The olefin mixture was characterized by conversion to the nitrosyl chloride addition products. The olefins (0.8 g.) were mixed with 2 ml. of freshly prepared ethyl nitrite at −7° and 1.5 ml. of concentrated hydrochloric acid added dropwise with stirring. After 1 hour, the blue precipitate was filtered and washed with cold ethanol. The filtrate, upon standing, deposited a mixture of blue and white crystals.

The first crop of blue crystals was dissolved in acetone, filtered hot and on cooling yielded 0.33 g. of blue crystals, m.p. 89.9–90.4° (lit.[3] 91°). The remaining crude material was dissolved in the acetone filtrate and on concentration an additional 0.08 g. of blue crystals was obtained, m.p. 88.0–90.2°. The total yield of 9-nitroso-10-chlorodecalin was 0.41 g. (34%). From the mother liquor a small amount of white crystals was obtained, m.p. 112° dec. (lit.[3] value for $\Delta^{1(9)}$-octalin nitrosochloride is 127°).

Δ^9-Octalin Epoxide (XVI).—Δ^9-Octalin[26] (6.2 g., 0.045 mole) was dissolved in 20 ml. of chloroform and added to a solution of 6.90 g. (0.05 mole) of perbenzoic acid in 100 ml. of chloroform. The reaction mixture was allowed to stand in the dark for 3 days at room temperature and then the chloroform solution neutralized with dilute sodium hydroxide solution. A white solid appeared which partially dissolved after the mixture had been shaken. The chloroform layer was separated, washed with water, dried and then the solvent removed. The Δ^9-octalin epoxide was distilled through a 10-plate column, yield 4.9 g. (71%), b.p. 88° (16 mm.), $n^{19}\text{D}$ 1.4851 (lit.[27] b.p. 82–83° (8–9 mm.), $n^{20}\text{D}$ 1.4847).

***trans*-9-Hydroxydecalin (XVII).**—A solution of 1.0 g. (6.6 mmoles) of Δ^9-octalin epoxide in 5 ml. of dry ether was allowed to react with 20 ml. of a 1 *M* solution of lithium aluminum hydride at room temperature for 12 hours. Water and alkali were added, the ether layer separated and the aqueous layer extracted twice with ether. The combined ethereal extracts were washed with water, dried and the solvent removed. The crude product was distilled, b.p. 61–62° (1.4 mm.) and the distillate solidified on standing, m.p. 35–45°, yield 0.49 g. (48%). Durland and Adkins[6] report a b.p. 57–59° (1 mm.) and m.p. 52°.

A solution of 0.2 g. of the crude alcohol was dissolved in 10 ml. of petroleum ether and stirred with a solution of 0.30 g. of chromic acid in 10 ml. of water for 2 hours. The organic layer was separated, washed with 5% sodium bicarbonate and then dried. After removal of the solvent, the residue crystallized. The solid was recrystallized from petroleum ether by cooling to −65° to yield 0.23 g. (62%) of yellow ester, m.p. 78–86° (lit.[26] m.p. 77–85°).

The ester (0.23 g.) was heated under reflux for 1 hour with a mixture of 0.25 g. of zinc dust, 4 ml. of acetic acid and 6 ml. of water. The product was recovered by steam distillation and extracted from the distillate with ether. The crude material was sublimed and the crystalline alcohol melts from 50.0–51.5°.

1,2-Di-(*trans*-9-decalyl)-ethylene Glycol (XIV).—*trans*-9-Decalincarboxylic acid (1.0 g.) was converted to the acid chloride in the usual manner and the chloride, dissolved in dry ether, was added slowly to a dark blue solution of sodium in liquid ammonia. The excess sodium was decomposed with ammonium chloride and ethanol and the solution allowed to warm to room temperature. Water was added, the solution partially concentrated, and then extracted with chloroform. The chloroform solution was concentrated, pentane added and the crystals which formed melt from 163–165°. The material was recrystallized from aqueous ethanol, yield 0.31 g. (52% based upon recovered acid), m.p. 167.7–168.7°.

Anal. Calcd. for $C_{22}H_{38}O_2$: C, 78.98; H, 11.45. Found: C, 79.00; H, 11.51.

The alkaline solution from the reaction upon acidification yielded 0.36 g. of starting acid.

Acknowledgment.—The authors wish to acknowledge the assistance given by Mr. Erwin Blanz during the progress of this work.

BERKELEY, CALIFORNIA

[CONTRIBUTION NO. 1919 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

On Some Dehydrogenation Products of α-Carotene, β-Carotene and Cryptoxanthin

BY G. KARMAKAR[1] AND L. ZECHMEISTER

RECEIVED JULY 9, 1954

By treatment of α-carotene, $C_{40}H_{56}$, β-carotene, $C_{40}H_{56}$, and cryptoxanthin, $C_{40}H_{55}OH$, with N-bromosuccinimide and (in part) with N-bromoacetamide, three new crystalline pigments, "dehydrocarotenes I–III," have been isolated, besides dehydro-β-carotene, bisdehydro-β-carotene and anhydro-eschscholtzxanthin. Dehydrocarotene I was obtained only from α-carotene, II from β-carotene and III from both carotenes. Their spectral curves are characterized by the lack of fine structure in the visible region. Upon treatment of dehydrocarotenes (or of desoxylutein I) with boron trifluoride etherate and subsequent chromatographic resolution, fine structure appears in the spectrum of the main product. Some structural, stereochemical and spectral features of these compounds are discussed.

