ture. The product was taken up in petroleum ether (b.p. 60–68°) and chromatographed on Florisil.[25] Elution with petroleum ether (b.p. 60–68°) gave a product which after methanol crystallization weighed 1.2 g. and showed only a single band at 3520 cm.$^{-1}$ This product was designated as VIa. The analytical sample from methanol gave m.p. 177–182°; $[\alpha]_D^{25}$ −82.5°, infrared spectrum shows bands at 3520 (bonded hydroxyl), 1736 (acetate), 990, 925, and 855 cm.$^{-1}$ (spiroketal side chain).

Anal. Calcd. for $C_{29}H_{46}O_5$: C, 73.38; H, 9.77. Found: C, 73.39; H, 9.91.

20α-Hydroxy-22β-O-cyclopseudosarsasapogenin acetate (VIb). Elution of the Florisil chromatography column, described under VIa above, with benzene gave a small quantity of a mixture in the early fractions. Continued elution with benzene and then chloroform gave a product which on crystallization from petroleum ether (b.p. 60–68°) yielded 1.6 g. of VIb with only one hydroxyl band at 3605 cm.$^{-1}$ The analytical sample from petroleum ether (b.p. 60–68°) gave m.p. 192–197°; $[\alpha]_D^{25}$ + 32.4; infrared spectrum shows bands at 3605 (nonbonded hydroxyl), 1735 (acetate), 988, 925, 910, 872 cm.$^{-1}$ (spiroketal side chain).

Anal. Calcd. for $C_{29}H_{46}O_5$: C, 73.38; H, 9.77. Found: C, 73.08; H, 9.95.

Conversion of VIa *to* VIb. To a solution of 0.1 g. of VIa in 5 ml. of methanol was added 1 ml. of glacial acetic acid. The solution was allowed to stand overnight at room temperature. The product was isolated by ethereal extraction in the usual manner. Infrared examination showed an almost complete conversion to VIb; about 5–10% VIa was present. Similar treatment of VIb gave only unchanged starting material.

$\Delta^{20(21)}$-22α-O-Sarsasapogenin acetate (VIIa). To a solution of 1.2 g. of VIa in 30 ml. of pyridine cooled in an ice bath was added 0.07 ml. of thionyl chloride. The solution began to darken immediately. After 5 min., the reaction product was diluted with water and given the standard ether extraction, yielding 0.6 g. of crude VIIa. The analytical sample was crystallized from methanol, m.p. 181–183°; $[\alpha]_D^{25}$ −85°, infrared spectrum shows absence of hydroxyl bands at 3080, and presence of bands at 1670, 895 (C=CH_2), 1737 (acetate), 986, 922, 852 cm.$^{-1}$ (spiroketal side chain).

(25) Mention of trade names does not signify recommendation over similar equivalent products.

Anal. Calcd. for $C_{29}H_{44}O_4$: C, 76.27; H, 9.71. Found: C, 76.29; H, 9.80.

Conversion of VIIa *to* VIa. A solution of 0.2 g. of VIIa and 0.11 g. of osmium textroxide in 6 ml. of benzene and 0.14 ml. of pyridine was stored in the dark at room temperature for 12 days. Work-up proceeded as in reference 5b compound III. Infrared examination of the crude product showed two hydroxyl groups at 3620 and 3515 cm.$^{-1}$ consistent with formation of 20α, 21β-dihydroxy-22α-O-sarsasapogenin acetate. The total crude product was dissolved in 0.3 ml. of pyridine to which was added 0.15 g. of *p*-toluenesulfonyl chloride. The mixture was heated briefly on the steam bath and then allowed to stand overnight at room temperature. After standard work-up the residue was treated with lithium aluminum hydride and reacetylated as in reference 5b, conversion of III to I. Crystallization from methanol gave 0.04 g. of VIa.

Catalytic hydrogenation of VIIa. A sample of 0.1 g. of VIIa was catalytically hydrogenated in the presence of 5% palladium on charcoal as described under the preparation of IV. The product obtained was exclusively the known cyclopseudosarsasapogenin acetate,[11] VIIIb. Catalytic hydrogenation under similar conditions in the presence of a trace of pyridine (1 drop) gave only unchanged VIIa, as did substitution of palladium–calcium carbonate for palladium-charcoal catalyst (no pyridine added to ether).

