for several hours under high vacuum over phosphorus pentoxide: yield 1 g. (76.5%), m.p. 210–211° dec.

Sodium Vitamin D_3 Phosphate (from Di-*t*-butyl Vitamin D_3 Phosphate).—Since it was not possible to obtain the pure sodium salt from vitamin D_3 dichlorophosphate, it was obtained from di-*t*-butyl vitamin D_3 phosphate. An ethereal solution of vitamin D_3 dihydrogen phosphate (from 1 g. of vitamin D_3) prepared as in the previous case was placed in a Thiele tube and shaken for 24 hours in the dark and in an atmosphere of nitrogen with a solution (50 cc.) of trisodium phosphate dodecahydrate (2 g.). The ether layer was then separated and the aqueous layer extracted several times with small portions of benzene. The benzene extracts were combined with the ether layer and the mixture concentrated to a small volume at room temperature and under reduced pressure. The concentrate, which was very cloudy, was filtered through a sintered glass funnel and the filtrate evaporated to dryness in vacuum; yield 1.3 g. This was further purified by triturating it with absolute ethanol, and the mixture filtered. The yellowish solid obtained was dissolved in anhydrous ether, the mixture filtered again and the ether removed in vacuum. The white solid residue was washed once with absolute ethanol and dried for 12 hours under a high vacuum in the presence of phosphorus pentoxide; yield 410 mg. (32.3%), m.p. 215–216° dec.

Anal. Calcd. for $C_{54}H_{91}P_3O_{13}Na_4$: P, 8.20; Na, 8.12; mol. wt., 1133. $C_{54}H_{89}P_3O_{12}Na_4$: P, 8.34; Na, 8.25; mol. wt., 1115. Found: P, 8.15; Na, 8.09; mol. wt. (in "exaltone"), 1082.

The sodium in the sodium vitamin D_3 phosphate was determined in water solution by flame photometry.[23]

The ultraviolet spectrum of this salt in water is shown in Table III, and the characteristic bands of its infrared spectrum are listed in Table II.

This salt is completely soluble in water, forming clear solutions; it is soluble in benzene, tetrahydrofuran and ether, difficultly soluble in alcohol, insoluble in aliphatic hydrocarbon solvents.

Barium Vitamin D_3 Phosphate (from the Sodium Salt).—A solution of sodium vitamin D_3 phosphate in ether was shaken with 5% phosphoric acid solution, then with water. It was then transferred into a Thiele tube and shaken for 24 hours in the dark and in nitrogen with an excess solution of 0.1 *N* barium hydroxide. The ether layer was then removed and the aqueous layer extracted several times with ether and the ether extracts combined and washed once with water. The ether was then removed in vacuum and the residue dried azeotropically with benzene. The light brown solid obtained was further purified by triturating with absolute alcohol and the mixture filtered. The solid obtained was dried for several hours under high vacuum and in the presence of phosphorus pentoxide; m.p. 193–194° dec.

Anal. Calcd. for $C_{81}H_{131}P_3O_{12}Ba_2$: P, 5.58; Ba, 16.52; mol. wt., 1664. Found: P, 5.25; Ba, 17.36; mol. wt. (in "exaltone"), 1581.

The extinction coefficient ($E_{1\,cm.}^{1\%}$) at 267 mμ in cyclohexane was found to be 178, and the characteristic bands of its infrared spectrum are listed in Table II.

The barium salt is insoluble in water, soluble in hydrocarbon solvents, slightly soluble in ethanol.

Barium Vitamin D_3 Phosphate (from Vitamin D_3 Dichlorophosphate).—This salt was prepared and purified according to the procedure given for the calcium salt (from vitamin D_3 dichlorophosphate) except the hydrolysis of vitamin D_3 dichlorophosphate which was accomplished with 0.1 *N* barium hydroxide solution. From 769.2 mg. of vitamin D_3 was obtained 1.065 g. (96%) of the purified barium salt, m.p. 175–180° dec. This salt is soluble in all hydrocarbon solvents, slightly soluble in ethanol, insoluble in water.

Anal. Calcd. for $C_{54}H_{92}P_2O_{10}Ba$: P, 5.63; Ba, 12.47; inorganic residue, 27.5. Found: P, 5.50; Ba, 12.20; inorganic residue found by combustion, 27.1.

Acknowledgment.—The authors wish to acknowledge with thanks some of the financial support for this investigation from the Research Corporation. They also wish to thank Dr. Nagy and his associates of this Institute for some of the analyses and the infrared spectra.

