

The point of attack by the dienophilic group is at the 4-carbon position in the diene skeleton. Desorption from the catalyst with subsequent ring closure would lead through a cyclic transition state, and with the spontaneous loss of hydrogen, to the final pyridinic product. The preferential formation of 2,4-dimethyl- and 2,4,6-trimethyl-pyridines when isoprene and methylpentadiene were used with acetonitrile can be understood from this viewpoint.

The influence of substituents on the structure and reactivity of nitriles in this reaction with butadiene has been considered.² It was found that the rate was increased in the presence of the catalyst, but that the enhancement was approximately the same for $R = H, CH_3, C_2H_5$ and C_6H_5 in RCN, and of the same order of magnitude as found for acetonitrile and butadiene in the present work. In view of the much greater effects observed with variation in diene structure, this suggests that the catalyst surface has little influence on the polarizability

of the nitrile and acts almost preferentially for the activation of the diene. The effect on the rate when $-E$ substituents are introduced into the nitrile is under investigation.

The thermodynamics of these reactions using benzonitrile and butadiene as a specific example, have been discussed in detail elsewhere.⁴ In the present work an estimate of the free energy change was made for the acetonitrile-methylpentadiene reaction. The method of group increments,^{12,13} taking cognizance where necessary of differences in the symmetry numbers and in the potential barriers restricting internal rotation, was used to calculate the data for methylpentadiene and trimethylpyridine. At 400°, the free energy change for the reaction was found to be -4.1 kcal. The equilibrium space-time yield predicted from this result is 0.24 mole/hr./100 cc. catalyst. The experimental space-time yield (Table II) was 1.9×10^{-2} mole/hr./100 cc., i.e., about 8% of the predicted value for reaction equilibrium.

Acknowledgment.—The support of this work in part by a grant-in-aid from Research Corporation (New York) is gratefully acknowledged. The authors wish to thank Dr. H. F. Herbrandson for stimulating discussions.

(12) D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **55**, 468 (1945).

(13) J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *ibid.*, **56**, 559 (1946).

TROY, NEW YORK

(CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS)

Stereochemistry of the Pyrrolizidine Bases

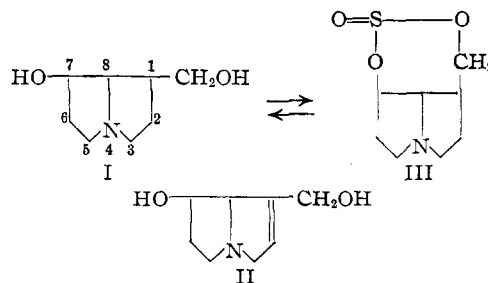
BY ROGER ADAMS AND BENJAMIN L. VAN DUUREN

RECEIVED JULY 16, 1954

Platynecine on treatment with thionyl chloride gives a new three-ring structure containing the sulfite ester group. This substance can be hydrolyzed readily to platynecine. From this and other evidence it may be deduced that the hydroxyl and hydroxymethyl groups in platynecine are both *trans* to the 8-hydrogen atom, that is, *cis* to each other. The diastereoisomer of platynecine, dihydroxyheliotridane, does not form a sulfite ester. Platynecine can be dehydrated with phosphorus oxychloride in benzene to anhydroplatynecine whereas dihydroxyheliotridane does not give the anhydro compound under identical conditions. It is deduced that in dihydroxyheliotridane the C_1-CH_2OH is *trans* to the 8-hydrogen atom, whereas the C_7-OH is *cis* to the 8-hydrogen atom. Since retronecine and heliotridine are reduced to platynecine and dihydroxyheliotridane, respectively, the stereoconfigurations of the former two bases are clarified. The stereochemistry of the necines is discussed on the basis of their relation to retronecine, platynecine, heliotridine and dihydroxyheliotridane.

