treated with ethanolic picrolonic acid to give 2.1 g. of yellow crystals, m.p. 213–215° dec. After recrystallization from ethanol, the picrolonate of XVIII was obtained as yellow crystals, m.p. 216–217° dec.

Anal. Calcd. for $C_{29}H_{37}N_5O_7$: C, 61.36; H, 6.57; N, 12.34. Found: C, 61.32; H, 6.28; N, 12.51.

Regeneration of the free base (XVIII) from the picrolonate followed by distillation using a short-path still gave a pale yellow oil, b.p. 150° (10^{-4} mm.), $[\alpha]^{25}$ +126.0°, $\lambda_{C=O}$ 5.85 μ.

Anal. Calcd. for $C_{19}H_{29}NO_2$: C, 75.20; H, 9.63; N, 4.62 $-OCH_3$, 10.23. Found: C, 75.21; H, 9.40; N, 4.51; $-OCH_3$ 10.35.

The Absolute Configurations of the Erythrina Alkaloids[1]

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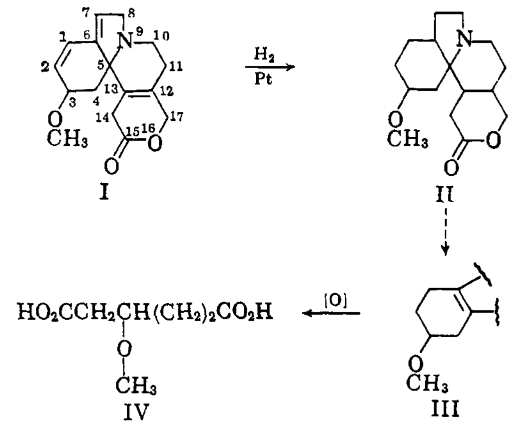
A degradation of β-erythroidine has been accomplished which allows a correlation between the absolute configuration of the asymmetric atom at C-3 of β-erythroidine and the levorotatory (3*S*)-3-methoxyadipic acid. This combined with other available data allows the assignment of the absolute configuration of β-erythroidine as 3*R*,5*S*. Further, the implications of these results with respect to the other erythrina alkaloids are discussed and absolute configurational assignments are made for these as well.

Although the erythrina alkaloids have been subjected to extensive degradative and synthetic investigations,[5] the relative and absolute configurations of these alkaloids have largely remained as important problems to be settled. In attempting to resolve these questions, we have approached the over-all problem from two points of view. First, the configurational relationships existing among the various erythrina alkaloids have been studied.[1] Secondly, we have undertaken the determination of the absolute configuration of one of the asymmetric atoms of one of the key alkaloids. The combination of data would thus allow complete configurational assignments for all the important erythrina alkaloids. The present communication presents the details of the accomplishment of these objectives.[6]

Of the asymmetric atoms present in the various erythrina alkaloids the most feasible one from the point of view of degradation and ease of correlation with a molecule of known absolute configuration appeared to be the asymmetric carbon at C-3 of β-erythroidine (I). From previous studies,[7,8] it was known that the spiro amine nitrogen is readily removed through a series of Hofmann degradations and by starting with tetrahydro-β-erythroidine (II) such a degradation might yield a derivative having the general features shown by III. Oxidation of III could then yield optically active β-methoxyadipic acid (IV) for which the absolute configuration of each enantiomorph is known[9] because of its role in the elucidation of the absolute configuration of steroids.[10,11]



