reaction mixture was poured onto ice, and the oil was separated from the ice–water. The oil was dried briefly over anhydrous sodium sulfate at ice temperature and analyzed by infrared. Initially the oil was virtually all 3-thiocyanocyclohexene and it gradually isomerized as the sample was kept at 32°. The half-life of 3-thiocyanocyclohexene was estimated to be approximately 2 hr. at 32°.

1-(2-Cyclohexen-1-yl)-2-thiourea.—Addition of aqueous–alcoholic ammonia to 3-isothiocyanocyclohexene yielded the thiourea, 78%, m.p. 133.5–135°, lit.[1] m.p. 133–134°.

1-(2-Cyclohexen-1-yl)-3-phenyl-2-thiourea.—To 1.39 g. (0.01 mole) of 3-isothiocyanocyclohexene was added 0.93 g. (0.01 mole) of aniline and 5 ml. of dioxane. The mixture was heated on a steam bath for 1 hr. and was then kept at room temperature for 60 hr. After dilution with water and cooling, a solid separated, 1.28 g., 55% yield. The product was recrystallized once from benzene–cyclohexane, decolorized in ethyl acetate solution with decolorizing carbon, and again recrystallized from benzene–cyclohexane. The snow white needles melted at 98.5–100°. The infrared spectrum of the compound in a potassium bromide disk showed bands at 3240 and 3140 cm.$^{-1}$.

Citrus Carotenoids. II. The Structure of Citranaxanthin, a New Carotenoid Ketone

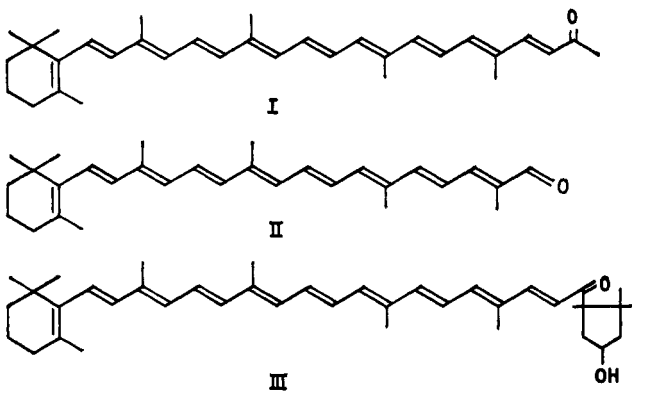
HENRY YOKOYAMA AND MICHAEL J. WHITE

Fruit and Vegetable Chemistry Laboratory,[1] *Pasadena, California*

Received February 23, 1965

During the course of recent investigations of the carotenoid constituents of the peel of the trigeneric hybrid, *Sinton citrangequat* (*Citrus sinensis* × *Poncirus trifoliata* × *Fortunella margarita*),[2] we isolated a small amount of a new carotenoid ketone, $C_{33}H_{44}O$, which we propose to call citranaxanthin.

The visible spectra (Figure 1) of citranaxanthin, recorded in petroleum ether and ethanol, were very similar to those of β-apo-8′-carotenal (II), though somewhat



longer in wave length. Their common spectral features strongly indicate the presence of a conjugated carbonyl group in citranaxanthin.[3] The visible spectrum of citranaxanthin also indicated a decaenone chromophore similar to that of kryptocapsin (III).[4–6]

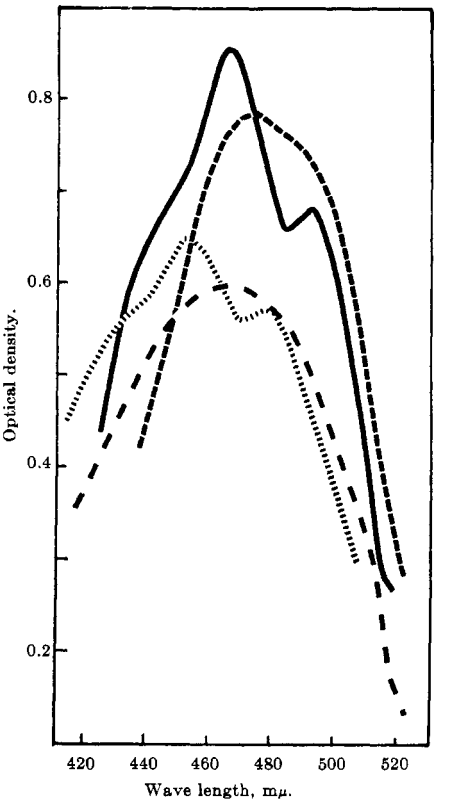


Figure 1.—Visible spectra of citranaxanthin: in petroleum ether, ———; in ethanol, ———; of β-apo-8′-carotenal: in petroleum ether, ▪▪▪▪▪▪▪▪▪▪; in ethanol, – – – –.

In the infrared spectrum of citranaxanthin a band at 1662 cm.$^{-1}$, characteristic of a conjugated carbonyl grouping,[4] confirmed the visible absorption data. Reduction of citranaxanthin with sodium borohydride gave a product which exhibited a hypsochromic shift in its absorption maxima.

