ponent. The remainder of the material (12.4 g.) and 40 g. of freshly fused sodium acetate in 200 ml. of acetic acid was heated at 100° for 5 hr. The solution was cooled, diluted with water, and extracted with chloroform. The resultant product, 13.1 g. of a halogen-free oil, was saponified in 100 ml. of methanol and 50 ml. of water containing 25 g. of potassium carbonate (1 hr. at reflux). Chloroform extraction of the reaction mixture yielded 10.7 g. of product. Crystallization and recrystallization from acetone afforded 4.08 g. of alcohol **1a**, m.p. 154–157°. Another recrystallization from acetone–cyclohexane afforded the analytical sample: m.p. 163–164°; λ_{max} 2.73, 5.72, 12.0 μ; λ_{max} 280 mμ (log ϵ 3.45), 286 mμ (log ϵ 3.45); $\Delta\nu$ 277 (CH_2OH), 397 (C-4 *H*), 432 (C-1 *H*) c.p.s.

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34. Found: C, 76.41; H, 8.13.

The mother liquors were chromatographed on silica. Fractions eluted with 10% ethyl acetate in benzene were combined and recrystallized twice from acetone, yielding 0.80 g. of **4-hydroxymethylestrone 3-methyl ether** (**2a**), m.p. 193–197°. Another recrystallization from acetone afforded the pure material: m.p. 200–202°; λ_{max} 2.84, 5.78, 12.3 μ; λ_{max} 282 mμ (log ϵ 3.37), 288 mμ (log ϵ 3.36); $\Delta\nu$ 282 and 287 (CH_2OH), 401, 410, 431, 440 (C-1 and C-2 *H*) c.p.s. On D_2O exchange the CH_2OH doublet became a singlet at 284 c.p.s.

Anal. Found: C, 76.40; H, 8.62.

When the chloromethylation product was hydrolyzed in aqueous dioxane containing potassium hydroxide, the yields of the two hydroxymethyl compounds (**1a** and **2a**) were lower. An amorphous material (20% of the total, mol. wt. 525) was eluted with 2% ethyl acetate–benzene. A portion crystallized and was recrystallized from acetone to yield a material (**3**): m.p. 208–210°; λ_{max} 5.76 μ; $\Delta\nu$ 275 ($-CH_2O$), 395 (C-4 *H*), 441 (C-1 *H*) c.p.s.; mol. wt. 561.

2-Methoxymethylestrone 3-Methyl Ether (**1b**).—The chloromethylation of 10 g. of estrone methyl ether was carried out as described above. The crude chloromethyl mixture was boiled for 4 hr. in 80 ml. of methanol and 40 ml. of water containing 20 g. of potassium carbonate. The product (11 g. of semicrystalline material) was isolated by ether extraction and chromatographed on silica. The fractions eluted with 5% ethyl acetate–benzene were recrystallized from acetone, yielding 1.32 g. of crystalline material, m.p. 110–118°. An additional recrystallization of this material from acetone–petroleum ether gave the pure ether **1b**: m.p. 123–125°; λ_{max} 5.73 μ; λ_{max} 281 mμ (log ϵ 3.44), 286 mμ (log ϵ 3.44); $\Delta\nu$ 204 (OCH_3), 227 (OCH_3), 267 (CH_2OCH_3), 395 (C-4 *H*), 435 (C-1 *H*) c.p.s.

Anal. Calcd. for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.52; H, 8.37.

In addition to **1b**, both hydroxymethyl compounds **1a** and **2a** were obtained.

2-Hydroxymethylestradiol 3-Methyl Ether (**1c**).—A solution of 0.46 g. of the hydroxymethyl compound **1a** in 5 ml. of tetrahydrofuran was added to a solution of 0.50 g. of lithium aluminum hydride in 40 ml. of ether. The mixture was stirred at room temperature for 1 hr. and then was diluted slowly with ethyl acetate. Water was added and the product was extracted with ether, yielding 0.42 g. of a crystalline product. Recrystallization from acetone yielded 0.35 g. of the 17-hydroxy compound **1c**, m.p. 195–198°, recrystallized from methanol–ethyl acetate to afford the pure diol, m.p. 198–200°, λ_{max} 3.02 μ.