CAMBRIDGE 39, MASSACHUSETTS

(23) J. U. White, *Anal. Chem.*, **24**, 394 (1952).

[CONTRIBUTION NO. 1214 FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

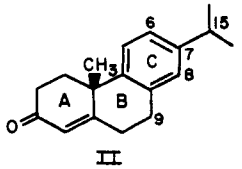
Chromic Acid Degradation of Methyl Dinitrodehydroabietate[1]

BY ERIK S. HANSEN AND HAROLD H. ZEISS[2]

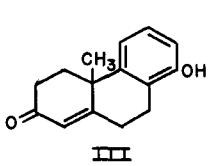
RECEIVED JANUARY 27, 1954

Chromic acid oxidation of methyl dinitrodehydroabietate leads to extensive rupture of the hydrophenanthrene ring system. The degradation products are characterized and assigned structures.

Stimulated by the successful conversion of dehydroabietic acid (I) into 2-keto-$\Delta^{1,11}$-nordehydroabietene (II) and by an encouraging stereochemical relationship of the C-12 methyl group,[3] our interest in the investigation of the diterpenic acids as source material for steroidal syntheses turned to the final obstacle, the modification of ring C. Starting with any of the abietic-type acids involves the task of removing the C-7 isopropyl group, while the use of *d*-pimaric acid leads to another set of difficulties. The intermediate III, obtained by Robinson and Cornforth[4] in their total synthesis of steroids, seemed to us to be the most suitable compound with which to establish rapport, both structural and stereochemical, between dehydroabietic acid and the steroids. The problem thus proposed was desisopropylation at C-7 and appropriate substitution at C-8.



II



III

Other workers have subjected I to various oxidative conditions. Drake has oxidized I with oxygen and persulfate catalyst in alkaline solution to 9-ketodehydroabietic acid.[5] The same keto acid was obtained from I by the action of alkaline permanganate by Pratt.[6] Air oxidation of methyl dehydroabietate in the presence of benzoyl peroxide by

(1) Taken from the dissertation submitted by E. S. Hansen to the Faculty of the Graduate School, Yale University, 1953, in candidacy for the Ph.D. degree.

(2) To whom correspondence may be addressed.

(3) H. H. Zeiss and W. B. Martin, Jr., THIS JOURNAL, **75**, 5935 (1953).

(4) R. Robinson and J. W. Cornforth, *J. Chem. Soc.*, 1855 (1949).

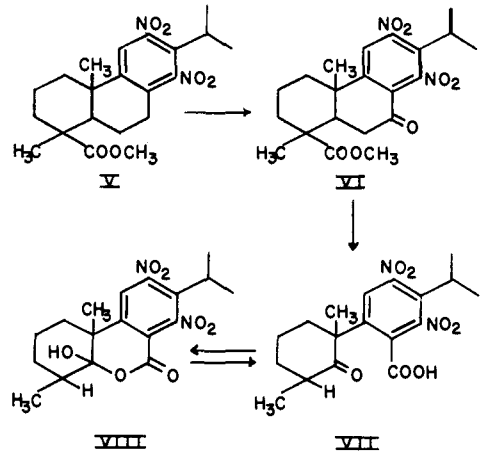
(5) A. E. Drake, U. S. Patent 2,434,643; *C. A.*, **42**, 2786*d* (1948).

(6) Y. T. Pratt, THIS JOURNAL, **73**, 3803 (1951).

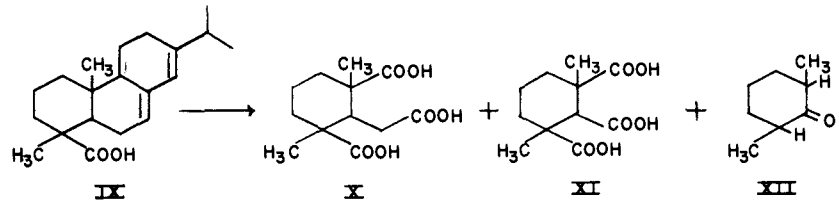
Ritchie, Sanderson and McBurney[7] yielded methyl 9-hydroperoxydehydroabietate as the main product, with some oxidation at the isopropyl site indicated. During the course of this present investigation these authors have attacked methyl dehydroabietate with chromic acid, air and benzoyl peroxide and finally with ferrous sulfate, by which sequence of reactions the isopropyl group is converted to an acetyl function.[8] As will be shown subsequently[9] this same conversion may be accomplished in one step more conveniently and with better yields by chromic acid alone. It was considered, therefore, that if I is oxidized at C-9 and at C-15 by a free radical mechanism, the introduction of nitro groups into positions *ortho* and *para* to the C-9 and C-15 carbon atoms would increase the rate of oxidation and possibly alter the proportion of C-15 product in a favorable manner. Accordingly, the oxidation of methyl 6,8-dinitrodehydroabietate (V)[10] with chromic acid was examined.