It has been reported recently, in collaboration with Wallcave,[2] that carbon tetrachloride solutions of β-carotene, $C_{40}H_{56}$, (11 double bonds), when refluxed with N-bromosuccinimide, showed marked deepening of the color and yielded, after chromatography, three crystalline pigments, *viz.*, dehydro-β-carotene,[3] $C_{40}H_{54}$, bisdehydro-β-carotene, $C_{40}H_{52}$, and anhydro-eschscholtzxanthin,[4] $C_{40}H_{50}$. We find that N-bromoacetamide is also an effective dehydrogenating agent for β-carotene, although it did not produce any anhydro-eschscholtzxanthin under the conditions applied.

Upon refluxing α-carotene with N-bromosuccinimide, bisdehydro-β-carotene and anhydro-eschscholtzxanthin were isolated while dehydro-β-carotene was absent from the reaction mixture. A similar treatment with N-bromoacetamide has resulted in the isolation of bisdehydro-β-carotene only (Table I).

The correct chromatographic separation of the three intensely colored products just mentioned required a strong developer, such as hexane plus 8% acetone, on the lime–Celite column; the chromatographic filtrate was then orange-yellow. Its pigment content could likewise be resolved when the weak developer hexane was used. This resulted in the isolation of two new crystalline pigments termed dehydrocarotenes I and III.

Dehydrocarotene III also was obtained from β-carotene besides a third crystalline compound,

---

[1] We wish to thank The Rockefeller Foundation for a Fellowship and a grant.

[2] L. Zechmeister and L. Wallcave, THIS JOURNAL, **75**, 4493 (1953).

[3] R. Kuhn and E. Lederer, *Ber.*, **65**, 637 (1932); P. Karrer and G. Schwab, *Helv. Chim. Acta*, **23**, 578 (1940).

[4] P. Karrer and E. Leumann, *ibid.*, **34**, 445 (1951).

TABLE I

YIELDS OF SOME DEHYDROGENATION PRODUCTS OF CAROTENOIDS

The figures refer to recrystallized compounds and indicate % of starting material.

Starting material	Reagent, N-bromo-	Recovd. unchanged starting material	Dehydro-β-carotene	Bisdehydro-β-carotene	Anhydro-eschscholtzxanthin	Dehydrocarotenes		
						I	II	III
α-Carotene	Succinimide	30	. .	0.75	0.14	2.7[a]	. .	0.14
α-Carotene	Acetamide	35	. .	0.25	. . .	3.5[a]	. .	0.21
α-Carotene	Phthalimide	25	. .	Trace	. . .	3.8[a]	. .	Trace
β-Carotene	Succinimide	8	2.0	1.5	0.67	. .	1.4[a]	0.24
β-Carotene	Acetamide	21	1.6[b]	2.1	. . .	. .	. .	. . .
Cryptoxanthin	Succinimide	. .	. .	0.73	0.93	. .	. .	0.4
Cryptoxanthin	Acetamide	. .	. .	1.4[c]	0.88[c]	. .	. .	. . .

[a] The photometrically established yield amounted to twice this value. [b] Crystalline neo-dehydro-β-carotene A was also isolated; yield 2.8%. [c] Identified and estimated spectroscopically; not crystallized.

dehydrocarotene II. The latter was, however, missing upon the interaction of N-bromoacetamide and β-carotene.

The group I–III is sharply differentiated, by the much lower adsorption affinity and weaker color intensity, from the group including dehydro-β-carotene, bisdehydro-β-carotene and anhydro-eschscholtzxanthin. Furthermore, the spectral curves of the dehydrocarotenes I–III are void of fine structure in the visible region; upon iodine catalysis they develop a marked *cis* peak in the ultraviolet region (Figs. 1–3); and in the resulting stereoisomeric mixture the *trans* configuration is preponderant. All these features differentiate the new compounds from the representatives of the other group.

A discussion of the dehydrocarotene structures follows.

Dehydrocarotene I (*ex* **α-Carotene**).—The analysis of this hydrocarbon indicates the formula $C_{40}H_{54}$ and catalytic hydrogenation showed the presence of twelve double bonds, *vs.* eleven in α-carotene. The melting point of dehydrocarotene I is markedly higher than that of α-carotene. Its adsorption affinity to lime–Celite stands between those of α- and β-carotene. Maximum extinction in hexane is observed at 10 mμ longer wave length than that of α-carotene. The strong *cis* peak effect mentioned (Fig. 1) points to a normal (*i.e.*, non-retro)[5] structure of the molecule. The infrared spectrum excludes the presence of acetylenic or cumulenic bonds or aliphatic isolated double bonds but indicates the presence of an isolated ring double bond.[6] Since it is reasonable to assume that the latter is identical with that contained in α-carotene, one terminal group remained unchanged in this dehydrogenation process.