Anal. Calcd. for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.86; H, 8.91.

4-Hydroxymethylestradiol methyl ether (**2c**) was prepared by a similar reduction of the ketone **2c**. Recrystallization of the very insoluble product from boiling Cellosolve afforded the pure compound, m.p. 259–263°, λ_{max} 3.04 μ.

Anal. Found: C, 76.04; H, 8.84.

Hydrogenolysis Experiments.[7]—A solution of 1.53 g. of the 2-hydroxymethyl derivative **1a** in 30 ml. of acetic acid and 1.0 g. of 5% palladium-on-carbon catalyst was stirred in an atmosphere of hydrogen. After 45 min., uptake of hydrogen ceased. The mixture was filtered, the solvent was distilled, and the resulting residue was recrystallized from hot petroleum ether (b.p. 60–70°) (Darco) to provide 0.83 g. of 2-methylestrone 3-methyl ether (**1d**): m.p. 152–153°; λ_{max} 5.76, 12.02 μ; $\Delta\nu$ 129 (Ar-CH_3), 392 (C-4 *H*), 422 (C-1 *H*) c.p.s.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.30; H, 8.63.

(7) The hydrogenations were performed by Mr. W. M. Selby and staff.

The same compound was prepared by O-methylation of 2-methylestrone,[8] using methyl iodide–potassium carbonate.

Reduction of 0.20 g. of the methoxy compound **1b** required 18 hr. and afforded 80 mg. of the pure 2-methyl compound **1d**.

The same procedure yielded **4-methylestrone methyl ether** (**2d**) when the hydroxymethyl derivative **2a** was used as substrate. The reduction product was recrystallized from petroleum ether–methanol to give 0.36 g. of the pure 4-methyl derivative **2d**: m.p. 159–160°; λ_{max} 5.78, 12.43 μ; $\Delta\nu$ 127 (ArCH_3) c.p.s.

Anal. Found: C, 80.83; H, 8.71.

Reduction of the 2-hydroxymethyl derivative **1c** during a 15-min. period and recrystallization of the product from petroleum ether yielded 50 mg. of **2-methylestradiol 3-methyl ether** (**1e**): m.p. 139–140°; λ_{max} 2.79, 11.6 μ.

Anal. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.91; H, 9.66.

The same compound was prepared in good yield by lithium aluminum hydride reduction of the 2-methyl compound **1d**.

4-Methylestradiol 3-methyl ether (**2e**) was obtained by hydrogenolysis of the hydroxymethyl derivative **2c** or preferably by lithium aluminum hydride reduction of the ketone **2d** (procedure given above). The product was purified by recrystallization from petroleum ether to yield the alcohol **2e**: m.p. 170–172; λ_{max} 2.84, 12.42 μ.

Anal. Found: C, 80.04; H, 9.59.

2-Formylestrone 3-Methyl Ether (**4**).—A solution of 0.65 g. of the hydroxymethyl derivative **1a** in 30 ml. of chloroform was stirred with 0.60 g. of manganese dioxide for 72 hr. The solution was filtered through Super-Cel and the filtrate was concentrated, yielding 0.40 g. of crystals, m.p. 155–160°. Recrystallization of this material from acetone–petroleum ether gave the pure aldehyde **4**: m.p. 170–172°; λ_{max} 5.77, 5.98 μ; λ_{max} 224 mμ (log ϵ 4.29), 266 (4.12), 332 (3.69); $\Delta\nu$ 400 (C-4 *H*), 463 (C-1 *H*), 622 (*CH*O) c.p.s.

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 77.05; H, 7.66.

