Phytochemistry, 1970, Vol. 9, pp. 1795 to 1797. Pergamon Press. Printed in England.

SHORT COMMUNICATION

CAROTENONE FORMATION IN *TRIPHASIA TRIFOLIA**

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(*Received* 6 *October* 1969, *in revised form* 2 *January* 1970)

Abstract—α- And β-carotene and cryptoxanthin, present in immature fruit of *Triphasia trifolia*, disappear on ripening and fully ripe fruit is pigmented by semi-α- and semi-β-carotenone, triphasiaxanthin (I) and β-carotenone.

INTRODUCTION

AS PART of an extended study of the plant pigments responsible for the color of citrus fruits, we now describe the results of a study of the more abundant carotenones of the *Citrus* relative, *Triphasia trifolia* (Rutaceae). It was of interest to establish the pattern of carotenone formation in the ripening fruit. The flesh (peel and endocarp) of the fully ripe fruit is crimson colored and the carotenoid yield is as high as 300 mg/100 g fr. wt. *T. trifolia* is undoubtedly one of the richest natural sources of carotenones.

The principal carotenone present in the fully ripe fruit has been structurally identified as the monocyclic diketone semi-β-carotenone[1] (Table 1). Less abundant and more polar

TABLE 1. COMPOSITION OF SOME CAROTENOIDS IN THE RIPENING FRUIT OF *T. trifolia*

Carotenoids	In % of total carotenoids*			
	Early green (dark green) color	Mature green (light green color with blotches of orange)	Early season (deep orange) color	Fully ripe (deep crimson) color
α-Carotene	1	4	2	—
β-Carotene	6	21	8	0·5
Semi-α-carotenone	—	—	2	4
Semi-β-carotenone	—	17	46	63
Triphasiaxanthin	—	—	3	6
β-Carotenone	—	—	7	21
Cryptoxanthin	2	6	3	—

* Total carotenoid content (mg/100 g wet wt.): Early green, *ca.* 10; mature green, *ca.* 90; early season, *ca.* 130; fully ripe, *ca.* 300.

* Part XI in the series "Citrus Carotenoids".

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[1] H. YOKOYAMA and M. J. WHITE, *Phytochem.* 7, 1031 (1968).

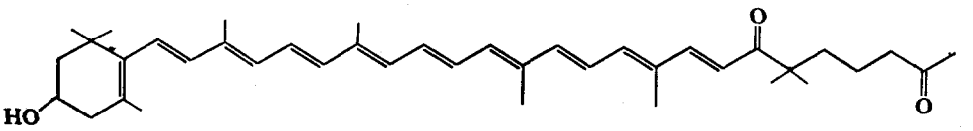
carotenones were the acyclic tetraketone β-carotenone[1] and the hydroxy derivative of semi-β-carotenone triphasiaxanthin.[2] In addition, semi-α-carotenone was present as a minor constituent. The natural occurrence of semi-α-carotenone was first shown in the fruit of another member of the Rutaceae, *Murraya exotica*.[3]

RESULTS

In the ripening fruit of *T. trifolia* the development of ripe color (carotenones) does not begin until the chlorophyll has dropped to a low level (Table 1). In the early (dark green color) stage of maturity there is a total absence of the carotenones. It is in the mature (light green color) fruit that the carotenones are first detected. The initial carotenones formed in detectable amounts consist principally of semi-β-carotenone (17% of total, 15·3 mg/100 g fr. wt.), accompanied by trace amounts of semi-α-carotenone and triphasiaxanthin.

The mature fruit contains relatively high concentration of β-carotene (*ca.* 21% of total, 18 mg/100 g wet wt.). α-Carotene and cryptoxanthin are present in lesser amounts (3·6 mg/100 g; 5·4 mg/100 g fr. wt.). With further ripening of the fruit these carotenoids decrease in concentration until only trace amounts are present in the fully ripe fruit. During this period of decreasing β-carotene content, semi-β-carotenone accumulates with maximum accumulation occurring in the fully ripe fruit. In the ripening fruit β-carotenone appears subsequent to the formation of semi-β-carotenone. β-Carotenone makes its initial appearance in the early season (orange color) fruit; no β-carotenone is found in the mature fruit.

On the basis of the chemical structure of the carotenones and the carotenone development observed, it is reasonable to suggest that partial oxidative degradation similar to that observed in the partial chromic acid oxidation of β- and α-carotene is operative in the ripening fruit of *T. trifolia*: β-Carotene → semi-β-carotenone → β-carotenone; α-carotene → semi-α-carotenone. The chemical structure of triphasiaxanthin (I) suggests that it probably results from the partial degradation of cryptoxanthin.



(I) Triphasiaxanthin

It is noteworthy that in *T. trifolia* α-carotene degrades from the β-ring endgroup to yield semi-α-carotenone, very similar to that observed in the partial chromic acid oxidation of α-carotene. Also, cryptoxanthin degrades from the unsubstituted β-end to yield triphasiaxanthin (I). Detailed examination of the carotenones of *T. trifolia* indicates that the preferred pathway is oxidative degradation of the unsubstituted β-ring endgroup. Major paprika pigments capsanthin, capsorubin and crypto capsin are formed in nature in a different manner.[4] The hydroxylated β-ring endgroup preferentially undergoes rearrangement to the cyclopentane, whereas in *T. trifolia* the unsubstituted β-ring endgroup is preferentially degraded.

[2] H. YOKOYAMA, H. C. GUERRERO and H. BOETTGER, *J. Org. Chem*, in press.
[3] H. YOKOYAMA and H. C. GUERRERO, *Phytochem.* **9**, 231 (1970).
[4] L. CHOLNOKY, K. GYÖRGYFY, E. NAGY and W. PÁNCZÉL, *Nature* **178**, 410 (1957); L. CHOLNOKY, J. SZABOLCS, R. D. G. COOPER and B. C. L. WEEDON, *Tetrahedron Letters* 1257 (1963).

EXPERIMENTAL

The fruits of *T. trifolia* at various stages of maturity were collected in January and February, 1969 by Mr.N. Almeyda at the Federal Experiment Station of the U.S. Department of Agriculture, Mayaguez, Puerto Rico. Early green refers to dark green immature fruits; mature green to light green fully developed fruits; early season to orange colored ripe fruits and fully ripe to the deep crimson ripe fruits.

The extraction and isolation of the carotenoids were carried out in the manner described previously.[1] The structural identity of the individual carotenoids was established by comparison with authentic samples by TLC and visible, i.r. and NMR spectroscopy.

Acknowledgements—The authors are indebted to Dr. H. M. Gaskins, Officer in Charge and Mr. N. Almeyda of the Federal Experiment Station, Mayaguez, Puerto Rico, for the fruit collections.