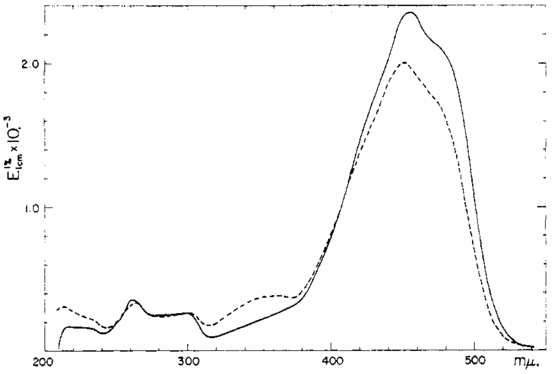
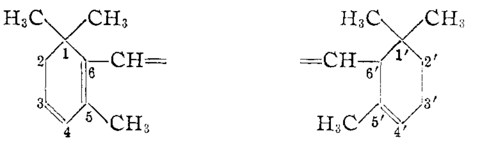


Fig. 1.—Extinction curves, in hexane, of dehydrocarotene I: ——, all-*trans;* and ----, after iodine catalysis.

The provitamin A potency of this compound in the rat, as kindly determined by Dr. H. J. Deuel, Jr., and Mr. A. F. Wells of the University of Southern California, amounted to roughly 15% of that of β-carotene, *i.e.*, about one-third of that of α-carotene.

On the basis of these data we propose that the very probable structure of dehydrocarotene I is that of 3,4-dehydro-α-carotene, in which only the β-ionone ring of α-carotene underwent dehydrogenation (*cf.* the formula). The lack of fine structure in the visible spectral region would be in accordance with the more depressed spectrum of vitamin A_2 as compared with A_1.[7]



Assumed end groups in dehydrocarotene I (3,4-dehydro-α-carotene)

Dehydrocarotene II (*ex* **β-Carotene**).—We believe that the relationship between this compound and β-carotene is the same as between dehydrocarotene I and α-carotene. This is illustrated, among other points, by the equal shift of λ_{max} in the two processes, β-carotene → dehydrocarotene II, and α-carotene → dehydrocarotene I (9–10 mμ, *cf.* Table II). Both dehydro compounds are adsorbed above the respective carotene zones on the lime–Celite column. Upon iodine catalysis very similar observations are made in both instances in the visible and ultraviolet spectral regions (Fig. 2) as well as with reference to the composition of the stereoisomeric mixtures obtained. The infrared curve of dehydrocarotene II shows the absence of isolated double bonds. Finally, according to Deuel and Wells, the biopotency of this dehydrocarotene amounts to 67% of that of β-carotene. Considering all these data,

---

(5) W. Oroshnik, G. Karmas and A. D. Mebane, THIS JOURNAL, **74**, 295 (1952).

(6) We are indebted to Mr. K. Lunde for the infrared curves mentioned in this paper.

(7) *Cf. e.g.*, N. A. Milas, in "The Vitamins," Vol. 1, edited by W. H. Sebrell, Jr., and R. S. Harris, Academic Press, Inc., New York, N. Y., 1954, p. 51, Fig. 11.

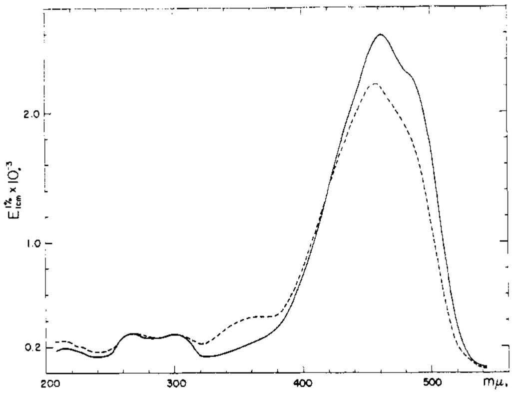


Fig. 2.—Extinction curves, in hexane, of dehydrocarotene II: ——, all-*trans;* and ----, after iodine catalysis.

the very probable structure of dehydrocarotene II is that of 3,4-dehydro-β-carotene. This seems to be confirmed by the analogous decrease of the biopotencies in the transitions, α- or β-carotene → dehydrocarotene I or II, and vitamin $A_1 \rightarrow A_2$.

TABLE II

WAVE LENGTH OF MAXIMUM EXTINCTION OF SOME CAROTENES AND DEHYDROCAROTENES (IN HEXANE)

	mμ
α-Carotene	445
Dehydrocarotene I	455
β-Carotene	452
Dehydrocarotene II	462
Dehydrocarotene III	471

Dehydrocarotene III (*ex* both Carotenes).—This minor component appears in the dehydrogenation product of either α- or β-carotene and is adsorbed on the column considerably above the I and II zones. It is assumed that both end groups of the molecule underwent dehydrogenation in this instance. For α-carotene this would also involve a migration of its isolated double bond into conjugation with the main chromophore as confirmed by the lack of indication of an isolated double bond in the infrared curve. In the visible region (Fig. 3), the shift (19 mμ) in the position of λ_{max} caused by the conversion, β-carotene → dehydrocarotene III, is the double of the value given for the processes, α-carotene → I, and β-carotene → II (Table II). If the present interpretation of dehydrocarotene III as 3,4,3′,4′-dehydro-β-carotene is confirmed by further studies, then bisdehydro-β-carotene,[2] for which two possible structures were evaluated, should be assigned the unsymmetrical constitution. Recently, Mr. F. J. Petracek has found in our laboratory a different and more advantageous route for the preparation of dehydrocarotene III, whose full clarification is thus to be expected.