The n.m.r. spectrum exhibited singlets at τ 7.72 (end-of-chain methyl group α to a carbonyl group), 8.02 (in-chain olefinic methyl group), 8.25 (methyl group attached to C=C in the cyclohexene ring), and 8.92 (*gem*-dimethyl group). Additionally no signal could be detected in the τ 0.3–0.6 region characteristic of aldehydic protons with α,β-unsaturation.[6] The doublet at τ 2.50 (J = 16 c.p.s.) indicates that the double bond to which the vinyl proton β to the carbonyl is attached has the *trans* configuration.[7,8]

On treatment with aqueous alcoholic potassium hydroxide, citranaxanthin underwent a retroaldol cleavage to yield acetone as a volatile component. The nonvolatile portion consisted of a compound identical with β-apo-8′-carotenal (II). Condensation of β-apo-8′-carotenal (II) with acetone in the presence of alcoholic potassium hydroxide afforded I. I did not separate from the natural pigment on thin layer chromatography and its infrared and n.m.r. spectra were identical with those of natural citranaxanthin.

These facts lead unambiguously to I as the structure of citranaxanthin. This compound is the first known naturally occurring carotenoid with a methyl ketone grouping in the side chain.

(1) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) H. J. Webber, "The Citrus Industry," Vol. 1, H. J. Webber and L. D. Batchelor, Ed., University of California Press, Berkeley and Los Angeles, Calif., 1943, p. 666.

(3) R. Kuhn and H. Brockmann, *Ber.*, **66**, 828 (1933).

(4) C. K. Warren and B. C. L. Weedon, *J. Chem. Soc.*, 3972 (1958).

(5) M. S. Barber, L. M. Jackman, C. K. Warren, and B. C. L. Weedon, *Proc. Chem. Soc.*, 19 (1960).

(6) M. S. Barber, J. B. Davis, L. M. Jackman, and B. C. L. Weedon, *J. Chem. Soc.*, 2870 (1960).

(7) L. M. Jackman and S. L. Jensen, *Acta Chem. Scand.*, **18**, 1403 (1964).

(8) M. S. Barber, A. Hardisson, L. M. Jackman, and B. C. L. Weedon, *J. Chem. Soc.*, 1625 (1961).

Experimental[9,10]

Isolation of Citranaxanthin (I).—The *Sinton citrangequat* fruit was collected when the flavedo had attained its deepest color (bright orange-red). Eight kilograms of peel was separated from the endocarp and extracted with acetone. The carotenoids were partitioned between petroleum ether (b.p. 30–60°) and 90% methanol. The epiphase was submitted to column chromatography on magnesium oxide–Hyflo Supercel (1:1 w./w.). The isolated ketone crystallized from petroleum ether, yielding 90 mg.: m.p. 156–156°; λ_{max} in petroleum ether 463 ($E^{1\%}_{1\,cm}$ 2145) and 495 mμ, in ethanol 475 mμ (shoulder at 489 mμ); infrared bands at 2900, 1662 (conjugated carbonyl), 1590, 1505, 1440, 1280, 1190, 1160, 1025, 960, 900, and 832 cm.$^{-1}$; n.m.r. signals[11] at τ 2.50 (J = 16 c.p.s.), 7.72, 8.02, 8.25, and 8.92.

Anal. Calcd. for $C_{33}H_{44}O$: C, 86.76; H, 9.74. Found: C, 86.6; H, 9.77.

Reaction of I with hydroxylamine hydrochloride–pyridine in ethanol and recrystallization from benzene–petroleum ether afforded the oxime derivative, m.p. 196–197°.

Alkali Cleavage of Citranaxanthin (I).—A solution of 50 mg. of I in 10 ml. of ethanol and 0.5 ml. of 1 *N* potassium hydroxide was distilled (heated at 55–65°) for 20 min. with vigorous stirring in a constant stream of nitrogen into a receiver containing a solution of 2,4-dinitrophenylhydrazine in ethanol. The precipitate was recrystallized from ethanol, furnishing the 2,4-dinitrophenylhydrazone of acetone, m.p. 125–126° (melting point of an authentic sample 125°). Admixture of authentic sample did not depress the melting point.

The nonvolatile mixture was extracted with petroleum ether and chromatographed on a column of magnesium oxide–Hyflo Supercel. Pure II was isolated and crystallized from petroleum ether; m.p. 137–138°. The substance did not depress the melting point of an authentic sample of β-apo-8′-carotenal (m.p. 138–139°), kindly furnished by Hoffmann-La Roche, and was identical with authentic β-apo-8′-carotenal by thin layer chromatography and infrared spectroscopy. The oxime had m.p. 178–179° (melting point of an authentic sample, 178–179°).

Reduction of Citranaxanthin.—To 0.5 mg. of citranaxanthin in 5 ml. of methanol was added 10 mg. of sodium borohydride under nitrogen. The mixture was shaken at *ca.* 10° for 60 min. whereupon a hypsochromic shift was observed. The carotenoids were transferred to petroleum ether. The petroleum ether extract was washed carefully with water and dried over anhydrous sodium sulfate. Chromatography on Microcel C furnished citranaxanthol, λ_{max} in petroleum ether 418, (sh), 442, and 469 mμ.

