Phytochemistry, 1970, Vol. 9, pp. 231 to 232. Pergamon Press. Printed in England.

SHORT COMMUNICATION

NATURAL OCCURRENCE OF SEMI-α-CAROTENONE[1]

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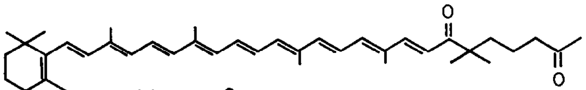
(*Received* 14 *July* 1969)

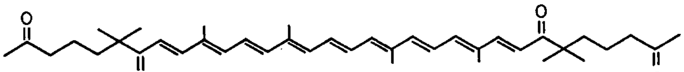
Abstract—Semi-α-carotenone was shown for the first time to occur in nature, in fruits of *Murraya exotica.*

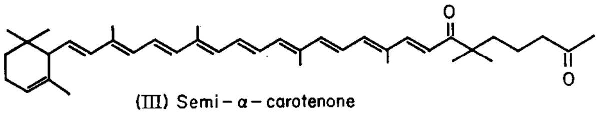
EARLIER WE reported on the natural occurrence of semi-β-carotenone(I) and β-carotenone(II).[3] In this communication, we report the natural occurrence of semi-α-carotenone as a minor carotenoid constituent in the fruit of the *Citrus* relative *Murraya exotica* (both Rutaceae). Semi-α-carotenone is formed as a partial oxidation product on chromic acid treatment of α-carotene.[4] However, the pigment has not heretofore been reported to occur in nature.

The i.r. spectrum indicated the presence of a saturated carbonyl group (1715 cm^{-1}) and a conjugated carbonyl group (1660 cm^{-1}). The visible absorption spectrum conformed to that of a nonaenone chromophore. Reduction with $LiAlH_4$ caused a hypsochromic shift (*ca.* 25 nm) in the visible absorption maxima.

The NMR spectrum of the isolated pigment contained 3 *C*-methyl resonances which were very similar in values to those recorded for the *C*-methyl resonances in the α-ring endgroup in α-carotene. The NMR signals at τ 9·15 and 9·00 (C-1′ geminal methyls, 3 H each) and 8·36 (C-5′ methyl, 3 H) established the α-ring endgroup in the isolated compound. In addition the NMR spectrum indicated the presence of 4 in-chain olefinic methyls at τ 8·04 (9 H) and 8·10 (3 H). There was also a methylketone methyl at τ 7·89 (3 H). Its mass measurement indicated a molecular ion at *m*/*e* 568 as required.


(I) Semi-β-carotenone


(II) β-carotenone


(III) Semi-α-carotenone

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[1] Part IX in the series "Citrus Carotenoids".

[2] A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

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

[4] P. KARRER, U. SOLMSSEN and O. WALKER, *Helv. Chim. Acta* **17**, 417 (1934).

On the basis of evidences presented structure III was suggested for the isolated pigment. The structure of the compound was subsequently confirmed by synthesis from α-carotene.

EXPERIMENTAL

Melting points were determined in evacuated sealed capillary tubes and are uncorrected. NMR spectra were obtained at 100 MH_z and were determined in deuterochloroform relative to internal tetramethylsilane. The fruit collections of *Murraya exotica* were made in February, 1968, by Mr. N. Almeyda at the Federal Experiment Station of the U.S. Department of Agriculture, Mayaguez, Puerto Rico. Mass spectral analysis was performed by West Coast Technical Service, San Gabriel, California.

Extraction of M. exotica

The carotenoid pigments were extracted from the fruits (600 g) in the usual manner[3] and phase-partitioned between light petroleum—90% methanol. The epiphase was submitted to column chromatography on MgO: HyFlo Supercel (1:2, w/w). The isolated pigment was crystallized from *n*-hexane, yielding 9 mg; m.p. 134–136°; λ_{max} ($CHCl_3$), nm ($\epsilon \times 10^{-3}$) 480 (90·7), 500sh, (81·3); λ_{max} (*n*-hexane) 438, 462, 490 nm; i.r. bands at 1715 (saturated carbonyl) and 1660 (conjugated carbonyl) cm^{-1}; NMR signals[5] at τ 9·15 (s, 3 H), 9·00 (s, 3 H), 8·36 (s, 3 H), 8·10 (s, 3 H), 8·04 (s, 9 H), and 7·89 (s, 3 H); mass measurement of parent ion in the mass spectrum *m/e* 568 (M.W. 568).

Reduction of the isolated pigment with $LiAlH_4$ in dry ether afforded the reduced product: λ_{max} (*n*-hexane) 412, 436, 465 nm.

Semi-α-carotenone (III, 20 mg, m.p. 134–136°) was synthesized by the partial oxidation of α-carotene (400 mg) with chromic acid. Comparison with natural sample showed the same TLC behavior; and they had identical visible, i.r., and NMR spectra.

Acknowledgements—The authors are indebted to Dr. Robert Lundin for the NMR spectra, and to Dr. M. H. Gaskins and Mr. N. Almeyda of the Federal Experiment Station for the fruit.

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[5] C-methyls only.