The alkaloids of the Senecio group are mono- or diesters of the pyrrolizidine bases or necines. The three most common bases are platynecine (I), retronecine and its diastereoisomer heliotridine (II). The structures of these bases have been established beyond doubt.¹

Recently Menshikov and Kuzovkov² reported the preparation of the diastereoisomer of platynecine by the catalytic reduction of heliotridine with Raney nickel and hydrogen as used previously by Adams and Rogers³ for the reduction of retronecine to platynecine. The name dihydroxyhelio-



tridane was suggested for this base.² This report deals with the stereochemistry of these four bases and of the necines related to them.

Konovalova and co-workers^{4,5} found that when

(4) A. Orechov, R. Konovalova and W. Tiedebel, *Ber.*, **68**, 1886 (1935).

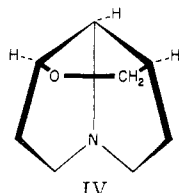
(5) R. Konovalova and A. Orechov, *ibid.*, **69**, 1908 (1936).

(1) N. J. Leonard, "The Alkaloids" (Editors R. H. F. Manske and H. L. Holmes), Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 108.

(2) G. P. Menshikov and A. D. Kuzovkov, *J. Gen. Chem., U.S.S.R.*, **14**, 1702 (1949).

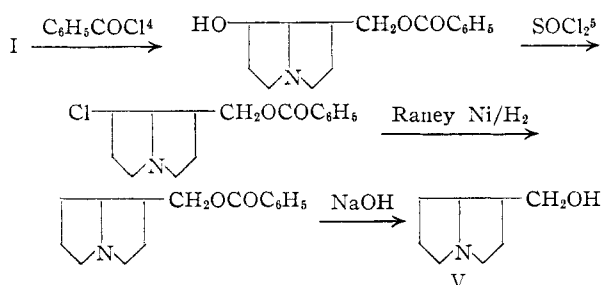
(3) R. Adams and E. F. Rogers, *THIS JOURNAL*, **63**, 537 (1941).

platynecine (I) is treated with a variety of reagents (phosphorus trichloride, phosphorus pentachloride, phosphorus oxychloride, thionyl chloride, sulfuric acid) a molecule of water is lost and a stable ether, anhydroplatynecine, is formed. Leonard and Felley⁶ concluded from a study of scale molecular models that anhydroplatynecine can exist only in the configuration, IV (and its mirror image).



In this structure the 1,7-oxymethylene bridge is *trans* to the 8-hydrogen atom. These authors considered that the reagents for the dehydration would not cause a change in configuration at the C₁-CH₂OH, although inversion of configuration might or might not take place on the C₇-OH, and hence deduced that the C₁-CH₂OH is *trans* to the 8-hydrogen in platynecine.

Platynecine was converted to *l*-isoretronecanol (V) by Adams and Hamlin⁷ by the series of reactions



l-Isoretronecanol was obtained also by Menshikov and Kuzovkov² from dihydroxyheliotridane by using the same method. Since it may also be assumed in these reactions that the conditions used are not likely to affect the C₁-CH₂OH bond it may be concluded that in dihydroxyheliotridane as in platynecine, the C₁-CH₂OH is *trans* to the 8-hydrogen atom. The hydroxyl group at C₇ must have opposite configurations in platynecine and dihydroxyheliotridane.

Dihydroxyheliotridane has not been obtained by the hydrolysis of any alkaloids. Heliotridine, however, is the basic moiety of heliotrine and lasiocarpine, both of which yield monobasic acids on hydrolysis.¹ Retronecine and platynecine occur in nature only in diesters of C₆-, C₈- or C₁₀-dicarboxylic acids.¹ This fact suggests that the orientations of the hydroxyl groups in retronecine and platynecine favor formation of diesters with eleven and twelve-membered rings more than the orientation of the hydroxyls in heliotridine and dihydroxyheliotridane.

It seems likely that in platynecine (I) both the C₁-CH₂OH and the C₇-OH are *trans* to the 8-hydrogen atom, whereas in dihydroxyheliotridane

the C₇-OH is *cis* to the 8-hydrogen and the C₁-CH₂OH *trans* to the 8-hydrogen atom. In other words, in platynecine the C₁-CH₂OH and the C₇-OH groups are *cis* to each other, whereas in dihydroxyheliotridane they are *trans*. The 8-hydrogen atom in all these necines can be in one position only as indicated in structure IV. Experimental support for these views now has been obtained.