Methyl 6,8-dinitrodehydroabietate (V), $C_{21}H_{28}O_6N_2$, was oxidized by chromic acid at 70° in acetic acid yielding two pure products, a ketone VI and an acid VII, and two constant melting acidic mixtures, A and B. The ketone, $C_{21}H_{26}O_7N_2$, showed split carbonyl absorption at 5.81 and 5.87 μ, conjugated carbonyl absorption at 244 and 302 mμ, and a negative iodoform test. Inasmuch as no carbon was lost during the oxidation and since the ketone is conjugated, VI must be methyl 9-keto-6,8-dinitrodehydroabietate. Reoxidation of VI gave mixture A. The acid VII, $C_{18}H_{22}O_7N_2$, was monobasic, dissolving in aqueous sodium bicarbonate, and gave a broad carbonyl band at 5.75–5.80 μ, two strong absorption peaks at 2.80 and 2.95 μ and two maxima at 240 and 300 mμ. Since three carbon atoms had been lost and one oxygen atom had been gained in the oxidation, it appeared that the desired desisopropylation (and decarboxylation) had occurred, accompanied by the usual C-9 ketonization. Strong infrared absorption by the nitro groups did not permit a determination of the presence or absence of the isopropyl group doublet at 7.24 and 7.31 μ. There remained to be explained, however, the acidity of VII and the infrared absorption bands of VII in the 2.8–4.0 μ range which were surprisingly well defined for a carboxylic acid. On the one hand it was improbable that a compound having the structure considered above would show high acidity,[11] and on the other the absence of typical carboxylic acid absorption did not support a free acid formulation.[12] The desisopropylated structure was discarded.

The alternate explanation of the structure and properties of VII had to lie in an extensive rupture of the hydrophenanthrene ring system. Starting with the well-founded assumption of the vulnerability of the C-9 position to oxidative attack, a progression of successive oxidations could be visualized. The consequence of the opening of ring B to a dicarboxylic acid would be considerable relief of steric strain existing at the C-1 carboxylate group, allowing ester hydrolysis. Hydroxylation of the tertiary C-11 position by oxidation to an α-hydroxy acid, followed by the loss of carbon monoxide and water would generate a β-keto acid and this in turn would lose carbon dioxide and be converted to the final product, VII. The structure proposed for VII is in accord with all the known facts since this keto acid is undoubtedly in equilibrium with the lactol form VIII.



Additional support for this degradation scheme is found in the vigorous oxidation of abietic acid (IX) by Ruzicka and Waldmann.[13] Among the products isolated were the C_{12}- and C_{11}-acids (X and XI) and a small amount of 2,6-dimethylcyclohexanone (XII). It would appear, therefore, that XII is formed from XI by α-hydroxylation and decarboxylation.



The course of oxidation above leading to VII required that 6,8-dinitrodehydroabietic *acid* (IV) must yield also VII on oxidation, since the carboxyl group, originally present as the tertiary ester, must be lost, and this proved to be the case.

The keto acid VII readily absorbed three moles of

(7) P. F. Ritchie, T. F. Sanderson and L. F. McBurney, THIS JOURNAL, **75**, 2610 (1953).

(8) P. F. Ritchie, T. F. Sanderson and L. F. McBurney, *ibid.*, **76**, 723 (1954).

(9) H. H. Zeiss and M. Tsutsui, unpublished results.

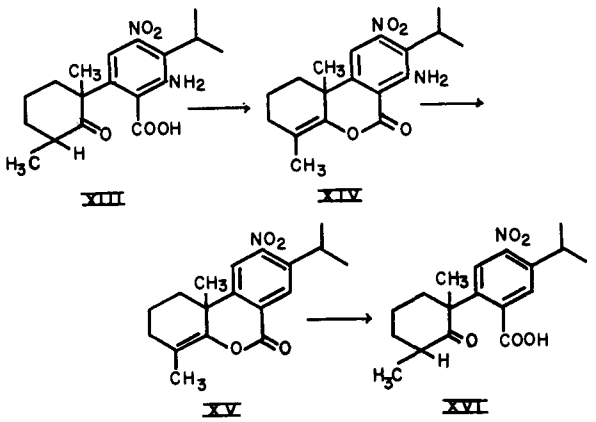
(10) W. P. Campbell and M. Morgana, THIS JOURNAL, **63**, 1838 (1941), deduce the dinitro derivative of I to be 6,8-dinitrodehydroabietic acid (IV). These authors place one nitro group at C-6 with certainty and the other at C-8 by analogy. While no serious doubt exists regarding the latter assignment, it is noted that a 5,6-dinitro structure is not excluded by the evidence; G. Schroeter, *Ann.*, **426**, 17 (1922), has found that the nitration of tetralin gives more 5,6- than 5,7-dinitrotetralin.