Citranaxanthin (I).—A solution of 0.5 g. of β-apo-8′-carotenal (II) in 5 ml. of acetone and 5 ml. of ethanol was added drop by drop in an atmosphere of nitrogen to a well-stirred mixture of 0.5 ml. of 1 *N* potassium hydroxide and 5 ml. of ethanol, and the reaction mixture was stirred at room temperature for 5 hr. The petroleum ether extract of the reaction mixture was chromatographed on a column of magnesium oxide–Hyflo Supercel. I was isolated and crystallized from petroleum ether, yielding 0.4 g., m.p. 155–156°, undepressed on admixture of natural citranaxanthin; both samples exhibited the same thin layer chromatographic behavior: λ_{max} in petroleum ether 463 and 495 mμ, in ethanol 475 mμ (shoulder at 488 mμ). The n.m.r. spectrum [singlets at 7.72, 8.02, 8.25, and 8.92; doublet at 2.50 (J = 16 c.p.s.)] is in full accord with structure I. Further proof of identity with natural citranaxanthin was established by infrared spectroscopy.

Anal. Calcd. for $C_{33}H_{44}O$: C, 86.76; H, 9.74. Found: C, 86.6; H, 9.70.

The oxime had a melting point of 196–197°. The substance did not depress the melting point of the oxime of natural citranaxanthin. Retroaldol cleavage with alkali yielded the same products, acetone and β-apo-8′-carotenal (II), as described above for natural citranaxanthin.

Acknowledgment.—The authors are indebted to Dr. David Dreyer of this laboratory for his helpful discussion and assistance in the n.m.r. analysis, and to Dr. J. Furr of the U. S. Department of Agriculture Date and Citrus Experiment Station, Indio, California, and Dr. E. Olson of the U. S. Department of Agriculture Crops Research Division, Weslaco, Texas, for fruit collections.

(9) All melting point determinations were carried out in evacuated capillary tubes on an Electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded in a KBr disk on Perkin-Elmer Models 137 and 521 spectrophotometers. Visible spectra were measured with a Cary Model 14 spectrophotometer. The n.m.r. spectra were determined in carbon tetrachloride on a Varian A-60 n.m.r. spectrometer, with tetramethylsilane as an internal standard. Analyses were provided by Mr. L. M. White.

(10) Use of trade names of specific materials or equipment does not constitute a recommendation by the U. S. Department of Agriculture to the exclusion of others which may also be available.

(11) Relative areas of n.m.r. peaks were consistent with assignments.

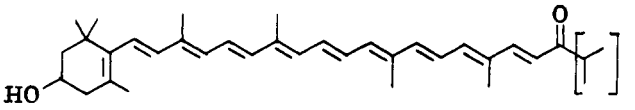
Citrus Carotenoids. III. The Structure of Reticulataxanthin

HENRY YOKOYAMA, MICHAEL J. WHITE, AND CARL E. VANDERCOOK

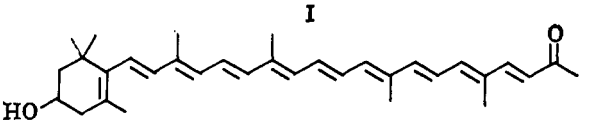
Fruit and Vegetable Chemistry Laboratory,[1] *Pasadena, California*

Received February 23, 1965

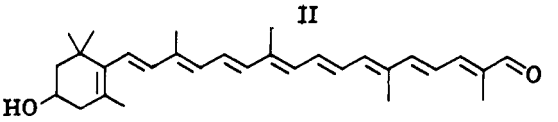
Curl[2] described the isolation and proposed a tentative structure (I) of a carotenoid pigment, reticulataxanthin from the peel of tangerine fruit (*Citrus reticulata*). He deduced structure I through chemical and visible



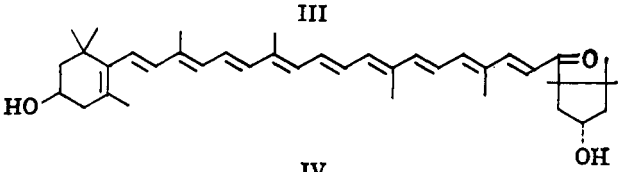
I



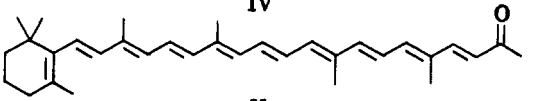
II



III



IV



V

spectral investigations. The nature of the terminal group attached to the carbonyl was uncertain. This ambiguity invited further investigation, and we report herein a more complete structural study of reticulataxanthin.

The pigment used in our study was extracted from the peel of the citrus hybrid, *Minneola tangor* (*Citrus reticulata* × *Citrus sinensis*) which proved to be a much richer source than tangerine. Column chromatography on magnesium oxide–Hyflo Supercel isolated and separated the pigment. Crystallization from peroxide-free ether–petroleum ether (b.p. 30–60°) furnished reticulataxanthin, $C_{33}H_{44}O_2$.

(1) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) A. L. Curl, *J. Food Sci.*, **27**, 537 (1962).