After heating platynecine under reflux with phosphorus oxychloride in benzene for two hours anhydroplatynecine can be distilled with steam from the reaction mixture in 20% yield. Dihydroxyheliotridane, on treatment with phosphorus oxychloride under identical conditions did not yield any anhydroplatynecine. It may thus be deduced that in platynecine the two hydroxyls are probably *cis* to each other.

Sulfite esters form readily from 1,2-diols^{8,9} and have also been prepared from 1,3-diols¹⁰ in the strophanthidine series. Platynecine on treatment with thionyl chloride at its boiling point gives a poor yield of dichloroplatynecine and anhydroplatynecine.⁴ In the present investigation platynecine was treated with thionyl chloride at 0° for 30 minutes. A colorless crystalline product was obtained which analyzed correctly for the hydrochloride of platynecine sulfite (III). The infrared absorption spectrum shows a band at 1195 cm.⁻¹, which can be ascribed to the S=O bond.^{8,9} Bands at 925, 955 and 980 cm.⁻¹ are due probably to this structure. There was no absorption in the hydroxyl region, although platynecine shows a strong band in this region.

When this hydrochloride was treated with dilute aqueous sodium hydroxide at room temperature, it dissolved and the water-insoluble oil that separated at first rapidly redissolved. From the aqueous solution, platynecine was obtained. Treatment of platynecine sulfite hydrochloride with dilute aqueous sodium bicarbonate solution in the cold gave an oil from which the free base could not be isolated. However, platynecine sulfite hydrochloride could be converted readily to a crystalline platynecine sulfite picrate.

A Fisher-Taylor-Hirshfelder model of platynecine sulfite indicates that only one such structure can be formed with very little strain, namely, that with the sulfite ester bridge *trans* to the 8-hydrogen atom, VI. The hydrolysis of the sulfite ester with dilute alkali to platynecine excludes the possibility of inversion of configuration during treatment with thionyl chloride and hence indicates that in platynecine the C₁-CH₂OH and C₇-OH groups are *cis* to each other and *trans* to the 8-hydrogen atom, VII. It follows that in dihydroxyheliotridane they are *trans* to each other and since the C₁-CH₂OH is *trans* to the 8-hydrogen atom, the C₇-OH is *cis* to the 8-hydrogen atom, VIII. Since dihydroxyheliotridane and platynecine are obtained by the catalytic reduction of retronecine (IX) and heliotridine (X), respectively, the configurations of all four bases may now be written.

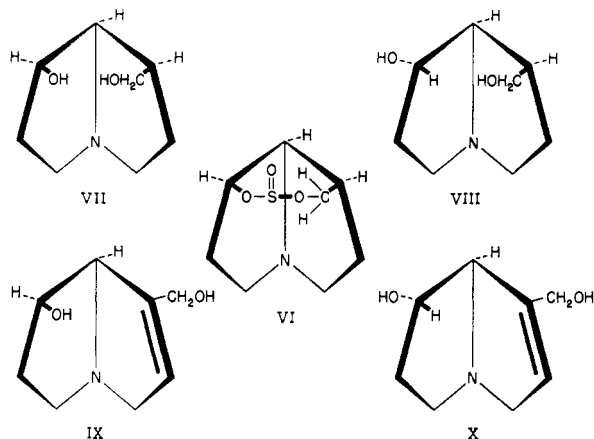
(8) R. Adams, P. R. Shafer and B. H. Braun, *ibid.*, **74**, 5612 (1952).

(9) R. Adams and B. L. Van Duuren, *ibid.*, **75**, 4638 (1953).

(10) C. T. Herzig and M. Ehrenstein, *J. Org. Chem.*, **17**, 724 (1952).

