bonate solution, and water, and dried ($MgSO_4$). Removal of the solvent gave a solid, m.p. 215–220°, which after several crystallizations from methylene chloride–methanol gave friedel-18-ene as needles (22 mg.): m.p. 241–243°, $[\alpha]_D$ +16° (*c* 1.1); lit.[15] m.p. 242–245°, $[\alpha]_D$ +17°.

B.—A solution of friedelane (186 mg.) in carbon tetrachloride (75 ml.) was heated under reflux by an infrared lamp, and bromine (147 mg., 2 mole equiv.) in carbon tetrachloride (6 ml.) was added. After heating for 1 hr., the mixture was cooled, and the solvent was removed under reduced pressure. To the residual solid, a solution of *m*-chloroperbenzoic acid (337 mg.) in chloroform (30 ml.) was added, and the mixture was allowed to stand at room temperature for 24 hr. A solution of potassium iodide (0.1 g.) in 0.4 *N* acetic acid (5 ml.) and water (50 ml.) were then added and the liberated iodine was titrated with standard sodium thiosulfate solution. (This indicated a 41% alkene content in the mixture.) The chloroform layer was separated, washed successively with water, sodium hydrogen carbonate solution, and water, dried, and evaporated. The solid residue (180 mg.) was dissolved in petroleum ether (b.p. 30–60°) and chromatographed on alumina (Savory and Moore, pH 8.5). Elution with this solvent (100 ml.) gave a solid (25 mg.), crystallized from methylene chloride–methanol as small needles, m.p. 239–240°, $[\alpha]_D$ +26° (*c* 0.35), R_f 0.72,[16] regarded as **18-bromofriedelane.** It did *not* give a color with tetranitromethane, but gave a positive Beilstein test. Continued elution with petroleum ether (70 ml.) gave a solid (6 mg.; 2 spots, R_f 0.71 and 0.60). Petroleum ether (35 ml.) and petroleum ether–benzene (4:1, 70 ml.) then yielded a solid (75 mg.) which on crystallization from methylene chloride–methanol gave **18,19-epoxyfriedelane** as needles, m.p. 254–256°, $[\alpha]_D$ +36° (*c* 0.66), R_f 0.60, with infrared spectrum (in KBr) identical with that of the previously reported specimen,[15] m.p. 260–261°. Elution with benzene and benzene–chloroform gave oils (71 mg.) shown to be mixtures by thin layer chromatography.

Conversion of 18-Bromofriedelane to Friedel-18-ene.—The bromofriedelane was extremely labile, losing hydrogen bromide on an attempted recrystallization and drying for analytical purposes.

Anal. Calcd. for $C_{30}H_{51}Br$: C, 73.28; H, 10.46. Calcd. for $C_{30}H_{50}$: C, 87.73; H, 12.27. Found: C, 80.87, 83.79; H, 11.89, 11.64.

We were unable to separate 18-bromofriedelane from its dehydrobromination product, friedel-18-ene, by thin layer chromatography; furthermore, 18-bromofriedelane could be quantitatively dehydrobrominated under certain chromatographic conditions.

A.—A solution of 18-bromofriedelane (19 mg.) in petroleum ether (1 ml.) was filtered through a column of Woelm neutral alumina (3 g.). Evaporation of the eluent (15 ml.) gave a product (negative Beilstein test, bright yellow color with tetranitromethane) which on two crystallizations from methylene chloride–methanol gave friedel-18-ene, m.p. 239–241°, $[\alpha]_D$ +18° (*c* 0.6), with an infrared spectrum identical with authentic hydrocarbon.

B.—When the total reaction product, obtained from friedelane (310 mg.) by bromination followed by peracid oxidation as in B above, was chromatographed on Florisil, elution with petroleum ether gave directly friedel-18-ene (26 mg.), m.p. 239–240°.

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[16] Each chromatographic fraction was examined by thin layer chromatography, using benzene as developing solvent and silica gel G (0.25-mm. layer) as adsorbent.

The Preparation and Isomerization of 3-Thiocyanocyclohexene

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Greenwood and James[1] reported the formation of 3-isothiocyanocyclohexene from 3-bromocyclohexene and sodium thiocyanate in methanol apparently without prior formation of 3-thiocyanocyclohexene. Displacement reactions leading initially to predominant yields of isothiocyanates are rare[2] except with acyl halides.[3] Some apparent exceptions have been studied, and the formation of trityl isothiocyanate[4] and *t*-butyl isothiocyanate[5] probably involve equilibrium control of the reaction since trityl and *t*-butyl carbonium ions are formed with ease.

We have investigated the reaction of 3-bromocyclohexene with potassium thiocyanate in dimethyl sulfoxide (DMSO) containing enough water so that the temperature could be lowered to 0° and with sodium thiocyanate in methanol at 0°. The resulting products were subjected to infrared analysis and displayed a sharp absorption band at 2155 cm.$^{-1}$, typical of alkyl thiocyanates. On attempted distillation at 0.6 mm. the product isomerized to 3-isothiocyanocyclohexene as shown by the appearance of a new absorption band at 2105 cm.$^{-1}$ and disappearance of the sharp band at 2155 cm.$^{-1}$. On the basis of these results we conclude that 3-bromocyclohexene reacts with potassium thiocyanate in DMSO–water or sodium thiocyanate in methanol at 0° to form 3-thiocyanocyclohexene which is extremely labile and rearranges to 3-isothiocyanocyclohexene, possibly by an allylic rearrangement, examples of which have previously been studied.[6–9] A rough estimate of the rate of isomerization of neat 3-thiocyanocyclohexene indicates a half-life of about 2 hr. at 32°.