(8) Dr. A. Goldkamp of these laboratories kindly furnished this sample which was prepared by the method of Patton.[3]

Citrus Carotenoids. IV. The Isolation and Structure of Sintaxanthin

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In a previous communication,[2] we have described the isolation and characterization of a new carotenoid ketone from the flavedo of the fruit of the trigeneric hybrid, *Sinton citrangequat* (*Citrus sinensis* × *Poncirus trifoliata* × *Fortunella margarita*). This pigment was designated citranaxanthin and shown to be 5,9,14,18-tetramethyl-20-(2,6,6-trimethylcyclohex-1-enyl)eicosa-3,5,7,9,11,13,15,17,19-nonaene-2-one; the unusual feature of citranaxanthin is the terminal methyl ketone grouping in the side chain.

We wish to report herein the isolation and elucidation of the structure of a second carotenoid ketone from the flavedo of the *Sinton citrangequat*. This pigment is similar to citranaxanthin but possessing a nonaenone chromophore. Accordingly, we propose to call this new carotenoid sintaxanthin.

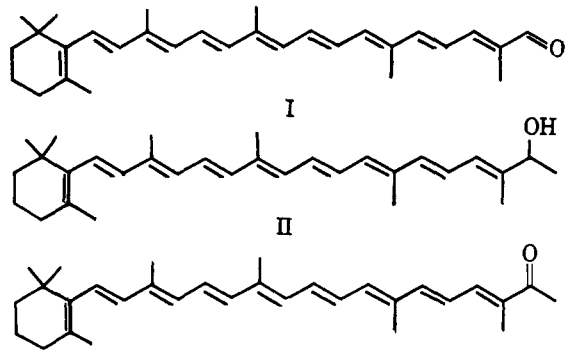
When the crude pigment extract of the flavedo of the *Sinton citrangequat* fruit collected in Feb. 1964 was

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

(2) H. Yokoyama and M. J. White, *J. Org. Chem.*, **30**, 2481 (1965).

chromatographed, a small amount of sintaxanthin (*ca.* 0.2% of the total carotenoids) was obtained. However, from the fruit collected in Feb. 1965, the yield of sintaxanthin was much higher (*ca.* 30% of total carotenoids) and the color of the flavedo appeared to be slightly less intense.

The visible spectrum (Figure 1) of sintaxanthin indicated a chromophore similar to that of β-apo-8′-carotenal (I).[3] The infrared spectrum of the isolated pigment exhibited a band at 1660 cm.$^{-1}$, characteristic



I II III

of a conjugated carbonyl grouping.[4] On iodine catalysis a hypsochromic shift of *ca.* 4 mμ in the absorption maxima of the pigment accompanied by 16% decrease in extinction value of the main absorption peak was observed, indicating an all-*trans* form. Reduction of sintaxanthin with sodium borohydride afforded a product which exhibited a hypsochromic shift in its absorption maxima and which was shown to be II by the identity of its visible, infrared, and n.m.r. spectra with those of the synthetic sintaxanthol (II) prepared by the action of methyllithium on β-apo-8′-carotenal (I).

The n.m.r. spectrum revealed a singlet at τ 7.72 which can be assigned to the end-of-chain methyl protons α to a carbonyl group. The signal at τ 8.10 is due to the in-chain vinyl methyl group on a carbon atom α to a carbonyl group deshielded by the latter.[5] Additional signals were detected at τ 8.01 (in-chain olefinic methyl group), 8.27 (methyl group attached to C=C in the cyclohexene ring), and 8.97 (*gem*-dimethyl group).

Oxidation of II with manganese dioxide in acetone gave III. III did not separate from the natural pigment on thin layer chromatography and its visible, infrared, and n.m.r. spectra were identical with those of natural sintaxanthin. The mixture melting point was undepressed. Elementary analysis of sintaxanthin was in agreement with the molecular formula, $C_{31}H_{42}O$.