Preliminary studies on the Hofmann degradation of tetrahydro-β-erythroidine (II), however, led to a mixture of products indicating that, in part, opening of the lactone ring was occurring followed by decarboxylation. To circumvent this the corresponding diol (V) was employed, but in this case the Hofmann reaction was accompanied by some dehydration, leading again to a mixture of products. Treatment of the diol V with phosphoric acid readily converted it to the dihydropyran derivative VI and this now underwent the Hofmann reaction smoothly and cleanly to give VII. The formation of VII being favored in the first step of the Hofmann reaction could be predicted by analogy to the behavior of tetrahydroerythraline[12] as well as from theoretical considerations.[13] The spectral properties of VII are in full accord with this assignment. In the infrared the characteristic absorption bands of a vinyl group are present at 900–915 and at 1000 cm.$^{-1}$. These disappear on hydrogenation. The ultraviolet absorption spectrum of VII has a broad maximum at 238 mμ (log ϵ 3.97) as would be expected.[14] Finally the n.m.r. spectrum of VII shows a clear quartet at τ 2.64 corresponding to the lone internal vinyl hydrogen and a pair of doublets centered at τ 5.07 corresponding to the terminal methylene protons. The approximate coupling constants for the *cis* and *trans* protons are 10.0 and 16.4 c.p.s.

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[1] Paper XIX in this series. For the preceding communication, see V. Boekelheide and M. Chang, *J. Org. Chem.*, **29**, 1303 (1964).

[2] University of Oregon, Eugene, Ore.

[3] Abstracted from the Ph.D. thesis of G. R. Wenzinger, University of Rochester, 1960.

[4] Research fellowship grants from Chas. Pfizer and Co., E. I. du Pont de Nemours, the Sherman Clarke Fund, the Elon Huntington Hooker Fund, and the National Science Foundation are gratefully acknowledged.

[5] For a summary of the chemistry of the erythrina alkaloids, see R. H. F. Manske, "The Alkaloids," Vol. VII, Academic Press, New York, N. Y., 1960, Chapter 11.

[6] For preliminary accounts, see G. R. Wenzinger and V. Boekelheide, *Proc. Chem. Soc.*, 53 (1963), and A. W. Hanson, *ibid.*, 52 (1963).

[7] V. Boekelheide and E. J. Agnello, *J. Am. Chem. Soc.*, **73**, 2286 (1951).

[8] J. Weinstock and V. Boekelheide, *ibid.*, **75**, 2546 (1954).

[9] M. Viscontini and P. Miglioretto, *Helv. Chim. Acta*, **38**, 930 (1955).

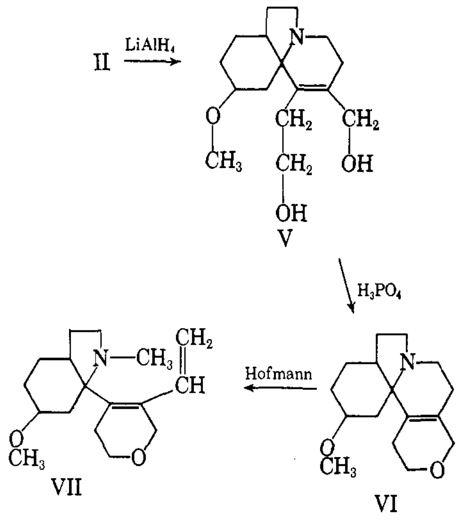
[10] S. Bergstrom, A. Lardon, and T. Reichstein, *ibid.*, **32**, 2 (1949).

[11] K. Brenneisen, Ch. Tamm, and T. Reichstein, *ibid.*, **39**, 1233 (1956).

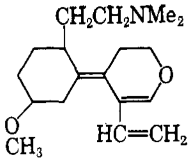
[12] G. W. Kenner, G. H. Khorana, and V. Prelog, *ibid.*, **34**, 1969 (1951).

[13] A. C. Cope and E. E. Schweizer, *J. Am. Chem. Soc.*, **81**, 4577 (1959); *cf.* D. V. Banthorpe, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 4054 (1960), and references cited therein.

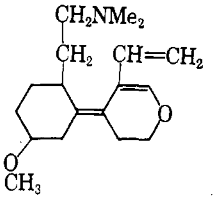
[14] R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).