Dehydration of VIb. A sample of 1.6 g. of VIb was dehydrated with 0.1 ml. of thionyl chloride as described under the preparation of VIIa. Crystallization of the crude product gave 0.7 g. of a crystalline mixture. The product could not be separated by chromatography on Florisil. Infrared analysis of the mixture showed absence of hydroxyl bands and presence of bands at 3080 and 1672 indicative of the presence of C=CH_2. Spiroketal bands were present but in a manner indicating that a mixture of two spiroketal types might be present. This was confirmed by $[\alpha]_D^{25}$ values ranging from −40° to −20° in various experiments indicating an approximately equal mixture of VIIa and the desired VIIb.

Hydrogenation of mixture of VIIa *and* VIIb. A sample of 0.1 g. of the above mixture was catalytically hydrogenated with 5% palladium charcoal in ether as described under the hydrogenation of VIIa. The exclusive product was cyclopseudosarsasapogenin acetate, VIIIb.

PHILADELPHIA 18, PA.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE, U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE]

Chemistry of the Spiroaminoketal Side Chain of Solasodine and Tomatidine. VI.[1] The Beckmann Rearrangement of the Oximino Derivatives

YOSHIO SATO AND NOBUO IKEKAWA[2]

Received July 12, 1961

The oximes of the pseudo derivative "B" of solasodine and tomatidine undergo an "abnormal" Beckmann rearrangement to yield amidonitriles which can be hydrolyzed to the respective 3β,16β-dihydroxy-5-bisnorcholenic and allobisnorcholanic 22 → 16-lactones. Alternatively, the lactones can be obtained from the rearrangement and hydrolysis of the 23-oximino alkamines.

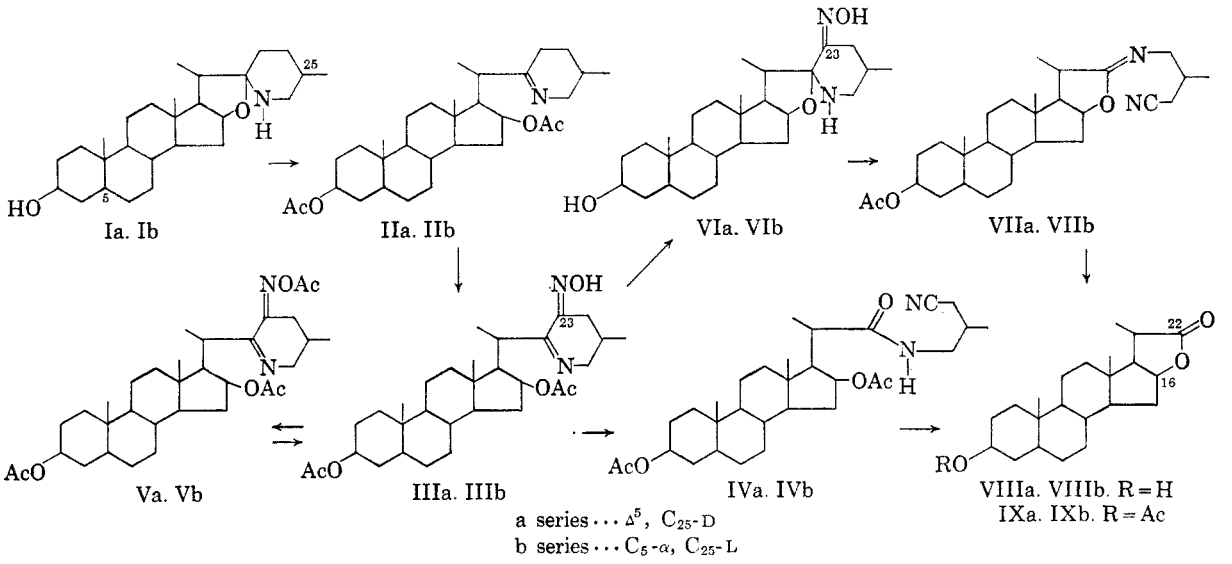
In the course of our studies of the so-called pseudo derivatives "B" of solasodine,[3] IIa, and tomatidine,[4] IIb, obtained from the treatment of the respective steroidal alkaloids, Ia and Ib, with

(1) For previous papers of this series see *J. Org. Chem.*, 26, 1945 (1961).