These facts lead to III as the structure of sintaxanthin.

Experimental Section[6]

All melting point determinations were carried out in evacuated sealed capillary tubes on a Electrothermal melting point apparatus and are uncorrected. Visible spectra were measured with a Cary Model 14 spectrophotometer. Infrared spectra were recorded in a KBr disks on Perkin-Elmer, Models 137 and 521, spectrophotometers. 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. Relative areas of n.m.r. peaks were consistent with assignments.

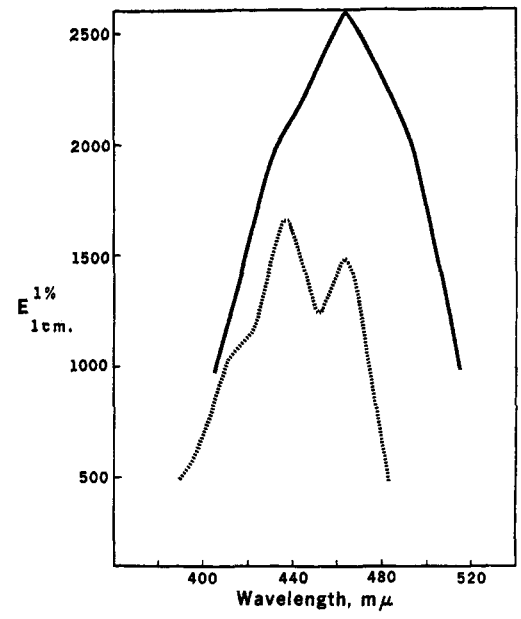


Figure 1.—Visible spectra of sintaxanthin (———) and sintaxanthol (▪▪▪▪▪▪▪▪▪▪) in benzene.

Isolation of Sintaxanthin.—The fruit of *Sinton citrangequat* was collected in Feb. 1965. The peel (8 kg.) was separated from the endocarp and extracted with several portions of acetone. The 5 l. of extract was concentrated *in vacuo* to 1 l. The carotenoid mixture was diluted with *n*-hexane, dried over anhydrous sodium sulfate, and partitioned between *n*-hexane and 90% methanol. The epiphase was submitted to column chromatography on magnesium oxide–Hyflo Supercel (1:1, w./w.). The isolated pigment (held fraction) crystallized from *n*-hexane, yielding 120 mg.: m.p. 144–145°; λ_{max} in *n*-hexane 425 (sh), 448, and 475 mμ, in benzene 436 (sh), 462 ($E^{1\%}_{1cm}$ 2588), and 485 mμ (sh); infrared bands at 2900, 1660 (conjugated carbonyl), 1610, 1585, 1545, 1440, 1370, 1335, 1010, and 970 cm.$^{-1}$; n.m.r. signals at τ 7.72, 8.01, 8.10, 8.27, and 8.97.

Anal. Calcd. for $C_{31}H_{42}O$: C 86.45; H, 9.83. Found: C, 86.3; H, 9.92.

Reaction of sintaxanthin with hydroxylamine–pyridine in ethanol and recrystallization from *n*-hexane–benzene yielded the oxime derivative, m.p. 203.5–204.5°.

Sintaxanthol (II).—A solution of 80 mg. of methyllithium in 15 ml. of ether was added dropwise in an atmosphere of nitrogen to a well-stirred mixture of 500 mg. of β-apo-8′-carotenal (I) in 15 ml. of dry ether. The reaction mixture was refluxed for 60 min. and cooled to *ca.* −10°, and cold water was added dropwise. The petroleum ether extract of the reaction mixture was chromatographed on a column of Microcel C. II was isolated and crystallized from peroxide-free ether–petroleum ether (b.p. 30–60°), yielding 350 mg.: m.p. 117–118°; λ_{max} in *n*-hexane 404, 425, and 451 mμ, in benzene 415, 437 ($E^{1\%}_{1cm}$ 1657), and 463 mμ; infrared bands at 3450 (hydroxyl), 1630, 1580, 1530, 1440, 1390, 1370, 1080, 1030, 1010, and 968 cm.$^{-1}$. The n.m.r. exhibited singlets at τ 8.07 (in-chain olefinic methyl group), 8.22 (in-chain vinyl methyl group on a carbon atom α to a carbinol group), 8.32 (methyl group attached to C=C in the cyclohexene ring), 8.97 (*gem*-dimethyl group); the doublet at τ 8.82 (J = 6 c.p.s.) is due to the coupling of the single carbinol proton and the end-of-chain methyl protons.