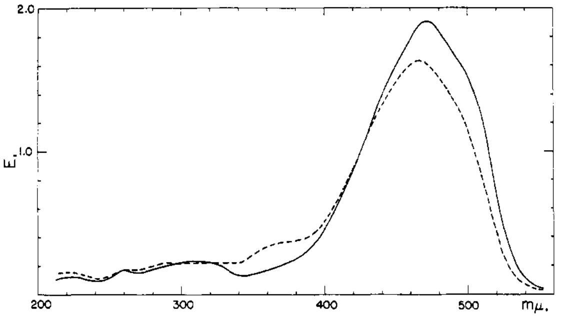


Fig. 3.—Extinction curves, in hexane, of dehydrocarotene III: ——, all-*trans*; and ----, after iodine catalysis.

Dehydrocarotenes and Boron Trifluoride Etherate.—Upon treatment with this reagent, pigment I or II rapidly forms a dark blue complex and, upon cautious hydrolysis, a mixture results in which but little starting material is included.[8] The main (crystalline) component was in each instance a hydrocarbon in whose visible spectrum the initial fine structure of the carotene, lost during the dehydrogenation process, has appeared again (Figs. 4–5). This rather surprising behavior could be explained simply by a migration of that double bond, which was formed by the dehydrogenation process, out of conjugation from the main chromophore, *i.e.*, by the rearrangement, 3,4-dehydro compound → 2,3-dehydro compound.

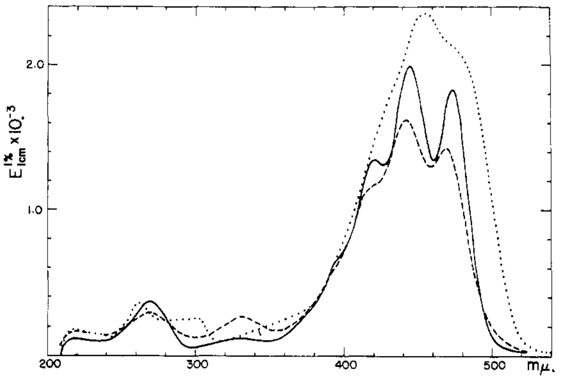


Fig. 4.—Extinction curves, in hexane, of a crystalline compound obtained by reaction of dehydrocarotene I with boron trifluoride etherate: ——, fresh solution; ----, after iodine catalysis; and ...., unreacted dehydrocarotene I.

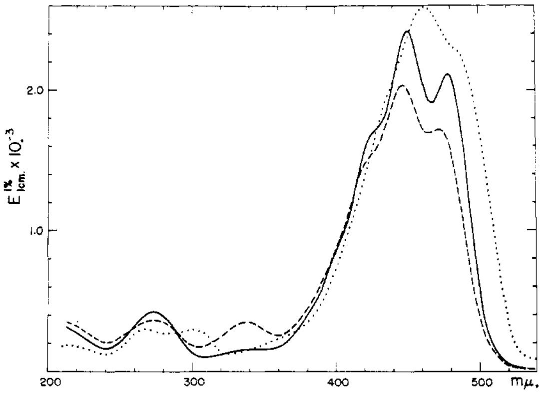


Fig. 5.—Extinction curves, in hexane, of a crystalline compound obtained by reaction of dehydrocarotene II with boron trifluoride etherate: ——, fresh solution; ----, after iodine catalysis; and ...., unreacted dehydrocarotene II.

This spectral behavior does not constitute a unique phenomenon, as can be shown by the ex-

---

(8) For other observations concerning carotenoid–boron trifluoride complexes and their cleavage products *cf.* L. Wallcave, J. Leemann and L. Zechmeister, *Proc. Nat. Acad. Sci.*, **39**, 604 (1953); L. Wallcave and L. Zechmeister, THIS JOURNAL, **75**, 4495 (1953).

ample of desoxylutein I, $C_{40}H_{56}O$, a structurally still unclarified pigment prepared in collaboration with J. W. Sease eleven years ago, by melting naturally occurring lutein, $(HO)C_{40}H_{54}(OH)$, with naphthalene and anhydrous boric acid.[9] It has now been observed that the spectral curve of this compound acquires fine structure upon formation and cleavage of its boron trifluoride complex (Fig. 6).

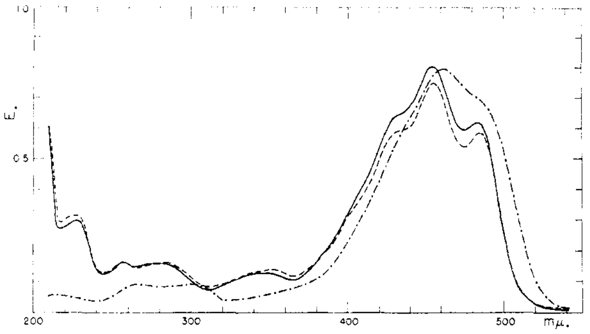


Fig. 6.—Extinction curves, in hexane, of an epiphasic compound obtained by treating desoxylutein I with boron trifluoride etherate: ——, fresh solution; ----, after iodine catalysis; and –·–·–, unreacted desoxylutein I.

Dehydrogenation of Cryptoxanthin.—This natural product (3-hydroxy-β-carotene) yielded in the N-bromosuccinimide reaction several crystalline compounds, among them dehydrocarotene III, bisdehydro-β-carotene, anhydro-eschscholtzxanthin, and a new pigment (λ_{max} at 486 mμ), while dehydro-β-carotene was absent (*cf.* Table I and the Experimental part).