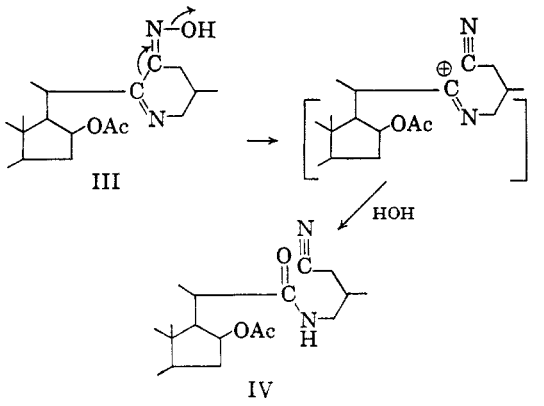
(2) Formerly Visiting Scientist, National Institutes of Health: present address, Institute of Physical and Chemical Research, Bunkyo-ku, Tokyo, Japan.

(3) Y. Sato, H. G. Latham, Jr., and E. Mosettig, *J. Org. Chem.*, 22, 1496 (1957).

(4) Y. Sato, H. G. Latham, Jr., and N. Ikekawa, *J. Org. Chem.*, 25, 1962 (1960).



a solution of zinc chloride, acetic anhydride, and acetic acid mixture, the effects of nitrous acid upon these derivatives (IIa and IIb) were investigated. With nitrous acid the pseudo derivatives IIa and IIb, form the C_{23} oximino derivatives IIIa and IIIb, respectively, in good yields. Support for the assignment of this formulation is derived from the spectral data $\lambda_{max}^{CHCl_3}$ 2.80, 3.05 μ, OH; 5.78 μ, O—Ac; 6.15 μ, —N=C—C=N, $\lambda_{max}^{C_2H_5OH}$ 232.5 mμ (log ϵ, 4.08) as well as from their elemental analyses and chemical transformations. When compound IIIa or IIIb is treated with *p*-toluenesulfonyl chloride in pyridine it readily suffers rupture of the C_{22}—C_{23} bond affording, after treatment with water, the cyanoamide derivative IVa or IVb ($\lambda_{max}^{CHCl_3}$, 2.90 μ, NH; 4.44 μ, C≡N; 5.77 μ, O—Ac; 5.95, 6.65 μ, HN—CO—). The course of the reaction is viewed as departure of the hydroxyl or its acylated counterpart with its pair of electrons accompanied by a shift of the C_{22}—C_{23} electron pair to form the nitrile and the resulting cation combining with water to form the amide (III → IV).



Thionyl chloride in benzene-chloroform as a medium also proved effective in promoting this rearrangement. This cleavage of the imino oximes is another instance of the so-called abnormal Beckmann rearrangement observed to occur in the α-diketone monooximes,[5,6] α-hydroxy ketone oximes,[7] tertiary ketone oximes,[8] 9,10-dihydro-9,10-(11-ketoethano)anthracene oxime,[9] spiroketoximes,[10] and 5-nitroso-6-aminopyrimidines.[11] Apparently the rearrangement of our compounds proceeds almost exclusively in the abnormal manner with these reagents. However, smaller amounts of what we believe to be normal rearrangement products were isolated along with the abnormal products when glacial acetic acid[12] was used as the medium for the rearrangement.

That the product from these rearrangements is a cyanoamide derivative was confirmed by conversion of IVa and IVb to the lactones, 3β,16β-dihydroxy-5-bisnorcholenic 22→16-lactone[13] (VIIIa) and 3β,16β-dihydroxyallobisnorcholanic 22→16-lactone[14] (VIIIb), respectively, by solvolysis with methanolic alkali. The ease in obtaining the unsaturated lactone VIIIa in good yields makes this method a most convenient route for the preparation of this rather inaccessible lactone.