The second step in the Hofmann degradation occurred smoothly with VII but did not lead to the desired introduction of a second vinyl group. Instead a mixture of two components resulted and these have been assigned structures VIIIa and VIIIb. This assignment was first deduced on a spectral basis. In the ultraviolet, the mixture of VIIIa and VIIIb showed a broad absorption maximum at 260 mμ (log ϵ 4.0), indicating a lengthening of the conjugated system. That the additional conjugation was due to an enol ether grouping was suggested by intense absorption in the infrared at 1588 cm.$^{-1}$.[15,16] In confirmation of this VIII was readily hydrolyzed by dilute acid to give a mixture of carbonyl compounds. Although the Hofmann decomposition to give the mixture of VIIIa and VIIIb was not anticipated, it is readily understandable simply as a vinylogous Hofmann reaction. Several eliminations of this type have been noted recently.[17-19]



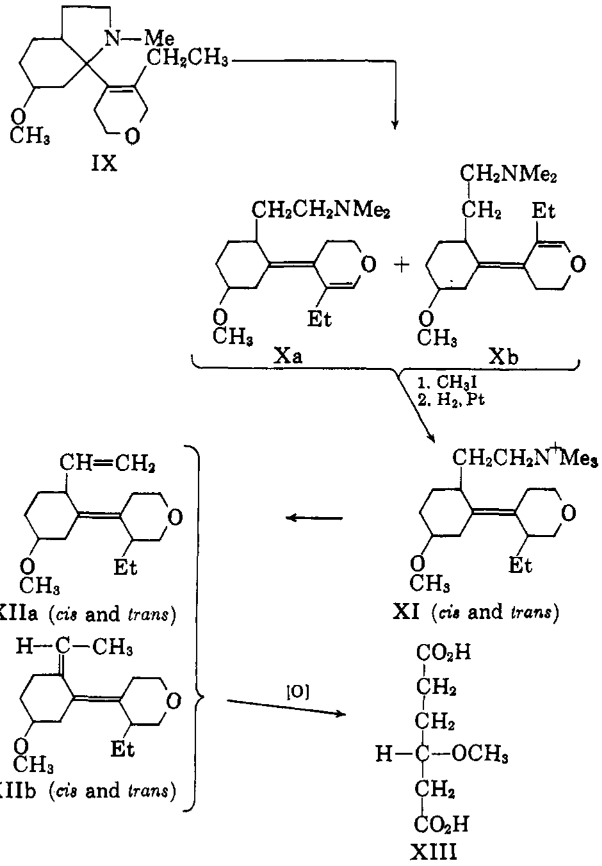
VIIIa



VIIIb

In the hope of altering the course of this Hofmann elimination, VII was first hydrogenated to give IX and then subjected to the Hofmann decomposition. But again, the product proved to be a mixture (Xa and Xb) in which the presence of the enol ether grouping was easily demonstrated. In the n.m.r., there was a signal for the single vinyl proton (τ 3.94) as well as appropriate signals for the other relevant features—the ethyl side chain (triplet, τ 9.09), the methoxyl (singlet, τ 6.72), and the dimethylamino group (6 protons, τ 7.82). The ultraviolet absorption spectrum was essentially the same as that for the mixture of VIIIa and VIIIb. A further Hofmann elimination of X gave products which were apparently aromatic. To avoid this, hydrogenation of X was carried out. The difference in rate of reduction of the tri- and tetrasubstituted double bonds is sufficiently large to allow a clean reduction of only the trisubstituted double bond. The resulting mixture was transparent in the ultraviolet and its other spectral characteristics were in keeping with structure XI. A final Hofmann degradation of XI then yielded trimethylamine and a mixture of hydrocarbons (XIIa and XIIb). The spectral characteristics of this mixture showed the presence of both the vinyl and ethylidene groups and, based on their integrated areas in the n.m.r. spectrum, the ratio of XIIa to XIIb is about 65:35. On hydrogenation XII absorbed 1 mole of hydrogen, transforming the vinyl and ethylidene side chains to a common ethyl group and causing the loss of the broad maximum at 240 mμ of the diene system. (See Scheme I.)

