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THE IDENTITY OF TROLLIXANTHIN AND TROLLIFLOR WITH NEOXANTHIN*

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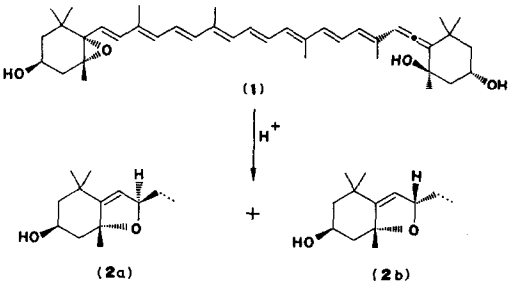
Key Word Index—*Trollius europaeus*; trollixanthin; trolliflor; neoxanthin; trollichrome; trolliflavin; neochrome.

Abstract—Trollixanthin and trolliflor have been shown to be identical with all-*trans*-neoxanthin from chromatographic and spectroscopic (visible, IR, NMR, mass, ORD and CD) evidence.

Karrer and co-workers isolated two pigments from the flowers of *Trollius europaeus* designated trollixanthin [1] and trolliflor [2]. Subsequently the occurrence of trollixanthin-like compounds has been reported in Valencia oranges [3, 4], navel oranges [5], tangerines [6], cling peaches [7] and apricots [8]. Trolliflor-like compounds are described from tomatoes [9], red bell peppers [10] and prunes [11].

Karrer and co-workers considered the elementary composition of trollixanthin and trolliflor as $C_{40}H_{56}O_4$ [12] and $C_{40}H_{56}O_5$ [2] respectively. Acid rearrangement of trollixanthin to trollichrome and of trolliflor to trolliflavin established the presence of an epoxy group in both pigments.

The identity of the visible spectra of trollixanthin and lutein-epoxide lead to the conclusion that trollixanthin was 6′-hydroxylutein epoxide [13]. Bonnet *et al.* [14] later suggested that trollixanthin or trolliflor was stereoisomeric with neoxanthin (**1**), differing in the relative configuration of the 3′-hydroxy and the 5′,6′-epoxy group. Recently Egger and Dabbagh [15] claimed the identity of trollixanthin with neoxanthin on the basis of chromatographic evidence including transformation to diadinoxanthin and failure to form an allylic methyl ether. Stereochemical relations were not considered.



The stereochemistry of neoxanthin (**1**) and the rearrangement products (**2a**, b) has been defined [17, 18]. We now report full evidence for the identity of trollixanthin and trolliflor with all-*trans*-neoxanthin (**1**) by chemical and spectroscopic, including chiroptical, methods. All experiments were carried out with original samples of Karrer and coworkers.

RESULTS AND DISCUSSION

Trolliflor has a visible light spectrum identical with that of all-*trans*-neoxanthin [16] (**1**). Its MS

* Part 9 in the series "Carotenoids of Higher Plants". For Part 8 see *Phytochemistry In press.*

exhibits the molecular ion at *m/e* 600·4180, correcting the molecular formula proposed earlier [2] to $C_{40}H_{56}O_4$. The fragmentation pattern corresponds to that of neoxanthin [16]. IR-absorption at 1925 cm^{-1} proves the allenic structure. The ^1H NMR spectrum is identical with that of all-*trans*-neoxanthin [16]. Trolliflor forms a diacetate and a diacetate-trimethylsilyl ether as expected for neoxanthin. These derivatives were identified by visible light and MS.

Concerning the absolute stereochemistry, the ORD spectrum of trolliflor is identical with that reported for all-*trans*-neoxanthin [16] supporting the same configuration at all chiral centres (C-3,5,6,3',5',6') and excluding geometrical isomerism e.g. 9-*cis*. [16]) in the polyene chain. This result is confirmed by the PMR spectrum of the mixed C-8' epimeric trolliflavin, (**2**a, b) prepared by acid rearrangement of trolliflor. The spectrum is fully consistent with the 3,5-*trans*-furanoxides [18] although the signal reported at 1·52 ppm for the 18'-methyl group appeared in our spectrum at 1·69 ppm.

Trollixanthin and its furanoxide trollichrome (two C-8'-epimers by TLC) are chromatographically indistinguishable from trolliflor (**1**) and trolliflavin (**2**a, b) respectively. The MS and IR spectra of trollixanthin are identical with those of trolliflor and the PMR spectra of trollichrome and trolliflavin are fully consistent. Identical CD spectra of trollixanthin and trolliflor further exclude stereoisomeric differences relative to neoxanthin.

In conclusion trollixanthin and trolliflor are identical with all-*trans* neoxanthin (**1**). The apparent difference in the visible light spectrum of these pigments reported earlier by Lippert and Karrer [2] was due to a mixture of trollixanthin and its furanoxide. The high oxygen content in the elementary analysis of trolliflor may partly be ascribed to the presence of two minor $C_{40}H_{56}O_5$ carotenoids. Their structures will be reported separately [19].

The differences in melting points reported for trolliflor=trollixanthin=neoxanthin, in the present work were at least, partly due to the solvent system used for crystallization, and to the presence of furanoid derivatives.

Neoxanthin (**1**), first described by Strain [20] is a widely distributed carotenoid, independently studied by the schools of Cholnoky under the name foliaxanthin [21, 22] and of Karrer as trollixanthin [1, 12, 13] and trolliflor [2].