(5) A. Werner and A. Piguet, *Ber.*, **37**, 4295 (1904).
(6) A. F. Ferris, *J. Org. Chem.*, **25**, 12 (1960).
(7) A. Werner and Th. Detscheff, *Ber.*, **38**, 69 (1905).
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(10) R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960).
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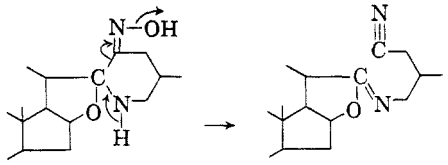
Acetylation of IIIa, IIIb with acetic anhydride and pyridine at low temperature (5°) affords the stable oxime acetates Va and Vb ($\lambda_{max}^{CHCl_3}$ 5.62 μ, =N—OAc[15]; 5.78 μ, OAc; 6.13, 6.20 μ), which revert readily to the original oximes either by chromatography over alumina or warming with aqueous acetic acid (90%).

Treatment of IIIa or IIIb with methanolic alkali effects cyclization as in the pseudo compounds "B"[3,4] to yield the C_{23} oximes of solasodine, VIa, or tomatidine, VIb. Interestingly, acetylation (acetic anhydride–pyridine, 5°) of these oximes, VIa or VIb, resulted in a concomitant occurrence of the abnormal Beckmann rearrangement (VI → VII) to produce the imino nitriles VIIa and VIIb.



VI VII

The infrared spectra of these compounds are characterized by the appearance of a band at 4.45 μ (—C≡N) and 5.88 μ (>C=N—).

Upon hydrolysis with aqueous acetic acid, they are easily converted to the corresponding lactone IXa and IXb obtained previously from IVa and IVb. The foregoing transformations illustrate some of the interesting and versatile reactions of the spiroaminoketal system present in these alkaloids.

EXPERIMENTAL[16]

23-Oximinopseudosolasodine "B" (IIIa). A solution of sodium nitrite prepared from 15 g. of the salt and 4 ml. of water was added dropwise to a solution of pseudosolasodine "B"[3] consisting of 800 mg. of the compound and 12 ml. of acetic acid. After standing overnight, the reaction mixture was poured on ice and made alkaline by addition of ammonium hydroxide. The product crystallized as plates (730 mg., 86%) from acetone-hexane and melted at 201–203°, $[\alpha]_D^{20}$ +25° (chloroform). Its infrared spectrum (chloroform) exhibited bands at 2.80, 3.05 μ (OH); 5.78 μ (O—Ac); 6.15 μ (—N=C—C=N—). The compound displayed an ultraviolet absorption maxima at 232.5 mμ (log ϵ, 4.08) in ethanol.

Anal. Calcd. for $C_{31}H_{46}O_5N_2$: C, 70.69; H, 8.80; N, 5.32. Found: C, 70.70; H, 8.88; N, 5.72.

The acetyl ester of the oxime IIIa (Va) was prepared by allowing 280 mg. of IIIa to stand in 3 ml. of pyridine and 1.5 ml. of acetic anhydride overnight at 5°. The product, which was poured on ice and collected, crystallized from ether-hexane to yield 262 mg. of needles of m.p. 151–153°, $[\alpha]_D^{20}$ +10.5° (chloroform), $\lambda_{max}^{C_2H_5OH}$ 223 mμ (log ϵ, 4.20), 303 mμ (log ϵ, 2.31); $\lambda_{max}^{CHCl_3}$ 5.62 μ (=N—OAc); 5.78 μ (OAc); 6.13, 6.20 μ.

Anal. Calcd. for $C_{33}H_{48}O_6N_2$: C, 69.69; H, 8.51; N, 4.93. Found: C, 69.40; H, 8.38; N, 5.07.