Experimental

Materials and Methods.—The adsorbents used were, Sierra Hydrated Lime, Superfine (U. S. Lime Prod. Corp., Los Angeles, Calif.); Adsorptive Powdered Magnesia "Seasorb" (Westvaco Chem. Div., N. Y.); Activated Alumina, Grade F, reground to −200 mesh (Aluminum Co. of America, Pittsburgh, Pa.); Calcium Carbonate, Precipitated (Mallinckrodt Chem. Works, Los Angeles, Calif.); and lime + Celite (No. 545, Johns-Manville Co.) 2:1. All elutions were carried out with acetone and the latter was washed out in the LeRosen continuous apparatus.[10] In order to eliminate ash from analytical samples, the hexane solutions were washed by shaking with conductivity water 25 times. "Partition behavior" (epi- or hypophasic) means distribution between hexane and 95% methanol. Spectral data refer to hexane solutions, unless stated otherwise. Visual spectra were observed in a Zeiss Evaluating Grating Spectroscope (Loewe–Schumm). The spectral data reported in chromatograms have been observed visually, all the others in the Beckman spectrophotometer. Infrared spectra refer to the Perkin–Elmer self-recording spectrophotometer. Melting points (cor.) were observed in evacuated capillaries in an electrically heated Berl block. Reagents: N-bromosuccinimide (Arapahoe Chem., Inc., Boulder, Col.); N-bromoacetamide (Matheson, Coleman and Bell, Rutherford, N. J.); and N-bromophthalimide (Sapon Labor., Brooklyn, N. Y.).

α-Carotene and N-Bromosuccinimide.—Five hundred mg. of pure, crystalline α-carotene was divided into ten portions. To a solution of 50 mg. of substance in 15 ml. of carbon tetrachloride, in a 25-ml. volumetric flask, were added 33 mg. of the reagent (2 mol. per mol. carotene) and 75 mg. of sodium bicarbonate, whereupon the liquid was refluxed over a 200 watt electric bulb for 6 hr. during which time it darkened considerably. After dilution with hexane to 25 ml. the solution was combined with the other nine similar portions. The solution was developed with hexane +8% acetone on five 30 × 8 cm. lime–Celite columns. (The figures on left indicate the width of the zones in mm.)

2 pale brown
125 interzone
15 pink: all-*trans*-bisdehydro-β-carotene (521, 489, 458 mμ)
11 interzone
13 purple: all-*trans*-anhydro-eschscholtzxanthin (534, 500, 468 mμ)
14 interzone
23 pink: a *cis*-bisdehydro-β-carotene (516, 485, 454 mμ)
5 interzone
9 light purple: a *cis*-anhydro-eschscholtzxanthin (529, 496, 463 mμ)
83 two pale pink zones (and interzones)
Filtrate: orange

The all-*trans*-bisdehydro-β-carotene and -anhydro-eschscholtzxanthin zones were cut out, eluted, and transferred into hexane by the addition of water. The solutions were dried with sodium sulfate, each combined with four similar ones (originating from parallel chromatograms) and rechromatographed as described. After evaporation both residues were dissolved in a little warm benzene, transferred into a centrifuge tube, concentrated in a nitrogen stream, and crystallized by dropwise addition of methanol, in a bath at 50°.

The combined five chromatographic filtrates (see above) were washed acetone-free, dried, concentrated to 500 ml., and developed with hexane on ten 30 × 8 cm. lime–Celite columns:

50 empty section
9 pink: dehydrocarotene III (about 473 mμ)
21 interzone
20 orange: unidentified
10 interzone
19 yellow: unidentified
49 interzone
39 orange: dehydrocarotene I (about 458 mμ)
35 pale yellow: unidentified
40 yellow: unchanged α-carotene (30% of the starting material)
8 empty section

Dehydrocarotenes III and I were rechromatographed, either as just described or on magnesia, and after evaporation of the hexane solutions crystallized from benzene–methanol.

All-*trans*-bisdehydro-β-carotene: dark purple, long, quadrangular plates, moderately glittering, m.p. 199–201°, mixed m.p. with a sample *ex* β-carotene, 200–201.5°.

Anal. Calcd. for $C_{40}H_{52}$: C, 90.18; H, 9.82. Found: C, 90.12; H, 9.88 (after correction for 0.95% ash); spectral maxima, 519, 487.5, 462.5 mμ; partition behavior, epiphasic. The substance did not separate on the column from a sample *ex* β-carotene.

All-*trans*-anhydro-eschscholtzxanthin: very dark-purple crystals forming parallel twins and bulky conglomerates, m.p. 211°; spectral maxima 532, 499, 470.5 mμ; partition behavior, epiphasic. No separation took place from a sample *ex* β-carotene on the column.

Dehydrocarotene III: deep-red, quadrangular (rhombic), faintly glittering plates (from benzene–methanol); the crystals appear slightly darker than those of dehydrocarotene II; m.p. 191–192.5°.

Anal. Calcd. for $C_{40}H_{54}$: C, 89.84; H, 10.16. For $C_{40}H_{52}$: C, 90.18; H, 9.82. Found: C, 89.67; H, 10.06 (after correction for 1.06% ash); maximum extinction: $E^{1\%}_{1\,\text{cm.}} = 2.37 \times 10^3$ at 471 mμ; and after iodine catalysis, 1.64×10^3 at 466 mμ (in hexane) (Fig. 3). This compound is markedly less soluble in hexane than β-carotene; it is insoluble in methanol; partition behavior, epiphasic. When developed with hexane plus 2–3% acetone on lime–Celite, it is adsorbed between the β-carotene and the dehydro-β-carotene zones.