For convenience the synonyms are cited below; the names neoxanthin and neochrome should be maintained. Neoxanthin (**1**)=folixanthin=trollixanthin=trolliflor. Neochrome (**2**a, b), furanoid rearrangement product of neoxanthin=foliachrome =trollichrome=trolliflavin.

EXPERIMENTAL

Materials and methods were as usually employed in the Norwegian laboratory and are summarized elsewhere [23]. Acetylation, silylation and acid rearrangement to the furanoxide were carried out by standard procedures [24].

Trolliflor, sample from Karrer's collection contained by TLC: sample 1, (100% trolliflor); sample 2, trolliflor (*ca* 76%); trolliflavin (*ca* 20%); and two compounds $C_{40}H_{58}O_5$ (*ca* 4%). Pure trolliflor had mp 145–147° (from acetone light petrol = APE), 166–168° (from C_6H_6, light petrol); λ_{max} (Me_2CO) 470, 441 and 417 nm; R_f (circular paper Whatman SG 81, 35% APE) 0·55; ν_{max} (KBr) 3030 *w*, 2975 *s*, 2910 *s*, 2860 *m*, 1925 *w*, 1566 *w*, 1470 *w*, 1450 *m*, 1380 *w*, 1363 *w*, 1290 *w*, 1245 *w*, 1220 *w*, 1150 *m*, 1120 *w*, 1067 *w*, 1040 *m*, 1002 *w*, 960 *s*, 952 *m*, 933 *w*, 910 *w*, 888 *w*, 860 *w*, 830 *w*, 817 *w* cm^{-1}; NMR δ ($CDCl_3$) 0·98 *s*, 1·16 *s* and 1·19 *s* (Me-16',17'18'), 1·08 and 1·35 *s* (Me-16, 17, 18), 1·81 *s*, (Me-19), 1·94 *s* and 1·97 *s* (Me-19', 20, 20'), 4·0–4·5 *m* (H-3, 3'), 5·9–6·9 (H-olefinic); MS. *m/e* 600, 4180 (100%, calc. 600·4179 for $C_{40}H_{56}O_4$), 582 (82%, M-H_2O); 564 (17%, M-2H_2O), 520 (8%, M-80), 508 (11%, M-92), 502 (45%, M-80-H_2O), 221 (96%), 181 (52%); CD ϕ (dioxane) 295 (−7200), 274 (−15300) tr, 264 (0), 251 (+8100) pk, 233 (+1800) tr, 222·5 (+14400) nm; $\Delta\epsilon$ (dioxane) 332 (0), 267·5 (−6·7) max, 238 (−0·4) min, 223 (−2·4) max nm.

Trolliflor diacetate λ_{max} (acetone) 471·5, 442·5, 417·5 nm; MS *m/e* 684 (100%, M), 666 (44%, M-H_2O), 624 (7%, M-HAc), 606 (20%, M-H_2O-HAc), 604 (10%, M-80), 592 (14%, M-92), 586 (56%, M-H_2O-80), 574 (5%, M-H_2O-92), 263 (70%, oxepinium), 223 (33% pyryllium), 203 (59% oxep.-HAc), 163 (52% pyryll.-HAc).

Trolliflor diacetate trimethyl silyl ether, λ_{max} (acetone) 471·5, 446, 421 nm. MS *m/e* 756 (100%, M) 696 (2%, M-60), 676 (9%, M-80), 666 (15%, M-$(Me)_3SiOH$), 664 (10%, M-92), 606 (6%, M-HAc-$(Me)_3SiOH$), 586 (19%, M-$(Me)_3SiOH$)-80), 263 (33% oxepinium), 223 (15% pyryllium), 203 (19% oxep.-HAc), 163 (19% pyryll.-HAc).

Trolliflavin, prepared from trolliflor, mp 193–195° (from C_6H_6, acetone); λ_{max}(EtOH) 448, 421, 398, 314, 303, 250 nm; R_f (SG 81, 35% APE) 0·66 and 0·60; NMR δ ($CDCl_3$, mixture of 8'-epimers) 1·08 *s* (Me-16), 1·18 *s* and 1·20 *s* (Me-16'), 1·35 *s* (Me-17,17',18), 1·62 and 1·69 (Me-18'), 1·73 and 1·81 (Me-19'), 1·81 *s* (Me-19), 1·96 *s* (Me-20,20'), 4·0–4·5 *m* (H-3,3'), 5·08, 5·18, 5·28 and 5·33 *m* (H-7',8'), 5·9–6·9 (H olefinic); MS. *m/e* 600 (28%, M) 582 (93%, M-H_2O), 564 (64%, M-2H_2O), 520 (5%, M-80), 508 (8%, M-92), 502 (47%, M-80-H_2O), 221 (100%) 181 (64%).

Trollixanthin, sample from Karrer's collection, chromatographically (TLC) pure, λ_{max} (EtOH) 471·5 (ϵ = 129000), 442·5 (136000), 418·5 (109000), 328 (31000), 265 (26000) nm; $\Delta\epsilon$(dioxane) 330 (0), 269 (−4·3) max, 238 (−0·4) min, 225 (−1·4) max nm; other data as for trolliflor.

Trollichrome, prepared from trollixanthin, data identical with those of trolliflavin.

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