Hydrolysis of the oxime acetate Va. Va (28 mg.) was dissolved in 2 ml. of 90% acetic acid and warmed on the water bath for 30 min. The product (22 mg.) which crystallized from acetone-hexane as plates melted at 201–204° and was identical with respect to melting point, mixture melting point and infrared spectra, with a sample of IIIa. Chromatography of Va over alumina (Woelm, Grade II) also afforded IIIa in good yields.

23-Oximinopseudotomatidine "B" (IIIb). To a solution of 940 mg. of pseudotomatidine "B" in 15 ml. of acetic acid was added dropwise, a solution of sodium nitrite prepared from 1.7 g. of the salt in 5 ml. of water. After standing at room temperature overnight, the solution was poured on ice and made alkaline by addition of aqueous ammonia. The compound, which was crystallized from acetone-hexane, formed plates (845 mg.) and melted at 205–208°, $[\alpha]_D^{20}$ +32° ($CHCl_3$), $\lambda_{max}^{C_2H_5OH}$ 232.5 mμ (log ϵ, 4.08). It exhibits the same principal infrared absorption bands as IIIa.

Anal. Calcd. for $C_{31}H_{45}O_5N_2$: C, 70.42; H, 9.15; N, 5.30. Found: C, 70.54; H, 9.17; N, 5.13.

The acetyl ester of the oxime IIIb (Vb) was prepared from 85 mg. of IIIb in 2 ml. of pyridine and 0.8 ml. of acetic anhydride in the same manner as with the corresponding solasodine series. The compound crystallized from ether-hexane to yield 80 mg. of needles, m.p. 157–159°, $[\alpha]_D^{20}$ +14.5 (chloroform), $\lambda_{max}^{C_2H_5OH}$ 223 mμ (log ϵ, 4.16), 303 mμ (log ϵ, 2.28), $\lambda_{max}^{CHCl_3}$ 5.62 μ (N—OAc); 5.78 μ (OAc), 6.13, 6.20 μ.

Anal. Calcd. for $C_{33}H_{50}O_6N_2$: C, 69.44; H, 8.83; N, 4.91. Found: C, 69.20; H, 8.70; N, 4.75.

The Beckmann rearrangement of IIIa (IVa). (a) To 100 mg. of IIIa in 2 ml. of pyridine was added 120 mg. of *p*-toluenesulfonyl chloride in 3 ml. of pyridine and the mixture was allowed to stand overnight at room temperature. The reaction mixture was poured on ice and the product crystallized from acetone-hexane. Plates (94 mg.) of m.p. 221–224°, $[\alpha]_D^{20}$ +21° (chloroform), $\lambda_{max}^{CHCl_3}$ 2.89 μ (NH); 4.44 μ (C≡N); 5.77 μ (OAc); 5.95 μ (—CONH—) were obtained. An analytical specimen melted at 222–224°.

Anal. Calcd. for $C_{31}H_{46}O_5N_2$: C, 70.69; H, 8.80; N, 5.32. Found: C, 70.88; H. 8.89; N, 5.33.

(b) To a solution of 37 mg. of IIIa in 1.5 ml. of benzene-chloroform mixture (1:1) was added 0.1 ml. of thionyl chloride reagent while the mixture was being cooled in ice. After standing overnight at room temperature, the reaction mixture was poured on ice. Ten milliliters of 1*N* sodium hydroxide was then added and the precipitate extracted with chloroform. The product which crystallized from acetone-hexane, m.p. 221–224°, was identical with IVa obtained by procedure (a). IIIa remained unchanged when allowed to stand overnight in a solution of 2% hydrogen chloride in acetic acid.

Beckmann rearrangement of IIIb (IVb). To a solution of 300 mg. of IIIb in 4 ml. of pyridine was added a solution of 360 mg. of *p*-toluenesulfonyl chloride in 6 ml. of pyridine. The mixture was allowed to stand overnight and poured on ice. The product which crystallized as plates (287 mg.) from acetone-hexane melted at 185–188°. An analytical sample melted at 188–189°, $[\alpha]_D^{20}$ +32.5° (chloroform), $\lambda_{max}^{CHCl_3}$ 2.90 μ (NH); 4.43 μ (C≡N); 5.77 μ (OAc); 5.95 μ (—CONH—).