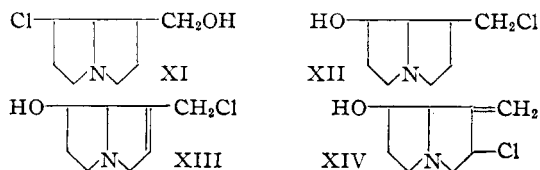
(6) N. J. Leonard and D. L. Felley, *THIS JOURNAL*, **72**, 2537 (1950).

(7) R. Adams and K. E. Hamlin, *ibid.*, **64**, 2597 (1942).



On treatment of dihydroxyheliotridane with thionyl chloride at 0° no sulfite ester was formed, but a new crystalline compound resulted. From the analysis it appears that one hydroxyl has been replaced by chlorine, so that the substance is the hydrochloride of chlorohydroxyheliotridane, namely 1-hydroxymethyl-7-chloropyrrolizidine (XI) or possibly the isomer, 1-chloromethyl-7-hydroxypyrrolizidine (XII). This difference in the reactivity of dihydroxyheliotridane and platynecine toward cold thionyl chloride is most likely due to stereochemical differences. Menshikov and Kuzovkov² reported that when the monobenzoyl derivative of dihydroxyheliotridane is treated with boiling thionyl chloride dehydration takes place at the secondary hydroxyl group.

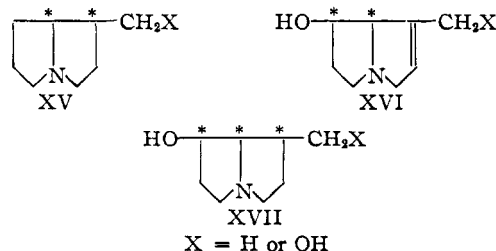
Scale molecular models indicate that the double bond in retronecine forces the two hydroxyl groups away from each other so that a sulfite ester bridge cannot be formed from this molecule. Treatment of retronecine with thionyl chloride at 0° gave a crystalline compound which analysis indicates has one hydroxyl replaced by chlorine. The substance is most likely the hydrochloride of monochlororetronecine (XIII) in which an allylic chloride group is present though a rearranged product XIV is not excluded.



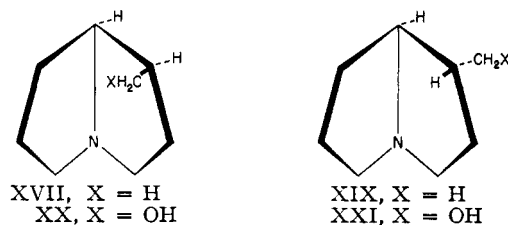
Platynecine and dihydroxyheliotridane may be acetylated readily by boiling under reflux with acetic anhydride for 30 minutes.¹¹ The diacetates could not be obtained crystalline but both gave crystalline picrates. Treatment of the diacetyl derivatives with alkali regenerated the original bases.

In 1-methyl- and 1-hydroxymethylpyrrolizidine (XV) both C₁ and C₈ are asymmetric, and two *dl*-pairs are possible in each. Since platynecine (XVII) has been degraded to *l*-heliotridane⁶ under conditions unlikely to affect the C₁-CH₃ bond,

(11) F. Barger, T. R. Seshadri, H. E. Watt and T. Yabuta [*J. Chem. Soc.*, 11 (1935)] acetylated retronecine by the same method and obtained an oily diacetate from which a crystalline picrate could be obtained.



Leonard and Felley concluded⁶ that the C₁-CH₃ in heliotridane is *trans* to the 8-hydrogen atom XVIII. *dl*-Pseudoheliotridane, the diastereoisomer of heliotridane which was also synthesized by these same investigators,^{6,12} would then be represented by XIX.



All four of the optically active forms of 1-hydroxymethylpyrrolizidine are known. These bases, together with the sources from which they have been obtained are listed in Table I.