Dehydrocarotene I: brownish-red glittering plates (from benzene–methanol); the color of the crystals is deeper than those of α-carotene; m.p. 188–190°. *Anal.* Calcd. for $C_{40}H_{54}$: C, 89.84; H, 10.16. For $C_{40}H_{52}$: C, 90.18; H, 9.82. Found: C, 90.00, 89.94, 89.64; H, 9.95, 9.87, 10.18. (The third sample was obtained with N-bromosuccinimide and the two others with N-bromoacetamide; they were free of ash.)

---

[9] L. Zechmeister and J. W. Sease, This Journal, **65**, 1951 (1943).

[10] A. L. LeRosen, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 165 (1942).

Catalytic hydrogenation (PtO_2, cyclohexane + glacial acetic acid 1:1): calcd. 12.0 double bonds; found 11.4 and 11.3. Under identical conditions α-carotene gave 10.4 and 10.3 double bonds (calcd.: 11.0).

Maximum extinction, $E^{1\%}_{1\text{ cm.}}$ 2.36 × 10^3 at 455 mμ; and after iodine catalysis, 2.00 × 10^3 at 450 mμ (Fig. 1). The spectrum remained essentially unchanged upon shaking the hexane solution with 20% methanolic KOH for 4 hr. and rechromatography, as well as upon refluxing benzene solutions with ethanolic sodium ethylate for 2 hr.

The compound is less soluble than α-carotene; it is insoluble in methanol; partition behavior, epiphasic. When developed with hexane on lime–Celite, it appears between the α- and β-carotene zones.

Stereoisomerization of Dehydrocarotene I.—The solution of 6 mg. of substance in 50 ml. of hexane was catalyzed with 0.08 mg. of iodine, illuminated for 30 min. and developed with hexane on a 30 × 8 cm. lime–Celite column. The following top-to-bottom sequence appeared: neo U (maximum at 450 mμ), neo V (445 mμ), unchanged all-*trans* (455 mμ), neo A (448 mμ), and neo B (445 mμ) (Fig. 7). All zones were separated by colorless interzones. Ratio of the stereoisomers in the recovered pigment (established photometrically, after iodine catalysis of each *cis* form), neo U: neo V:unchanged all-*trans*:neo A:neo B = 7.5:1.5:67.5:6.0:17.5. Upon 45 min. refluxing of an all-*trans* solution, the ratio was 1.5:0:90.0:5.0:3.5. Each *cis* isomer yielded upon iodine catalysis and chromatography the all-*trans* compound that did not separate from an authentic sample in the mixed chromatogram test.

α-Carotene and N-Bromoacetamide.—These experiments were conducted under conditions similar to those with N-bromosuccinimide; however, the mole ratio of pigment: reagent was 1:1.2, and the refluxing was shortened to 1 hr. Fifty mg. of α-carotene in 5 ml. of carbon tetrachloride was treated with 15 mg. of the reagent in the presence of 2 ml. of ether. During the last minute no condenser was used, while the ether evaporated. The chromatograms were similar to those described above but no anhydro-eschscholtzxanthin zone was present; for yields *cf.* Table I.

α-Carotene and N-Bromophthalimide: mole ratio, carotene:reagent = 1:2; *e.g.*, 50 mg. of carotene and 42 mg. of reagent in 7.5 ml. of carbon tetrachloride were refluxed for 30 min.; for yields *cf.* Table I. Dehydrocarotene I was identified by its m.p. (189–190°), mixed m.p. (187–189)°, and a mixed chromatogram test.[11]

Interaction of Dehydrocarotene I and Boron Trifluoride.—To a solution of 12 mg. of substance in 12 ml. of chloroform, contained in a 50-ml. volumetric flask, 1.2 ml. of distilled boron trifluoride etherate was added and shaken vigorously for a minute. Immediately upon mixing with the reagent the orange solution turned greenish and then deep blue within a minute. After some ice-cold water had been introduced, the liquid was washed over with cooled hexane into a separatory funnel, shaken vigorously and washed acid-free. The hexane solution was dried, then developed with hexane + 5% acetone on a 24 × 4.6 cm. lime-Celite column:

41 two weak yellow zones and interzones
20 light orange, main product (476, 445 mμ; with I_2, 472, 443 mμ)
132 several light yellow zones, among them a *cis* form of the main product (473, 444 mμ; with I_2, 473, 442 mμ)
Filtrate: fluorescent; after rechromatography on alumina, single maximum at 228 mμ

The 20-mm. zone was rechromatographed, the hexane solution thus obtained was dried, evaporated, and the residue crystallized from benzene +95% methanol; yield 2.4 mg., m.p. 171–172°

Anal. Calcd. for $C_{40}H_{56}$: C, 89.48; H, 10.52. For $C_{40}H_{54}$: C, 89.84; H, 10.16. Found: C, 89.59; H, 10.43; spectral maxima, 474, 444.5, 421 mμ; maximum extinction, $E^{1\%}_{1\text{ cm.}}$ 1.99 × 10^3 at 444.5 mμ; and after iodine catalysis, 1.62 × 10^3 at 442.5 mμ (Fig. 4).

When a hexane solution was mixed with 1 vol. 20% methanolic KOH and refluxed for 2 hr., both the visual spectrum and the chromatographic homogeneity remained unchanged.