(11) A literature search revealed no data on systems of this kind. We therefore prepared 6,8-dinitro-α-tetralone and found it to be alkali-insoluble; E. S. Hansen and H. H. Zeiss, unpublished results.

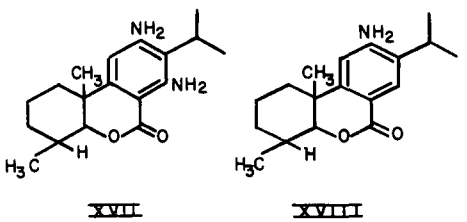
(12) That the source of the acidity did not arise from the hydrolysis of the hindered tertiary ester was demonstrated by the recovery of the ester from acetic acid solution maintained under oxidation conditions.

(13) L. Ruzicka and H. Waldmann, *Helv. Chim. Acta*, **16**, 842 (1933).

hydrogen with platinum to give the nitro amine XIII, soluble in aqueous sodium bicarbonate and concentrated hydrochloric acid. Upon refluxing in methanolic or ethanolic hydrochloric acid, XIII lost a mole of water, yielding the enol lactone XIV, which was non-acidic but soluble in hydrochloric acid. The enol lactone system was confirmed by two strong bands in the infrared carbonyl region at 5.80 and 5.98 μ.[14] The amino group of XIV was diazotized normally and deaminated smoothly in ethanol. The mononitro enol lactone XV dissolved slowly in 20% aqueous sodium hydroxide on the steam-bath to give the keto acid XVI having a single carbonyl band at 5.78 μ and a hydroxyl band at 2.76 μ (lactol form).[15]



Reduction of XV in ethanol under Clemmensen conditions gave the non-acidic, acid soluble amino lactone XVIII having single carbonyl absorption at 5.82 μ. The absence of nitro group absorption now brought under observation the *isopropyl group* at 7.24 and 7.30 μ, substantiating the survival of this carbon branch in the oxidation. Compounds VII, XIII and XIV on Clemmensen reduction all yielded the same diamine XVII characterized as its diacetate. Both constant melting mixtures, A and B, before mentioned, also gave XVII on similar treatment. Also, mixture B, on catalytic hydrogenation, gave XIII.



Acknowledgment.—We wish to express our indebtedness to the Research Corporation of New York for the encouragement and support which made this work possible.

(14) An analogy to this system is found in the enol lactone intermediate (5.79 and 5.92 μ) occurring in the total steroid synthesis reported by R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4223 (1952).

(15) Choice of formulation of compounds XIII–XVI as 6-nitro rather than 8-nitro derivatives was permitted on the basis of the oxidation of methyl 8-nitrodehydroabietate to the keto acid and subsequent cyclization to an enol lactone which was non-identical with XV; *cf.* reference 8.

Experimental[16]

Methyl 6,8-Dinitrodehydroabietate (V).—Finely powdered methyl dehydroabietate (25 g.), m.p. 62–63°, was nitrated according to the procedure of Fieser and Campbell.[17] Crystallization of the crude dinitro derivative from ether yielded 23 g. (69%) of pure product, m.p. 190–191° [α] +53° (α, 0.53°).

Oxidation of V.—The dinitro ester (30.6 g., 0.0757 mole) in 3 l. of stirred glacial acetic acid at 70° was oxidized with dropwise additions of 59.0 g. (0.590 mole) of chromium trioxide in 40 ml. of water and 1 l. of acetic acid over a period of 6 hours. This addition was followed by continued agitation of the solution at the same temperature for 1 hour and at 90° for 1 hour. After cooling to room temperature overnight the solution was stripped of acetic acid *in vacuo*, the residue puffed almost dry and the solid material treated with 25 ml. of sulfuric acid and 200 ml. of sulfurous acid in 800 ml. of water. The acid mixture was repeatedly extracted with ether, the resultant ether extracts being first washed with water and then exhaustively extracted with 1% sodium hydroxide solution.