TABLE I	
DIASTEREISOMERIC 1-HYDROXYMETHYLPYRROLIZIDINES	
Base	Source
<i>l</i> -Isoretronecanol	Transform. of platynecine ⁷
	Transform. of dihydroxyheliotridane ⁸
<i>d</i> -Isoretronecanol	Hydrol. of alk. lindelofine and lindelofamine ¹³
<i>l</i> -Trachelanthamidine	Hydro. of the alk. trachelanthamine ^{13,14}
<i>d</i> -Trachelanthamidine (Laburnine)	Alkaloid from <i>Cytisus laburnum</i> ¹⁵

Since platynecine has been converted to *l*-isoretronecanol under conditions unlikely to affect the C₁-CH₂OH bond, Leonard and Felley⁶ assigned to isoretronecanol structure XX so that trachelanthamidine can be represented by structure XXI.

The two diastereoisomers of structure XVI (X = OH), *viz.*, retronecine and heliotridane have been discussed already. Desoxyretronecine, obtained by the hydrogenolysis of retronecine esters such as monocrotaline with one mole of hydrogen⁸ (platinum catalyst) can be represented by structure XXII and its diastereoisomer (which has not been synthesized yet or obtained from plants) by structure XXIII.

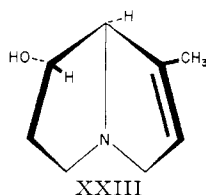
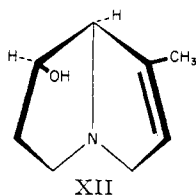
Structure XVII (X = OH) has three asymmetric carbon atoms, and four *dl*-pairs are possible. The optically active forms of two of these are known *viz.*, platynecine (VII) and dihydroxyheliotridane

(12) N. J. Leonard and D. L. Felley, *THIS JOURNAL*, **71**, 1758 (1949).

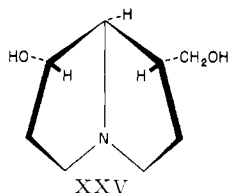
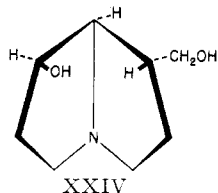
(13) G. P. Menshikov and G. M. Borodina, *J. Gen. Chem. U.S.S.R.*, **15**, 225 (1945).

(14) (a) G. P. Menshikov and G. M. Borodina, *ibid.*, **11**, 209 (1941); (b) G. P. Menshikov, *ibid.*, **16**, 1311 (1946); **17**, 343 (1947).

(15) G. Galinovskiy, H. Goldberger and M. Pöhm, *Monatsh.*, **80**, 550 (1949).

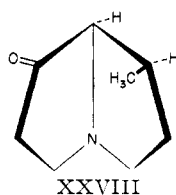
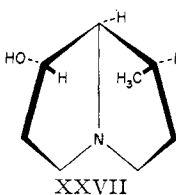
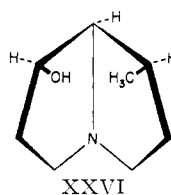


(VIII), discussed above. The other two possible forms are represented by structures XXIV and XXV. In both of these structures the C_1-CH_2OH is *cis* to the 8-hydrogen atom.



It is quite possible that XXIV or/and XXV represent the structural formulas of the bases mikanecine and hastanecine, both of which have the same empirical formula as platynecine and dihydroxyheliotridane. Manske¹⁶ reported that the alkaloid mikanoidine from *Senecio mikanoides* (Walp) Otto yielded on hydrolysis a base, $C_8H_{15}O_2N$, isolated as its picrate. Kononov and Menshikov¹⁷ reported that the alkaloid hastacine, $C_{13}H_{27}O_5N$, obtained from *Cacalia hastata* L., yielded on hydrolysis a new isomeric base, $C_8H_{15}O_2N$, m.p. 113–114°, $[\alpha]_D -9.07^\circ$, for which the name hastanecine was proposed.