Anal. Calcd. for $C_{31}H_{48}O_5N_2$: C, 70.42; H, 9.15; N, 5.30. Found: C, 70.24; H, 9.25; N, 5.32.

3β,16β-Dihydroxy-5-bisnorcholenic acid 22→16-lactone (VIIIa). IVa (47 mg.) was refluxed with 10% potassium hydroxide in methanol (20 ml.) for 6 hr. After partial concentration *in vacuo*, water was added and the resulting mixture acidified with 6*N* hydrochloric acid. The product crystallized from aqueous methanol as needles (29 mg.) m.p. 225–227°, $[\alpha]_D^{20}$ −86° (chloroform).

(15) H. Bredereck, A. Wagner, D. Hummel, and H. Kreiselmeier, *Chem. Ber.*, 89, 1532 (1956).

(16) Melting points were taken on the Kofler block and are uncorrected. Microanalyses were performed by the Microanalytical Services Unit of this laboratory under the direction of Mr. Harold G. McCann. The infrared spectra were taken on the Model 21 Perkin-Elmer Infrared Spectrometer by Mr. H. K. Miller and Mrs. A. H. Wright of this Laboratory. "Woelm" alumina grade 1 was used as adsorbent for chromatography unless otherwise stated.

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.51; H, 9.61.

The *acetate* of VIIIa prepared in the usual manner (pyridine–acetic anhydride) afforded needles from acetone-hexane of m.p. 212–215°. It agreed in melting point, mixture melting point, and infrared spectrum, with an authentic specimen of the compound prepared in another manner.[17]

3β,16β-Dihydroxybisnorallocholanic acid 22→16-lactone (VIIIb). The cyanoamide, IVb (100 mg.), was refluxed with 10% potassium hydroxide in methanol (30 ml.) for 6 hr. The product was worked up in the same manner as described above for VIIIa. It crystallized as needles (62 mg.) from aqueous ethanol and melted at 232–236°. Recrystallization raised the m.p. to 235–236°, $[\alpha]_D^{20}$ −43° (chloroform). The melting point, infrared spectra, and rotation agreed with an authentic sample of tigogenin lactone.[14]

23-Oximinosolasodine (VIa). IIIa (360 mg.) was refluxed with 10% potassium hydroxide in methanol (100 ml.) for 7 hr. After removal of the methanol *in vacuo*, water was added and the precipitate collected by centrifugation. The compound crystallized from methanol yielding 256 mg. (85%) of plates m.p. 180–183°, $[\alpha]_D^{20}$ −93° (chloroform), $\lambda_{max}^{C_2H_5OH}$ 231 mμ (log ε, 3.63).

Anal. Calcd. for $C_{27}H_{42}O_3N_2$: C, 73.26; H, 9.56; N, 6.33. Found: C, 73.33; H, 9.67; N, 6.26.

When the compound was recrystallized from acetone-hexane, needles which melted at 194–198° were obtained. If this substance was recrystallized from ethyl alcohol, needles of m.p. 161–164° were formed

Anal. Calcd. for $C_{27}H_{42}O_3N_2 \cdot {}^1/_2C_2H_5OH$: C, 72.22; H, 9.72; N, 6.01. Found: C, 71.90; H, 10.04; N, 5.87.

The compound of m.p. 180–183° was converted into the substance of m.p. 161–164° when recrystallized from ethanol.

23-Oximinotomatidine (VIb). Three hundred milligrams of the oximinopseudo compound IIIb, was refluxed for 7 hr. with 80 ml. of a solution of 10% potassium hydroxide in methanol. The product which crystallized from slightly moist methanol as needles melted at 207–209°, $[\alpha]_D^{20}$ −54° (chloroform), $\lambda_{max}^{C_2H_5OH}$ 231 mμ (log ε, 3.70). The substance is a hydrate as shown by the analyses.

Anal. Calcd. for $C_{27}H_{44}O_3N_2 \cdot H_2O$: C, 70.09; H, 10.02; N, 6.06. Found: C, 70.00; H, 10.16; N, 5.89.