(a) **Isolation of Methyl 9-Keto-6,8-dinitrodehydroabietate (VI).**—The ether layer above, freed of acidic product, was evaporated leaving 1.84 g. of VI, m.p. 216–218°, [α] +80° (α, 0.80°). Recrystallization of the dinitro ketone from ether, aqueous acetone or ethanol did not change this m.p.

Anal. Calcd. for $C_{21}H_{26}O_7N_2$: C, 60.28; H, 6.26; N, 6.70. Found: C, 60.44; H, 6.34; N, 7.12.

(b) **Isolation of Keto Acid VII.**—The wine-red alkaline extracts obtained above were filtered and acidified with cold, dilute hydrochloric acid. The pale yellow solid which precipitated was washed, dried (20.5 g., m.p. 140–146°) and a sample dissolved in hot methanol. On cooling an oil was deposited which, when seeded with a crystal of VII (*vide infra*), gradually crystallized. Recrystallization of the semi-crystalline mass once from methanol and three times from ethanol gave VII whose infrared and ultraviolet spectra were the same as the keto acid obtained later; m.p. and mixed m.p. 203–204°, [α] +164° (α, 1.64°).

(c) **Isolation of Mixtures A and B.**—The crude solid from above (m.p. 140–146°) was crystallized five times from ether–hexane to give 6.3 g. of mixture A, m.p. 171–171.5° dec., [α] −80°.

Anal. Calcd. for $C_{20}H_{24}O_9N_2$: C, 55.04; H, 5.54; N 6.42. Found: C, 55.06; H, 5.66; N, 6.08.

Mixture A was dissolved in ether, treated with Norit and crystallized a total of seven times from ether–hexane. From this treatment a second constant melting material, mixture B, was obtained, m.p. 186.5–187.5°, [α] +181.5°.

Anal. Found: C, 58.59, 58.31, 57.96; H, 6.25, 6.31, 6.08; N, 7.51, 7.50, 7.11.

Clemmensen Reduction of Acidic Oxidation Product from Methyl 6,8-Dinitrodehydroabietate.—Crude acidic oxidation product (60 g.) from V was dissolved in toluene and added to a mixture of 300 g. of amalgamated zinc, 225 ml. of water, 300 ml. of concentrated hydrochloric acid and 50 ml. of glacial acetic acid. After refluxing for 24 hours, during which hourly additions of 50 ml. quantities of hydrochloric acid for the first 4 hours were made, the mixture was cooled, and the toluene and aqueous layers were separated. The aqueous layer was extracted twice with ether, and the ether and toluene layers were then combined.

(a) **Isolation of the Keto Acid (VII).**—The combined ether–toluene solutions were extracted with 1% sodium hydroxide solution. Acidification of the dark red, alkaline extracts with cold, dilute hydrochloric acid caused the precipitation of an almost colorless solid which, after 6 recrystallizations from aqueous ethanol, amounted to 19.3 g. of colorless needles of VII, m.p. 203–205°, [α] +165° (α, 1.72°).

Anal. Calcd. for $C_{18}H_{22}O_7N_2$: C, 57.13; H, 5.86; N, 7.40. Found: C, 57.15; H, 5.66; N, 7.68.

(16) All melting points are corrected. Optical rotations (D line) were measured in 95% ethanol in a 1-dm. tube at room temperature. Ultraviolet spectra were measured in 95% ethanol and infrared spectra in chloroform. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(17) L. F. Fieser and W. P. Campbell, THIS JOURNAL, **60**, 159 (1938).

(b) **Isolation of Diamino Lactone XVII.**—The aqueous acidic layer after the ether extraction described above was made alkaline with concentrated sodium hydroxide solution and extracted with ether. The ether solution was extracted with 5% aqueous hydrochloric acid, and the acid solution filtered and made alkaline. The light brown precipitate was washed, dried and dissolved in anhydrous ether. Passage of hydrogen chloride gas through the ether caused the precipitation of the white, extremely hygroscopic **dihydrochloride of XVII**, m.p. *ca.* 282° dec. The free amine was regenerated in alkaline solution, filtered, washed and dried over phosphorus pentoxide. It was then put into a column of alumina with dry benzene and eluted with 1:1 benzene–chloroform solution. The light yellow oil obtained was reconverted to its dihydrochloride and regenerated, m.p. 64–67°, $[\alpha]$ +186°. No suitable solvent was found for crystallization of XVII to purity.