Two diastereoisomers of structure XVII (X/H) are known. Retronecanol is obtained by the hydrogenation of desoxyretronecine³ (XXII) or by the hydrogenolysis of monocrotaline with two moles of hydrogen in the presence of Raney nickel catalyst.¹⁸ The diastereoisomer, oxyheliotridane, was obtained by the hydrogenolysis of heliotrine¹⁹ by the same method. It was indicated by Adams and Leonard²⁰ that these reductions are asymmetric. From the methods of preparation it follows that the C_7-OH in retronecanol is *trans* to the 8-hydrogen whereas it is *cis* in oxyheliotridane. Furthermore, since both retronecanol²¹ and oxyheliotridane¹⁹ have been converted to *l*-heliotridane (XVIII) under conditions unlikely to affect the C_1-CH_3 bond, it follows that the C_1-CH_3 group is *trans* to the 8-hydrogen atom in both these structures. Thus retronecanol can be represented by structure XXVI and oxyheliotridane by structure XXVII.



(16) R. H. F. Manske, *Can. J. Research*, **14B**, 6 (1936).

(17) V. S. Kononov and G. P. Menshikov, *J. Gen. Chem., U.S.S.R.*, **15**, 328 (1945).

(18) R. Adams and E. F. Rogers, *THIS JOURNAL*, **61**, 2815 (1935).

(19) G. P. Menshikov, *Ber.*, **68**, 1051 (1935).

(20) R. Adams and N. J. Leonard, *THIS JOURNAL*, **66**, 257 (1944).

(21) R. Adams and E. F. Rogers, *ibid.*, **63**, 228 (1941).

Both retronecanol and oxyheliotridane have been oxidized to the same retronecanone XXVIII under conditions unlikely to affect the C_1-CH_3 bond. Adams and Hamlin⁷ oxidized retronecanol by the Oppenauer method. Menshikov and Kuzovkov² oxidized oxyheliotridane with chromic acid. The other two possible diastereoisomers of XVII (X = H) are not known.

A generous sample of heliotrine was kindly supplied us by Dr. C. C. J. Culvenor, Melbourne University, Australia; for this the authors are much indebted. The bases heliotridine and dihydroxyheliotridane were prepared by the hydrolysis and hydrogenolysis, respectively, of the alkaloid.

Acknowledgment.—The authors wish to thank Mr. J. Nemeth, Mrs. Lucy Chang and Mrs. Esther Fett for the microanalyses, and Miss Helen Miklas for the determination of the infrared absorption spectra.

Experimental

All melting points are corrected.

Heliotridine.—Heliotrine²² was hydrolyzed with barium hydroxide as described by Menshikov. Heliotridine was obtained as colorless plates, m.p. 116–118° (lit.²² m.p. 116.5–118°).

Rotation.—0.0182 g. made up to 1.60 ml. with 95% ethanol at 35° gave $\alpha_D +0.45^\circ$, l 1; $[\alpha]_D^{35} +34.6 \pm 1.0^\circ$ (lit.²² $[\alpha]_D +31^\circ$ (methanol)).

Dihydroxyheliotridane.—Heliotridine was reduced with Raney nickel and hydrogen by the method of Adams and Rogers.³ The product crystallized with difficulty from acetone and always was obtained as oily prisms, m.p. 69–73° (lit.² m.p. 76–77°). The picrate was obtained as yellow needles, m.p. 151–153° (lit.² m.p. 157–158°).

Rotation.—0.1170 g. made up to 10 ml. with 95% ethanol at 35° gave $\alpha_D -0.25^\circ$, l 1; $[\alpha]_D^{35} -21.3 \pm 1.0^\circ$ (lit.³ $[\alpha]_D -34^\circ$).

The product in hand was obviously contaminated with a small amount of impurity which seriously affected its melting point and rotation. The Russian investigators obtained the melting point they reported only by careful purification of the picrate which was then hydrolyzed. Even hydrolysis of the sharply melting diacetoxyheliotridane picrate reported in this communication resulted in a dihydroxyheliotridane which melted about the same as that reported above.

Retronecine.—Monocrotaline was hydrolyzed with barium hydroxide and the base isolated by the usual method,¹⁸ m.p. 121–122° (lit.¹⁸ m.p. 121–122°).

Platynecine.—Retronecine was hydrogenated with Raney nickel catalyst by the method of Adams and Rogers.³ The product was recrystallized from acetone, m.p. 148° (lit.³ m.p. 148–149°).