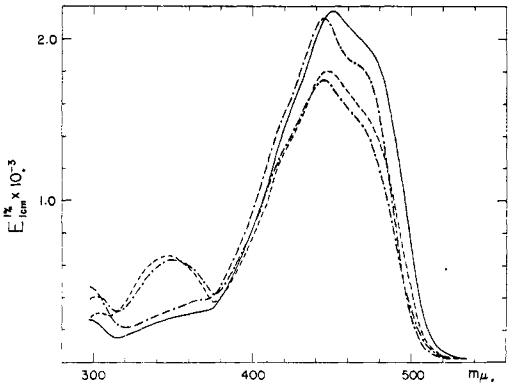


Fig. 7.—Extinction curves, in hexane, of some *cis* isomers of dehydrocarotene I: ——, neo U; —·—, neo V; ----, neo A; and -·-·-, neo B.

This compound is more easily soluble in benzene than either β-carotene or dehydrocarotene I; it is very sparingly soluble in methanol; partition behavior, epiphasic.

β-Carotene and N-Bromosuccinimide.—This conversion was carried out as described earlier[12] except that ten 100-mg. portions were treated and the liquid was refluxed for only 2 hr. The resulting solution, corresponding to 1 g. of β-carotene, was developed with hexane +2% acetone on five 30 × 8 cm. lime–Celite columns:

7 brownish
70 dehydro-β-carotene, bisdehydro-β-carotene, anhydro-eschscholtzxanthin and some *cis* forms, separated by interzones
33 interzone
9 faint pink
8 interzone
13 pink: dehydrocarotene III
14 orange
12 interzone
25 orange: dehydrocarotene II
13 yellowish orange
6 interzone
37 unchanged β-carotene (8% of the starting material)
5 interzone
25 yellow

The three components contained in the 70-mm. section were separated, rechromatographed, crystallized and identified as described earlier. Yields (pure crystals): 20 mg. of dehydro-β-carotene, 14.5 mg. of bisdehydro-β-carotene, and 6.5 mg. of anhydro-eschscholtzxanthin. The dehydrocarotenes II and III were rechromatographed on magnesia–Celite 3:1 (developer, hexane +10% acetone). The dried hexane solutions were evaporated, the residues dissolved in benzene and crystallized by the addition of methanol. The yields were (from 1 g. of β-carotene), 14 mg. of II (m.p. 186–187.5°); and 2.4 mg. of III (m.p. 191–192°, mixed m.p. with a sample *ex* α-carotene, 189.5–191.5°). The samples III obtained, respectively, from α- and β-carotene did not separate in the mixed chromatogram test.

Dehydrocarotene II forms deep-orange red, thick hexagonal plates. The color of the glittering crystals is about that of β-carotene.

Anal. Calcd. for $C_{40}H_{54}$: C, 89.84; H, 10.16. For $C_{40}H_{52}$: C, 90.18; H, 9.82. Found: C, 89.97; H, 10.01; maximum extinction, $E^{1\%}_{1\text{ cm.}}$ 2.59 × 10^3 at 462 mμ; and after iodine catalysis, 2.21 × 10^3 at 458 mμ (Fig. 2).

This spectrum was not altered by refluxing the benzene solution with sodium ethylate in ethanol for 2 hr. Dehydrocarotene II is less soluble in hexane than β-carotene; it is epiphasic in the partition test. It can be differentiated easily from dehydrocarotene I on the lime–Celite column where I is adsorbed below but II above the β-carotene zone.

Stereoisomerization of Dehydrocarotene II.—Iodine catalysis yielded the following three *cis* forms: neo U (maximum at 455 mμ), neo A (451 mμ), and neo B (451 mμ) (Fig. 8). Ratio in the recovered pigment, neo U:unchanged all-*trans*:neo A:neo B = 22:48.5:26.5:3.

---

(11) Under similar conditions N-bromomethylphthalimide or chloranil does not dehydrogenate carotene; *p*-quinone in glacial acetic acid displays a weak effect.

(12) Ref. 2, p. 4494.

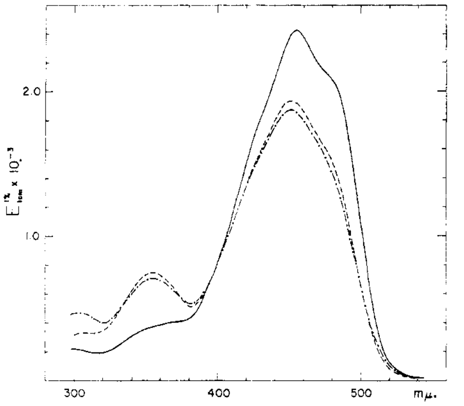


Fig. 8.—Extinction curves, in hexane, of some *cis* isomers of dehydrocarotene II: ——, neo U; ---- neo A; and —·—, neo B.

The interaction of dehydrocarotene II and boron trifluoride was carried out with 16 mg. of substance as described for dehydrocarotene I, but hexane +8% acetone was used as a developer. The main zone was rechromatographed and recrystallized from benzene +98% methanol; yield 1 mg., m.p. 163.5–164.5°; spectral maxima, 479, 451 mμ; maximum extinction, $E^{1\%}_{1\,\text{cm.}}$ 2.42 × 10^3 at 451 mμ; and after iodine catalysis, 2.03 × 10^3 at 447 mμ (Fig. 5).