The diamino lactone was refluxed with 3.5 ml. of acetic anhydride for 10 minutes. After cooling the solution was diluted with 25 ml. of water, and the mixture was warmed on the steam-bath. An almost colorless solid slowly crystallized from solution as the acetic anhydride was hydrolyzed. After cooling the **diacetate** was collected, dried and recrystallized from methanol as very small needles, m.p. 235–236°.

Anal. Calcd. for $C_{22}H_{30}O_4N_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.10; H, 7.66; N, 6.99.

The dilute acetic acid filtrate remaining after the isolation of the diacetate was made alkaline, causing the precipitation of a colorless solid. **This monoacetate** was collected, washed, dried and crystallized from aqueous methanol, m.p. 264° dec.

Anal. Calcd. for $C_{20}H_{28}O_3N_2$: C, 69.74; H, 8.19; N, 8.13. Found: C, 70.48; H, 8.62; N, 7.94.

The mono- and diacetates were reconverted to the diamino lactone XVII by hydrolysis in 10% hydrochloric acid.

Catalytic Reduction of Dinitro Keto Acid VII to Nitro Amine XIII.—The dinitro keto acid (251 mg.) was hydrogenated in 100 ml. of ethanol with 9 mg. of platinum oxide at atmospheric pressure and room temperature. After 3 hours a total of 3 mole equivalents of hydrogen was absorbed and no further hydrogen uptake occurred. The catalyst was filtered from the alcoholic solution, and the alcohol was removed until the nitro amine began to crystallize. Recrystallization of XIII from aqueous methanol gave 186 mg. (81%) of product, m.p. 289° dec., $[\alpha]$ +240° (α, 2.40°).

Anal. Calcd. for $C_{18}H_{24}O_5N_2$: C, 62.05; H, 6.94; N, 8.04. Found: C, 62.48; H, 6.68; N, 8.23.

The nitro amine (302 mg.) was reduced with 5 g. of amalgamated zinc in 15 ml. of ethanol, 4 ml. of water and 25 ml. of concentrated hydrochloric acid. After 1.5 hours the solution had become colorless and was worked up as in the Clemmensen reduction described earlier. A total of 105 mg. (40%) of diamino lactone XVII, m.p. 62–65°, was obtained.

Formation of Enol Lactone XIV from Nitro Amine XIII.—A solution of 1.155 g. of nitro amine, dissolved in 90 ml. of ethanol and 160 ml. of concentrated hydrochloric acid, was refluxed under nitrogen for 16 hours. The reaction mixture was cooled, saturated with hydrogen chloride and refluxed for an additional 24 hours, during which small additions of alcohol were made to keep precipitating solid in solution. The solution was cooled in an ice-bath saturated with hydrogen chloride, filtered and made slightly alkaline by the addition of 10% sodium hydroxide. The suspended solid was extracted with ether and removed from its ether solution with concentrated hydrochloric acid. After filtration the acidic solution was made basic causing the precipitation of a pale yellow solid, m.p. 210–215°. This was dissolved in a minimum quantity of methanol, filtered and diluted with water. Crystallization of the enol lactone was induced by seeding or by scratching the flask wall. After 7 recrystallizations 355 mg. (32.5%) of XIV was obtained as colorless plates, m.p. 263.5° dec., $[\alpha]$ −208° (α, 2.08°).

Anal. Calcd. for $C_{18}H_{22}O_4N_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.60; H, 6.40; N, 8.78.

The alkaline solutions above contained unreacted XIII which could be recycled to obtain more XIV.

Clemmensen reduction of XIV (208 mg.) as described for XIII gave 94 mg. (46.5%) of the diamino lactone XVII, m.p. 61–66°.

Deamination of Enol Lactone XIV to Mononitro Enol Lactone XV.—A solution of the enol lactone (85 mg.) in 5 ml. of concentrated hydrochloric acid at 0° was treated with 20 mg. of sodium nitrite in 6 drops of water. A 3° rise in temperature and development of green color ensued. Stirring at 0° was continued for 30 minutes after which 10 ml. of cold sirupy phosphoric acid was added dropwise over a 10-minute period at 0°. After 30 minutes more at the same temperature the solution was treated with 100 mg. of urea and then added dropwise to 25 ml. of ethanol at room temperature causing a slow evolution of nitrogen. Warming the solution to 80° increased the rate of evolution and changed the color of the solution to light brown. After concentration of the alcoholic solution to 15 ml. it was cooled and diluted with water to a volume of 50 ml. The colorless precipitate was extracted with ether, and its ether solution was washed with base, acid and water before drying over sodium sulfate. Evaporation of the ether left a colorless solid which, after one crystallization from aqueous ethanol, amounted to 30 mg., m.p. 152–154°. Eight recrystallizations from the same solvent yielded 20 mg. (24%) of the mononitro enol lactone, m.p. 167–168°, $[\alpha]$ +29.1° (α, 0.26°).