After the compound was dried at 150° for 20 hr. *in vacuo*, the m.p. rose to 234–237°.

Anal. Calcd. for $C_{27}H_{44}O_3N_2$: C, 72.93; H, 9.97; N, 6.30. Found: C, 72.90; H, 10.27; N, 6.60.

Imino nitrile, VIIa. A solution of 180 mg. of VIa in 7 ml. of pyridine and 2 ml. of acetic anhydride was allowed to stand overnight at 5° and poured on ice. The product which crystallized from ether-hexane yielded 152 mg. (80%) of needles, m.p. 145–148°. An analytical sample recrystallized from the same solvent system melted at 147–150°, $[\alpha]_D^{20}$ −6.5° (chloroform), $\lambda_{max}^{CHCl_3}$ 4.55 μ (—C≡N); 5.78 μ (—OAc) 5.88 μ[18] (—C=N—).

Anal. Calcd. for $C_{29}H_{42}O_3N_2$: C, 74.64; N, 9.07; N, 6.00. Found: C, 74.76; H, 9.37; N, 6.20.

Imino nitrile, VIIb. One hundred milligrams of VIb in 1 ml. of acetic anhydride and 3 ml. of pyridine was treated in the same manner as described above for VIIa. The product which was crystallized from hexane yielded 86 mg. of prisms of m.p. 126–128°, $[\alpha]_D^{20}$ +1.7° (chloroform); $\lambda_{max}^{CHCl_3}$ 4.55 μ (C≡N); 5.80 (OAc); 5.88 μ (—C=N—).

Anal. Calcd. for $C_{29}H_{44}O_3N_2$: C, 74.32; H, 9.46; N, 5.98. Found: C, 74.47; H, 9.56; N, 6.17.

3β-Acetoxy-16β-hydroxy-5-bisnorcholenic 22→16-lactone (IXa) *from the imino nitrile*, VIIa. A solution of 65 mg. of VIIa in 10 ml. of 90% acetic acid was refluxed for 30 min. and the solvent removed *in vacuo*. The residue was dissolved in methylene chloride and washed with 1*N* sodium bicarbonate solution. After removal of the solvent, the residue, which crystallized from methanol, yielded 49 mg. IXa, m.p. 208–212°. By recrystallization from acetone-hexane, plates of m.p. 212–215° were obtained. The melting point, mixture melting point, and infrared spectra were identical with that of the specimen prepared from the acetylation of the hydrolysis of the cyanoamide, IVa.

3β-Acetoxy-16β-hydroxybisnorallocholanic 22→16-lactone (IXb) *from the imino nitrile*, VIIb. VIIb (48 mg.) was treated in the same manner as reported above for the preparation of IXa. Needles (35 mg.) of m.p. 210–214° were obtained from aqueous ethanol. Recrystallization from the same solvent raised the m.p. to 216–218°, $[\alpha]_D^{20}$ −48° (chloroform). Its properties (melting point, mixture melting point, infrared spectra, and rotation) were in agreement with an authentic specimen of the acetate of tigogenin lactone.

BETHESDA, MD.

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[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

Spectra of Eschscholtzxanthin and Other Carotenoid Pigments

HAROLD H. STRAIN, MARY R. THOMAS, AND JOSEPH J. KATZ

Received April 6, 1961

The spectra in the visible region and the chromatographic behavior show that the twelve double bonds of eschscholtzxanthin occur in one conjugated system. The infrared spectra indicate that this xanthophyll is a derivative of *sym*-dehydro-β-carotene (dehydroretrocarotene) with a central single bond.

In 1938, eschscholtzxanthin, a remarkably labile dihydroxy carotenoid with twelve all-*trans* double bonds, was isolated from the golden yellow petals of the California poppy.[1] In 1948 Karrer and Jucker[2] proposed that eschscholtzxanthin is a dihydroxy-γ-carotene even though the absorption maxima of γ-carotene occur at wave lengths some 10 mμ shorter than those of the poppy xanthophyll.[1-3] In 1951, Karrer and Leumann[4] postulated

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