Dehydration of Platynecine.—One gram of platynecine was suspended in 50 ml. of dry benzene, 0.5 ml. of phosphorus oxychloride added and the mixture boiled under reflux for 2 hours. The solvent and excess reagent were removed under reduced pressure, 25 ml. of 50% aqueous sodium hydroxide added and the anhydroplatynecine steam distilled into 10 ml. of concentrated hydrochloric acid. When the volume of steam distillate had reached 500 ml., no more material distilled over. The steam distillate was taken to dryness under reduced pressure. The residue was dissolved in a minimum of absolute ethanol, an ethereal solution of picric acid added and the precipitated anhydroplatynecine picrate filtered off; 0.50 g. (20%), m.p. 260–265° dec. (lit.^{4,5} m.p. 265–270°). The residue in the steam distillation flask was worked up for unchanged starting

(22) The alkaloid heliotrine as obtained from *Heliotropium europaeum* L. growing in Australia differs in optical rotation from that reported by Menshikov for heliotrine of Russian origin from *Heliotropium lasiocarpum* F. and M. Thus E. M. Trautner and O. E. Neufeld [*Austr. J. Sci.*, **11**, 211 (1949)] reports $[\alpha]_D +49.3^\circ$. G. P. Menshikov [*Ber.*, **68**, 1051 (1935)] reports $[\alpha]_D -75^\circ$. According to Trautner and Neufeld the hydrolysis and hydrogenolysis products of their heliotrine are identical with those from Menshikov's alkaloid.

material. The oily product, 0.38 g., could not be crystallized.

Treatment of Dihydroxyheliotridane with Phosphorus Oxychloride.—One gram of dihydroxyheliotridane was treated with phosphorus oxychloride under conditions exactly identical with those described above for the dehydration of platynecine. No anhydroplatynecine picrate was obtained. From the residue in the distillation flask 0.5 g. of an oil was obtained. No crystalline product could be isolated from this oil.

Platynecine Sulfite Hydrochloride.—Five grams of platynecine was added slowly to 15 ml. of redistilled thionyl chloride at 0°. The mixture was kept at 0° for 30 minutes and the excess thionyl chloride then removed under reduced pressure without heating. The crystalline solid was washed with benzene and dried in a vacuum desiccator over sodium hydroxide for 12 hours. The crude product, 7.50 g. (98.7%), was recrystallized from absolute ethanol; colorless flakes, m.p. 197° dec.

Anal. Calcd. for $C_8H_{13}O_3NS \cdot HCl$: C, 40.08; H, 5.84; N, 5.84; S, 13.36. Found: C, 40.18; H, 6.02; N, 5.74; S, 13.60.

Rotation.—0.0165 g. made up to 1.60 ml. with 95% ethanol at 36° gave $\alpha_D -0.93^\circ$, l 1; $[\alpha]^{36}_D -90.2 \pm 1.0^\circ$.

Platynecine Sulfite Picrate.—The hydrochloride, dissolved in ethanol was treated with ethanolic picric acid. Fine yellow needles separated. The product was recrystallized from absolute ethanol; m.p. 249° dec.

Anal. Calcd. for $C_8H_{13}O_3NS \cdot C_6H_3O_7N_3$: C, 38.88; H, 3.70; N, 12.96. Found: C, 39.16; H, 3.87; N, 13.23.

Alkaline Decomposition of Platynecine Sulfite.—A solution of 0.5 g. of platynecine sulfite hydrochloride in 5 ml. of water was treated with 0.5 g. of sodium hydroxide in 1.0 ml. of water at room temperature. A water-insoluble oil separated and rapidly redissolved. After standing for one hour the solution was taken to dryness under reduced pressure. Anhydrous magnesium sulfate was added and the dry solid extracted repeatedly with acetone. The acetone extract was filtered and evaporated to 10 ml. On standing colorless prisms separated, m.p. 148°. The product gave no depression of melting point on admixture with an authentic sample of platynecine.