Anal. Calcd. for $C_{18}H_{21}O_4N$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.39; H, 6.45; N, 4.36.

The mononitro enol lactone (8.1 mg.) was warmed on the steam-bath for 24 hours in 1 ml. of 20% sodium hydroxide. The mixture was centrifuged, and the clear alkaline decantate was diluted to 3 ml. and acidified with hydrochloric acid. The almost colorless precipitate of keto acid XVI was collected by centrifugation, washed with water and dried *in vacuo;* 5.3 mg. (62%).

Reduction of the Nitro Enol Lactone XV to Amino Lactone XVIII.—The mononitro enol lactone (200 mg.) was reduced with 3 g. of amalgamated zinc in 10 ml. of ethanol, 2.5 ml. of water and 15 ml. of hydrochloric acid. The crude amino lactone (104 mg.), m.p. 70–76°, was isolated by procedures already described in other Clemmensen reductions. This product was put onto a column of alumina with benzene, and elution with the same solvent gave only a carbonyl-free fraction (48 mg.). Successive elutions with an increasing ratio of chloroform to benzene began with a 1:19 mixture. At about a 7:13 ratio three successive fractions were obtained which yielded 4.8, 31.0 and 10.2 mg., respectively, of a pale yellow oil. Although the infrared spectra of the three were almost identical, only the middle fraction finally crystallized, m.p. 100–104°. Five recrystallizations of the amino lactone from aqueous methanol gave 11 mg. (6%) of fine needles, m.p. 128–129°, $[\alpha]$ +51.2° (α, 0.26°).

Anal. Calcd. for $C_{18}H_{25}O_2N$: N, 4.87. Found: N, 5.01.

Oxidation of 6,8-Dinitrodehydroabietic Acid (IV).—The nitration of 20 g. of dehydroabietic acid was performed by the method of Fieser and Campbell[17] and afforded 17.5 g. (68%) of the dinitro acid, m.p. 168–170°. This acid (3 g.) was oxidized with 6 g. of chromic trioxide in 400 ml. of acetic acid as described in the oxidation of the methyl dinitro ester V. The light yellow, amorphous precipitate obtained weighed 2.1 g., m.p. 130–136°. Attempted crystallization of this crude acidic product from ethanol gave only oil.

The crude oxidation product (1.5 g.) was dissolved in 20 ml. of toluene and reduced with 6 g. of amalgamated zinc in 5 ml. of water, 20 ml. of hydrochloric acid and 10 ml. of glacial acetic acid by the method previously described. The toluene layer yielded a residue, as did the ether extract of the aqueous acidic layer, whose infrared spectrum was the same as that of the keto acid VII. A solution of this product in ethanol, when diluted with water to turbidity and seeded with VII, gave a crystalline precipitate which, after recrystallization from aqueous ethanol, melted constantly at 201–202.5°, mixed m.p. with VII 202–203°; 104 mg. (11%).

The aqueous acid layer was worked up as before and gave 320 mg. (21.5%) of the diamino lactone XVII, m.p. 62–66°.

Oxidation of Methyl 9-Keto-6,8-dinitrodehydroabietate (VI).—The 9-keto dinitro ester (1.0 g.) was oxidized with 0.858 g. of chromic trioxide in 0.5 ml. of water and 15 ml. of acetic acid. The acidic product was collected and dried as a light yellow solid (386 mg.), m.p. 145°. Crystallization of this solid from ether–hexane gave material melting between 171–171.5° alone or when mixed with mixture A.

Clemmensen Reduction of Mixtures A and B.—Separate reductions of 0.475 g. of mixture A and 0.500 g. of mixture

B were carried out with 10 g. of amalgamated zinc in 10 ml. of ethanol, 7.5 ml. of water and 10 ml. of concentrated hydrochloric acid. Small additions of hydrochloric acid were made during the 23-hour refluxing period. The product in each case was worked up as described in the reduction of the keto acid VII. From mixture A, 66 mg. of the diamino lactone XVII was obtained, m.p. 64–67°. After further purification by chromatography on alumina and elution with 1:1 chloroform–benzene solution, 56 mg. (14%) of XVII was obtained having ultraviolet and infrared spectra identical to that of the XVII isolated before. From mixture B 43 mg. (11%) of XVII was recovered.