Anal. Calcd. for $C_{31}H_{44}O$: C, 86.05; H, 10.25. Found: C, 86.1; H, 10.3.

Sintaxanthin (III).—A solution of sintaxanthol (II, 0.2 g.) in acetone (50 ml.) was shaken in an atmosphere of nitrogen with manganese dioxide (5 g., undried[4]) for 6 hr. Isolation of the product by column chromatography on magnesium oxide–Hyflo Supercel (1:2, w./w.) and crystallization from petroleum ether

(3) R. Rüegg, M. Montavon, G. Ryser, G. Saucy, U. Schwieter, and O. Isler, *Helv. Chim. Acta*, **42**, 854 (1959).

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

(5) M. S. Barber, J. B. Davis, L. M. Jackman, and B. C. L. Weedon, *ibid.*, 2870 (1960).

(6) Reference to a company or product does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

gave the ketone (0.15 g.), m.p. 144–145°, undepressed on admixture of natural sintaxanthin, and both samples displayed the same thin layer chromatographic behavior: λ_{max} in *n*-hexane at 425 (sh), 448, and 473 mμ, in benzene (at 436 (sh), 462, and 485 (sh) mμ. The n.m.r. spectrum (signals at τ 7.72, 8.01, 8.10, 8.27, and 8.97) is in full accord with structure III. The infrared spectrum was superimposable on that of the natural sample.

Anal. Calcd. for $C_{31}H_{42}O$: C, 86.45; H, 9.83. Found: C, 86.5; H, 9.72.

The oxime had m.p. 203–204°. The substance did not depress the melting point of oxime of natural sintaxanthin.

Reduction of Natural Sintaxanthin.—Reduction of the naturally occurring sintaxanthin (40 mg.) in the usual manner[7] with sodium borohydride, removal of the catalyst and solvent, and chromatography of the carotenoid mixture on a column of Microcel C afforded the reduced product, m.p. 117–118°, undepressed on admixture of synthetic sample, and both samples exhibited the same thin layer chromatographic behavior. The visible, n.m.r., and infrared spectra were identical with those of the synthetic sample (II).

Iodine Catalysis of Natural Sintaxanthin.—A solution of sintaxanthin (0.1 mg.) in *n*-hexane (5 ml.) containing a trace of iodine, was irradiated under a 100-w. lamp for 1 hr. The mixture was washed with 5% sodium thiosulfate solution and water and dried over anhydrous sodium sulfate, and the visible spectrum was determined. A hypsochromic shift of *ca.* 4 mμ in the absorption maxima, accompanied by 16% decrease in extinction value of the main absorption peak, was observed.

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(7) H. Yokoyama and M. J. White, *J. Org. Chem.*, **30**, 2481 (1965).

Photochemical Hydrogen Abstraction by the Nitro Group

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The lowest lying singlet and triplet excited states of simple aromatic nitro compounds have been shown to have their origin in an n → π* transition.[1,2] This suggests that the photochemistry of these compounds might prove to be analogous to the reactions observed for ketones having lowest lying n–π* excited states.