Chlorohydroxyheliotridane Hydrochloride (XI or XII).—Dihydroxyheliotridane, 0.5 g., was treated with an excess of thionyl chloride as described above for the preparation of platynecine sulfite hydrochloride. The light-brown oily product was dissolved in absolute ethanol, decolorized with Darco and filtered. On addition of ether to the solution, colorless prisms separated; 0.45 g. (60%). After four crystallizations from ethanol-ether, the product was pure, m.p. 158°.

Anal. Calcd. for $C_8H_{14}ONCl \cdot HCl$: C, 45.28; H, 7.07; N, 6.60. Found: C, 45.17; H, 7.07; N, 6.55.

Rotation.—0.0150 g. made up to 1.90 ml. with 95% ethanol at 36° gave $\alpha_D -0.04^\circ$, l 1; $[\alpha]^{36}_D -5.1 \pm 1.0^\circ$.

Monochlororetronecine Hydrochloride (XIII or XIV).—One gram of retronecine was treated with thionyl chloride as described in the previous experiment. The resinous product was dissolved in absolute ethanol, decolorized with Darco and filtered. On addition of ether, colorless needles separated; 0.75 g. (50%). The product was recrystallized several times from absolute ethanol-ether; m.p. 152–153°.

Anal. Calcd. for $C_8H_{12}ONCl \cdot HCl$: C, 45.71; H, 6.19; N, 6.66. Found: C, 45.63; H, 6.28; N, 6.70.

Rotation.—0.0109 g. made up to 1.60 ml. with 95% ethanol at 36° gave $\alpha_D -0.44^\circ$, l 1; $[\alpha]^{36}_D -64.7 \pm 1.0^\circ$.

Diacetylplatynecine Picrate.—A solution of 0.5 g. of platynecine in 10 ml. of acetic anhydride was boiled under reflux for 30 minutes. The excess acetic anhydride was removed under reduced pressure and the resultant oil dried in a vacuum desiccator. The oil was converted to a picrate by addition of an ethanolic solution of picric acid to the solution of the oil, also in ethanol. Fine yellow needles separated immediately. The picrate was recrystallized from absolute ethanol; m.p. 81°, yield 0.60 g. (40%).

Anal. Calcd. for $C_{12}H_{19}O_4N \cdot C_6H_3O_7N_3$: C, 45.95; H, 4.68; N, 11.89. Found: C, 45.96; H, 4.96; N, 12.19.

Alkaline Hydrolysis of Diacetylplatynecine.—An aqueous solution of 0.50 g. of the picrate described above was acidified with 2 ml. of concentrated hydrochloric acid and extracted with ether. The colorless aqueous solution was made alkaline with 10% aqueous sodium hydroxide and heated on a steam-bath for 3 hours. The solution was then taken nearly to dryness under reduced pressure, anhydrous magnesium sulfate added and the dry solid extracted repeatedly with acetone. The acetone extract was filtered, taken to dryness, 0.15 g. (99%), and recrystallized from dry acetone, m.p. 148°. The product gave no depression of melting point on admixture with an authentic sample of platynecine.

Diacetoxyheliotridane Picrate.—Two grams of dihydroxyheliotridane was acetylated with acetic anhydride in exactly the same manner as described above for platynecine. The oily diacetate was converted to a picrate; 3.80 g. (63%). The product was purified by recrystallization from absolute ethanol; m.p. 133–134°.

Anal. Calcd. for $C_{12}H_{19}O_4N \cdot C_6H_3O_7N_3$: C, 45.95; H, 4.68; N, 11.89. Found: C, 46.15; H, 4.94; N, 11.71.

Alkaline Hydrolysis of Diacetoxyheliotridane.—Three grams of the picrate described above was converted to the hydrochloride and hydrolyzed with alkali as described for diacetylplatynecine. The product crystallized on standing in a vacuum desiccator; 0.95 g. (99.5%), m.p. 69–73°. The substance gave no depression of melting point on admixture with an authentic sample of dihydroxyheliotridane.

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