Experimental

All melting and boiling points are corrected. 3-Bromocyclohexene was prepared as previously described,[1] b.p. 54–63° (10 mm.).

Reaction of 3-Bromocyclohexene with Potassium Thiocyanate in DMSO–Water at 0°.—To 10 ml. of DMSO were added 0.6 g. (0.0062 mole) of potassium thiocyanate and 0.5 g. (0.028 mole) of water. The solution was chilled in an ice bath and 1.0 g. (0.0062 mole) of 3-bromocyclohexene was added dropwise with shaking. The reaction mixture was poured onto ice, and an oil was separated from the ice–water. After brief drying over anhydrous sodium sulfate at ice temperature, a sample of the oil was subjected to infrared analysis. The strong band at 2155 cm.$^{-1}$ and the absence of a strong band at 2105 cm.$^{-1}$ showed the material to be almost exclusively 3-thiocyanocyclohexene. After heating the sample at 95° for 0.5 hr., a very strong band at 2105 cm.$^{-1}$ appeared accompanied by the disappearance of a separate band at 2155 cm.$^{-1}$. On attempting to distil a larger sample of 3-thiocyanocyclohexene prepared in the same way, material boiling at 47–50° (0.6 mm.) was obtained and infrared analysis showed it to be 3-isothiocyanocyclohexene.

Reaction of 3-Bromocyclohexene with Sodium Thiocyanate in Methanol.—To 0.81 g. (0.01 mole) of sodium thiocyanate dissolved in 20 ml. of absolute methanol chilled to 0° was added 1.61 g. (0.01 mole) of 3-bromocyclohexene. After 15 min. the

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[1] F. L. Greenwood and W. J. James, *J. Am. Chem. Soc.*, **73**, 4495 (1951).

[2] H. L. Wheeler, *Am. Chem. J.*, **26**, 345 (1901).

[3] A. E. Dixon, *J. Chem. Soc.*, **69**, 1593 (1896).

[4] R. W. Taft, Jr., and L. G. Cannell, 129th National Meeting of the American Chemical Society, Dallas, Texas, April 1956, Abstracts of Papers, Organic Division, p. 40-N.

[5] E. Schmidt, W. Striewsky, M. Seefelder, and F. Hitzler, *Ann.*, **568**, 192 (1950).

[6] O. Mumm and H. Richter, *Ber.*, **73B**, 843 (1940).

[7] A. Iliceto, A. Fava, and U. Mazzucato, *Tetrahedron Letters*, **No. 1**, 27 (1960).

[8] P. A. S. Smith and D. W. Emerson, *J. Am. Chem. Soc.*, **82**, 3076 (1960).

[9] NOTE ADDED IN PROOF.—It has been demonstrated by A. Fava, A. Iliceto, A. Ceccon, and P. Koch [*J. Am. Chem. Soc.*, **87**, 1045 (1965)] that 4,4′-dimethylbenzhydryl thiocyanate isomerizes to the isothiocyanate through the intermediacy of a tight ion pair. On the basis of existing data, such a mechanism cannot be discounted as a possibility in the present case.

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

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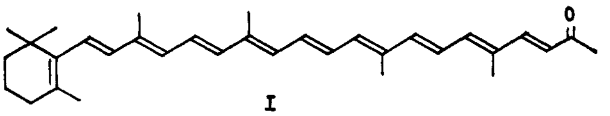
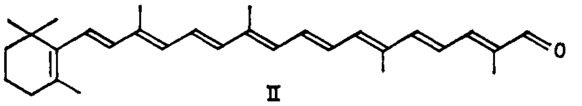
During the course of recent investigations of the carotenoid constituents of the peel of the trigeneric hybrid, *Sinton citrangequat* (*Citrus sinensis* × *Poncirus trifoliata* × *Fortunella margarita*),[2] we isolated a small amount of a new carotenoid ketone, $C_{33}H_{44}O$, which we propose to call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


I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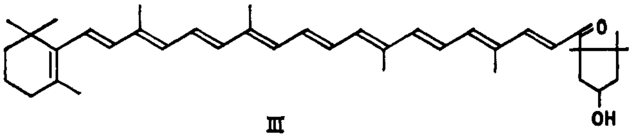
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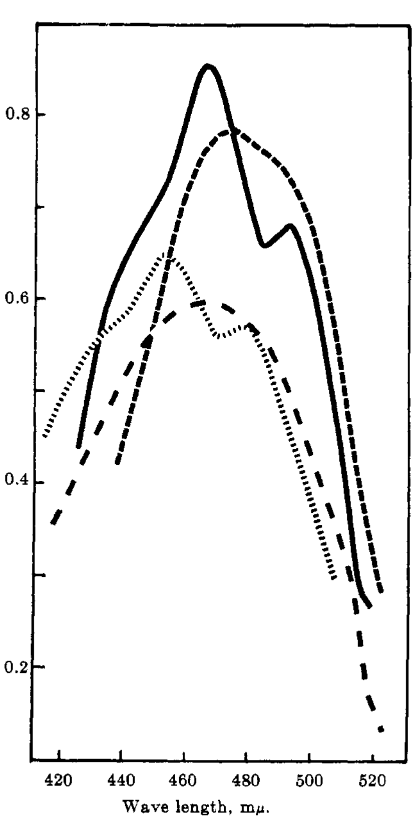

Figure 1.—Visible spectra of citranaxanthin: in petroleum ether, ———; in ethanol, ———; of β-apo-8′-carotenal: in petroleum ether, ⋯⋯⋯; in ethanol, - - - -.

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.

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(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).