Desoxylutein "I" and Boron Trifluoride.—When 7 mg. of substance was treated with the reagent as described for dehydrocarotene I and chromatographed on lime–calcium carbonate–Celite 1:1:1 (developer, hexane + 10% acetone), two main zones were observed; both showed marked fine structure; spectral maxima: upper zone (hypophasic), 474, 447 mμ; and lower zone (epiphasic) 484, 455 mμ (Fig. 6), corresponding roughly to the location of the spectral bands of α- and β-carotene.

β-Carotene and N-Bromoacetamide.—Fifty mg. of pigment in 5 ml. of carbon tetrachloride, 15 mg. of the reagent and 2 ml. of ether were refluxed for 20 min. (during the last min. no condenser was used). The combined yields of twenty such experiments were developed with hexane + 8% acetone on ten 56 × 8 cm. lime–Celite columns. The chromatograms were similar to those obtained with N-bromosuccinimide but anhydro-eschscholtzxanthin and dehydrocarotene II were missing. The dehydro-β-carotene crystals (m.p. 192–193°; maxima at 502.5, 471.5, 445.5 mμ) showed the following composition.

Anal. Calcd. for $C_{40}H_{54}$: C, 89.84; H, 10.16. Found: C, 89.55; H, 10.33 (after correcting for 0.28% ash).

A crystalline sample of neo-dehydro-β-carotene A[13] was also isolated; m.p. 159–161°; maxima, 496, 466, 442 mμ.

Cryptoxanthin and N-Bromosuccinimide.—To a solution of 20 mg. of crystalline cryptoxanthin (*ex* persimmons)[14] in 6 ml. of carbon tetrachloride 13 mg. of the reagent and 30 mg. of sodium bicarbonate were added. The liquid was then refluxed for 45 min., diluted with hexane and developed with hexane + 8% acetone on a 24 × 4.6 cm. lime–Celite column. The corresponding zones obtained from eight such experiments (*ex* 160 mg. of cryptoxanthin) were combined and worked up as described above. Four crystalline products could be isolated: *viz.*, bisdehydro-β-carotene, anhydro-eschscholtzxanthin, a small amount of dehydrocarotene III, and a new, deep-red compound whose spectral curve was void of fine structure: $\lambda_{\max}$ at 486 mμ; and after iodine catalysis, at 476 mμ. It showed essentially epiphasic behavior and was adsorbed on lime–Celite above the bisdehydro compound (yields, Table I).

Acknowledgment.—We wish to thank Professor A. J. Haagen-Smit, Mr. G. Swinehart and Dr. A. Elek for microanalyses and Mr. K. Lunde for infrared curves.

[13] L. Zechmeister and L. Wallcave, THIS JOURNAL, **75**, 5341 (1953).

[14] H. J. Deuel, Jr., E. R. Meserve, A. Sandoval and L. Zechmeister, *Arch. Biochem.*, **10**, 491 (1946); A. Chatterjee and L. Zechmeister, THIS JOURNAL, **72**, 254 (1950).

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Absorption Spectra of Tetracyclones. IV[1,2]

BY STEPHEN B. COAN, DONALD E. TRUCKER AND ERNEST I. BECKER

RECEIVED MAY 21, 1954

A series of tetracyclones has been synthesized in order to study absorption spectra. Substituents were introduced singly, in pairs and in quadruplet in the *p*-position of the phenyl rings. The syntheses of a number of substituted benzoins, benzils and 1,3-diphenyl-2-propanones are described as well as tetraphenylphthalic anhydrides which are derivatives for the tetracyclones. Previous observations were confirmed in that *p*-substituents in the 2- and/or 5-phenyl rings affect mainly the absorption maximum at 512 mμ, while *p*-substituents in the 3- and/or 4-phenyl ring affect mainly the maximum at 342 mμ. The shifts of the maxima are enhanced with the disubstituted compounds, while with tetrasubstituted compounds the maxima lie between those of the two corresponding disubstituted compounds. It is further suggested that the absorption maximum at 260 mμ is associated with a twinned stilbene type of resonance exclusive of the carbonyl group.

Introduction

This investigation is a continuation of a study which has already indicated that the two major absorption peaks of tetracyclone at 342 and 512 mμ can be related to resonance through the 3- and 4-phenyl rings and through the 2- and 5-phenyl rings, respectively. The earlier work dealt with several *p*-chlorosubstituted tetracyclones[1a]: a series of singly, *p*-substituted tetracyclones with electron-releasing groups[1b] and a series of *o*-chlorosubstituted tetracyclones.[1c] The purpose of the present work was to examine tetracyclones with substituents in pairs and in quadruplet employing electron-attracting as well as electron-releasing groups.

Syntheses of Tetracyclones

Most of the required intermediate benzils and 1,3-diphenyl-2-propanones were prepared by methods already in the literature. The preparation of 1,3-

---

[1] (a) Part I, F. J. Thaller, D. E. Trucker and E. I. Becker, THIS JOURNAL, **73**, 228 (1951); (b) part II, S. B. Coan, D. E. Trucker and E. I. Becker, *ibid.*, **75**, 900 (1953); (c) part III, E. L. Shapiro and E. I. Becker, *ibid.*, **75**, 4769 (1953).

[2] Taken from part of the Dissertation of D.E.T. (1951) and S.B.C. (1954) presented to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree. The spectra referred to in this paper have been deposited as Document number 4331 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $2.50 for photoprints, or $1.75 for 35 mm. microfilm payable to: Chief Photoduplication Service, Library of Congress.