Catalytic Reduction of Mixture B.—Mixture B (0.30 g.) was reduced with 0.01 g. of platinum oxide in 100 ml. of ethanol at atmospheric pressure and room temperature until hydrogen uptake had ceased (6 hours). The alcoholic solution was filtered and evaporated *in vacuo* at 50° to a light brown resin. This was dissolved in a small volume of ether from which it soon began to crystallize. This was recrystallized 6 times from methanol. The product (126 mg., 42%) proved to be the nitro amine XIII, m.p. 287° dec.; mixed m.p. 287° dec.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION NO. 1912 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Infrared Spectra and *cis–trans* Configurations of Some Carotenoid Pigments

BY K. LUNDE AND L. ZECHMEISTER

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Infrared spectra in relationship to *cis–trans* configurations are reported for some representatives of the following stereoisomeric sets: β-carotene, zeaxanthin, lycopene, α-carotene, γ-carotene, dimethylcrocetin and methylbixin. The influence of the spatial configurations on these spectra is manifest in the regions ~7.25, 10.0–10.6 and ~13 μ. Considering the new data, some configurations proposed earlier on the basis of spectral phenomena, observed in the visible and ultraviolet regions, have been confirmed while some others had to be revised.

The aim of the present paper is duofold. On one hand, we wish to contribute to the correlation of infrared spectra and *cis–trans* configurations of polyenes and, on the other, we endeavored to test, and where necessary to revise, in the field of the carotenoids, our earlier configuration assignments which were made without the benefit of the information given by infrared spectra.

While some reliable data have been reported concerning infrared spectra of *cis–trans* isomers of short conjugated systems,[1] relatively little is known about the influence of the configuration on vibrational spectra of long-chain polyenes.[2] Recently, we have studied along these lines the available members of the stereoisomeric diphenyl-ethylene, -butadiene, -hexatriene and -octatetraene sets,[2] after some new *cis* forms of the two latter compounds had been prepared in our laboratory.[3]

It has been pointed out[2] that the influence of the spatial configuration of a diphenylpolyene on its infrared curve becomes manifest in the following three regions: 7.0–7.1 μ (in-plane vibration of CH being part of a *cis* CC double bond); 12.84–12.95 μ (the analogous out-of-plane vibration); and 10.0–10.6 μ (out-of-plane vibration of CH in the corresponding *trans* grouping).

When evaluating our curves the following two features should be taken into consideration: (a) whereas in a diphenylpolyene molecule each C=C carries two hydrogens, in carotenoids several aliphatic double bonds carry a hydrogen and a methyl (*cf.* the formulas); (b) infrared spectra of diphenylpolyenes contain a great number of bands due to the presence of phenyl groups, while the carotenoid curves are simpler, although some configuration assignments encounter serious difficulties.

For the sake of convenience we will introduce the following terms: "methylated double bond" for a double bond located in a —(CH_3)C=CH— group, and "unmethylated double bond" for one in a —CH=CH— group.

In the present paper we will discuss first the symmetrical C_{40}-carotenoids, β-carotene $C_{40}H_{56}$, zeaxanthin $(HO)C_{40}H_{54}(OH)$, and lycopene $C_{40}H_{56}$; then two non-symmetrical ones, *viz.*, α-carotene $C_{40}H_{56}$ and γ-carotene $C_{40}H_{56}$; and, finally, the lower-molecular symmetrical pigments, dimethylcrocetin $CH_3OOC{\cdot}C_{18}H_{22}{\cdot}COOCH_3$, and methylbixin $CH_3OOC{\cdot}C_{22}H_{26}{\cdot}COOCH_3$.

While Fig. 1 gives a general impression of an infrared carotenoid curve, in Figs. 2–4 only the stereochemically significant regions appear.

In the numbering of the carbon atoms we are following Karrer's nomenclature (*cf.* the β-carotene formula).

Stereoisomeric β-Carotenes (I) (Figs. 1–2).—Four spatial forms have been studied in this set, *viz.*, all-*trans*-β-carotene (natural product); central-mono-*cis*-β-carotene (absolute configuration established by Inhoffen, *et al.*, by total synthesis[4]); and the neo forms U and B obtained by iodine catalysis of the all-*trans* compound.[5,9]

Within the 10.0–10.6 μ region some bands (designated below briefly as "*trans*"-bands) have been assigned by earlier authors[6] to out-of-plane vibrations of the two hydrogen atoms contained in a *trans* C—CH=CH—C grouping. It is also known that conjugation of this grouping to an analogous *cis* group, *i.e.*, the formation of a *trans–cis*-diene

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