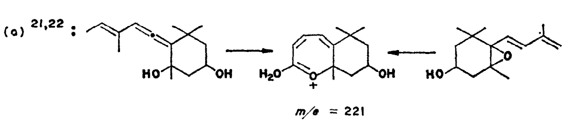


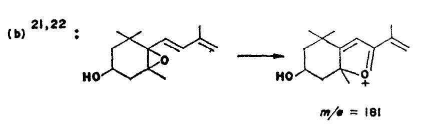
Scheme 1. Reactions of neoxanthin from *Taraxacum*, *Helianthus* and *Impatiens*. $R_1 = CH_3CO$; $R_2 = Et$; $R_3 = Me_3SiCl$.

Fraction B. This pigment had the same R_f in several chromatographic systems as neoxanthin from *Euglena*. With EtOH plus HCl, its spectrum showed a hypsochromic shift of 22 nm. The other reaction products are depicted in Scheme 1. The tertiary allylic hydroxyl group was eliminated from the diacetate with $POCl_3$ in pyridine. The spectrum of the resulting pigment did not differ from the untreated xanthophyll. The allenic pigments deepoxineoxanthin, mimulaxanthin, vaucheriaxanthin and fucoxanthin,[15–19] behaved the

Table 1. Comparison of the MS fragmentation patterns of Fraction B from *Helianthus* and *Taraxacum* with authentic neoxanthin from *Euglena* and Maple leaves

m/e	600	582	567	564	546	520	508	502	490	352	299	287	221	181	57	43	
	7	8	2	3	1	8	5	15	2	7	8	8	14	17	100	40	*Helianthus*
	5	9	2	3	2	9	3	16	2	6	9	11	25	30	100	45	*Taraxacum*
	6	8	1	2	1	4	6	22	3	13	3	3	20	25	100	40	*Euglena*
	8	11	2	5	1	—	12	—	—	—	—	—	—	—	—	100	Maple[10]
	—	M-18	M-18-15	M-18-18	M-18-18	M-80	M-92	M-18-80	M-18-92	—	—	—	a	b	—	—	





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same, which is consistent with the main polyene chromophore being in a plane at right angles to, and therefore not conjugated with, the newly introduced unsaturation on the opposite side of the allene group.[10] The allene was readily detected in the IR (1925 cm^{-1}). The MS fragmentation patterns of *Fraction B* are shown in Table 1. Due to practical difficulties, the reproducibility of the relative peak heights in the MS (especially in the lower mass region) is not good. Nevertheless, the data are in good agreement with those found for neoxanthin by Cholnoky *et al.*[10] According to Kuhn and Lederer,[23] *Impatiens nolitangere* is the best source for taraxanthin. We therefore made a quantitative analysis; the data (Table 2) agree with Kuhn's statement. Nevertheless, the question whether taraxanthin is really identical with the now isolated neoxanthin can only be answered by a re-examination of the original sample.

TABLE 2. QUANTITATIVE COMPARISON OF NEOXANTHIN ISOLATED FROM *Taraxacum*, *Helianthus* AND *Impatiens* PETALS

Species	Source	Content of neoxanthin (mg)	Neoxanthin/ kg fr. wt (mg)
Taraxacum	10 kg	12·6	1·26
Helianthus	10 kg	26·1	2·61
Impatiens	800 g	3·3	4·13

Fraction C. The pigments of this strongly adsorbed fraction gave a diacetate but the spectrum was not changed by acids. From the IR spectrum, they are free from allene groups; the MS gave $m/e = 616$ and others. The chromophore absorbed at 418, 395 and 373 nm in EtOH; the shape of the spectrum resembled that of auroxanthin. Whether these pigments contain in-chain epoxides, recently isolated by oxidation of canthaxanthin with monoperphthalic acid,[24,25] is under investigation.

EXPERIMENTAL

Isolation and *chromatographic* procedures are described in detail elsewhere.[14,16] The operations were done, whenever possible, under N_2. Only redistilled solvents were used. MS were recorded with a Varian MAT CH 5 at 70 eV (for minimizing secondary fragmentations and exact mol peak measurement at 30 eV), an ion source temperature at 290° and the probe heater at 170° using the direct inlet system for the crystallized sample (from Et_2O–light petrol.). The fragmentation patterns were compared with perfluorokerosene. IR spectra were run on a Leitz III G machine with crystallized pigment in KBr.

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