Phytochemistry, 1973, Vol. 12, pp. 2293 to 2294. Pergamon Press. Printed in England.

A NEW BETAXANTHIN FROM *GLOTTIPHYLLUM LONGUM**

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(*Received* 27 *February* 1973. *Accepted* 19 *March* 1973)

Key Word Index—*Glottiphyllum longum*; Aizoaceae; betaxanthins.

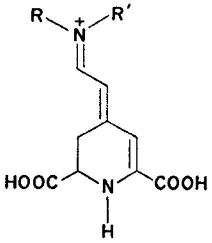
Abstract—The new betaxanthin (II) dopaxanthin was isolated from flowers of *Glottiphyllum longum.* Its structure was confirmed by chemical synthesis.

INTRODUCTION

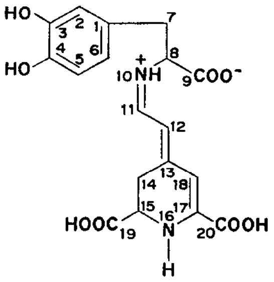
Previous investigation on the yellow water-soluble Centrospermae pigments resulted in the isolation and structural determination of several betaxanthins,[1–3] based on the general formula (I). We here report the isolation and characterization of the hitherto unknown betaxanthin (II) from petals of *Glottiphyllum longum* (Haw.) N.E.Br. (Aizoaceae).

METHODS AND RESULTS

The new betaxanthin was isolated and purified from crude extracts of *G. longum* by ion exchange and polyamide chromatography, and obtained as an orange-coloured amorphous material which could not be crystallized. The small amount available (3 mg) precluded NMR spectroscopical examination. The UV spectrum (water) showed, in addition to the absorption peak at 483 nm (shoulder at 470 nm) common to all betaxanthins, peaks at 267 and 225 (inflection) nm. The batho- and hyperchromic shift upon addition of borate (to 292 and 237 nm) indicated the presence of *ortho* phenolic hydroxyls, which was confirmed by the enhancement of the electrophoretic mobility in borate buffer (migration in paper electrophoresis relative to indicaxanthin: 0·82 in 0·2 M phosphate buffer pH 6·8 and 1·28 in 0·2 M borate buffer pH 7·7).



(I)



(II)

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* Part XVII of the series "Pigments of Centrospermae". For part XVI see Impellizzeri, G. and Piattelli M. (1972) *Phytochemistry* **11,** 2499. This work was supported by the Consiglio Nazionale delle Ricerche.

[1] Piattelli, M., Minale, L. and Prota, G. (1964) *Tetrahedron* **20,** 2325.

[2] Piattelli, M., Minale, L. and Prota, G. (1965) *Phytochemistry* **4,** 121.

[3] Piattelli, M., Minale, L. and Nicolaus, R. A. (1965) *Phytochemistry* **4,** 817.

Hydrogen peroxide oxidation of the pigment yielded pyridine-2,4,6-tricarboxylic acid. On acid hydrolysis, the compound gave 3,4-dihydroxyphenylalanine (DOPA), which was identified by co-chromatography in several systems and co-electrophoresis.

On the basis of these data, structure II and the name dopaxanthin are proposed for the compound. Confirmation of the structure was obtained by synthesis from betanin through a base exchange reaction with DOPA. The synthetic pigment had spectral, chromatographic and electrophoretic properties identical with those of the natural compound.

EXPERIMENTAL

Isolation of dopaxanthin (II). Petals of *Glottiphyllum longum* (10 g), collected from plants growing at the Botanic Garden of Catania, were extracted with 50% aq. MeOH. The extract was adjusted to pH 3 and applied to a column of Dowex 50W X2 (H^+ form). After washing with 0·1% HCl, pigment was eluted with H_2O. The eluate was rotary evaporated to a small vol. and column chromatographed on polyamide (5% aq. citric acid). The yellow band, which had a retention time remarkably longer than those of the known betaxanthins, was freed from citric acid by resin treatment and evaporated to dryness giving an amorphous orange-coloured residue (3 mg).

Oxidative degradation and acid hydrolysis of dopaxanthin. Methods described in an earlier publication were used.[1] DOPA was identified by co-chromatography in several systems (ninhydrin, $FeCl_3$ and diazotized 1-amino-2-methoxy-4-nitrobenzene as chromogenic reagents).

Synthesis of dopaxanthin. A slow stream of N_2 was passed for 1·5 hr, through a wash bottle containing 15% NH_3 solution, into a de-aerated suspension of betanin (50 mg) and DOPA (200 mg) in H_2O (10 ml). Much of the NH_3 was then stripped off by a stream of pure N_2, and the yellow pigment separated from betanin and excess DOPA by column electrophoresis (0·05 M phosphate buffer, pH 6·8; potential gradient 10 V/cm). The yellow band was desalted with resin and evaporated to dryness, giving an orange-coloured residue which was not crystallized. Yield 20%. NMR (60 MHz, CF_3COOD, τ): 1·30 (*d*, *J* 12 Hz, H-11). 3·17 (*m*, H-2, H-5, H-6), 3·50 (*s*, H-18), 3·65 (*d*, *J* 12 Hz, H-12), 5·55 (*m*, H-8, H-15), 6·70 (*m*, 2 H-7, 2 H-14).