One photochemical process which is particularly well documented as characteristic of such ketones is the abstraction of a hydrogen atom by the carbonyl oxygen. There is, in fact, considerable evidence in the literature which suggests that the nitro group, upon irradiation, also can abstract hydrogen atoms. Thus, the photochromic nature of nitro aromatics has been extensively studied[3] and spectral data presented implicating *aci*-nitro tautomers as the colored species. In addition, a number of photochemical rearrangements of nitro compounds have been rationalized by postulating an initial hydrogen abstraction step.[4] Despite the considerable volume of data, however, a definitive, chemical demonstration of hydrogen abstraction by the nitro group has been lacking; the frequency with which such a step is invoked in mechanistic rationales makes such an unambiguous demonstration all the more desirable. It was towards this goal that the experiments below were directed.

o-Nitrotoluene, dissolved in a mixture of deuterium oxide and *p*-dioxane, was irradiated through a Pyrex filter for 48 hr. The solvent was removed and starting material was recovered by molecular distillation and preparative v.p.c. The infrared spectrum of the recovered material was characterized by the appearance of a new doublet centered at 4.3 μ (C–D stretch) and by the marked decrease in intensity of a peak at 11.7 μ. Examination of the n.m.r. spectrum revealed that an average of 1.6 deuterium atoms/molecule had been incorporated into the methyl group. The mass spectrum gave the following isotopic composition: no deuteration, 10%; monodeuterated, 33%; dideuterated, 40%; and trideuterated, 17%.

No exchange was observed in the dark under comparable conditions. Furthermore, the possibility of exchange owing to some photolytically produced catalyst was eliminated by irradiating the *o*-nitrotoluene for 24 hr., removing half of the solution, and allowing the remainder to stand in the dark for 48 hr. Work-up of both solutions gave *o*-nitrotoluene with identical incorporation (0.79 deuterium atoms/molecule). Finally, the intramolecular nature of the abstraction process was demonstrated by irradiating *p*-nitrotoluene in a deuterium oxide–*p*-dioxane solution for 48 hr. The recovered starting material was examined by infrared, n.m.r., and mass spectroscopy; the spectra obtained gave no evidence for any incorporation of deuterium.

Experimental Section

All photolyses were conducted under an atmosphere of nitrogen using a 450-w. Hanovia high-pressure immersion lamp and a cylindrical Pyrex filter. Infrared spectra were obtained from a Beckman IR-8, n.m.r. spectra from a Varian A-60 using tetramethylsilane as an internal standard. Mass spectra were recorded on a Bendix time-of-flight mass spectrometer.

Photolysis of *o*-Nitrotoluene.—A solution of *o*-nitrotoluene (1.0 g.) in 10.0 ml. of D_2O (Columbia Organic Chemical Co., 99.5%) and 110 ml. of *p*-dioxane (Matheson Coleman and Bell, Spectrograde) was irradiated for 48 hr. The solvent was removed and the residue, upon molecular distillation (80° and 0.6 mm.), afforded 0.35 g. of *o*-nitrotoluene. Further purification was effected by preparative v.p.c. on a Carbowax 20M 10 ft. × 3/8 in. column at 200°. The *o*-nitrotoluene thus prepared was shown to be 98.5% pure by v.p.c. N.m.r. absorptions were at δ 2.57, 7.38, and 7.88 (relative area, 1.4:3.0:0.8). The mass spectrum had peaks at 137, 138, 139, and 140 (relative areas, 1.0:3.4:4.0:1.8).

(1) A. I. Kiss and G. Horvath, *Acta Chim. Acad. Sci. Hung.*, **39**, 39 (1963).

(2) M. Kasha, *Radiation Res., Suppl.*, **2**, 243 (1960).

(3) (a) For leading references, see G. Wettermark, E. Black, and L. Dogliotti, *Photochem. Photobiol.*, **4**, 229 (1965); (b) for a review of photochromism, see R. Dessauer and J. P. Paris, "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 275.

(4) For example, see P. DeMayo and S. T. Reid, *Quart. Rev.* (London), **16**, 393 (1961).