SCHEME I



Various attempts to separate the mixture of hydrocarbons represented by XIIa and XIIb, including vapor phase chromatography, were unsuccessful. Therefore, methods of oxidizing the mixture which would lead directly to β-methoxyadipic acid were explored. The most feasible proved to be direct oxidation with acid permanganate. The resulting mixture of acids was separated by countercurrent distribution and the fraction identified as β-methoxyadipic acid was isolated as the crystalline (*S*)-benzylthiuronium salt. The infrared solution spectrum of this derivative was shown to be essentially superimposable with that of an authentic specimen of the (*S*)-benzylthiuronium salt of β-methoxyadipic acid. Although the rotation of our sample from the degradation was low, it was definitely levorotatory and establishes the acid to be (3*S*)-3-

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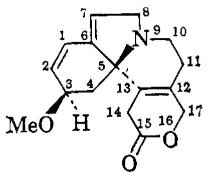
[15] G. D. Meakens, *J. Chem. Soc.*, 4170 (1953).

[16] W. H. T. Davidson and G. R. Bates, *ibid.*, 697 (1960).

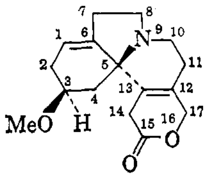
[17] H. E. Winberg, F. S. Fawcett, W. E. Mochel, and G. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

[18] L. A. Errede, *ibid.*, **83**, 949 (1961).

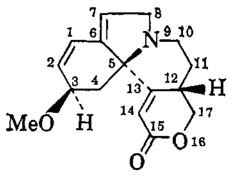
[19] W. von Philipsborn, H. Schmid, and P. Karrer, *Helv. Chim. Acta*, **38**, 1067 (1955).



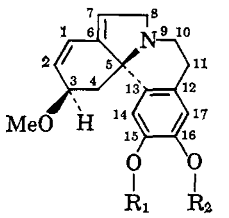
(3*R*,5*S*)-β-Erythroidine



(3*R*,5*S*)-Dihydro-β-erythroidine



(3*R*,5*S*,12*S*)-α-Erythroidine



3*R*,5*S* aromatic erythrina alkaloids
Erysopine, $R_1 = R_2 = -H$
Erythraline, $R_1 = R_2 = -CH_2-$
Erysodine, R_1 or $R_2 = -H$
Erysovine, R_1 or $R_2 = -CH_3$

methoxyadipic acid. This in turn establishes the asymmetric carbon at C-3 in β-erythroidine as having the absolute *R* configuration.

It is possible by a series of logical arguments to deduce the configuration of the spiro carbon at C-5 relative to C-3.[20a] This then leads to the complete assignment of absolute configuration as (3*R*,5*S*)-β-erythroidine. Fortunately, this matter has now been settled beyond question by the recent X-ray crystallographic investigation of dihydro-β-erythroidine hydrobromide by Hanson.[6] These studies established the. relative configuration of dihydro-β-erythroidine to be as shown and as predicted for β-erythroidine. In addition Hanson was able to establish the absolute configuration as well and these are 3*R* and 5*S* in verification of the conclusions of the present chemical study.

Although the well-established methods of X-ray crystallography and chemical interrelationship of configuration leave no doubt that the absolute configuration of β-erythroidine is 3*R*,5*S*, Weiss and Ziffer have recently proposed the opposite absolute configuration for β-erythroidine based on arguments from optical rotatory dispersion measurements.[20b] These arguments assume a definable connection between the sign of the Cotton effect and the chirality of the transoid diene chromophore, neglecting contributions from the C-3 and C-5 asymmetric carbons. Although the reasons for the discrepancy in applying the chirality rule to β-erythroidine are not clear, it is apparent that their choice of compounds was unfortunate. Application of their arguments to the corresponding triene, desmethoxy-β-erythroidine, gives an opposite result from that of β-erythroidine. Thus, as we have shown,[1] the sign of the Cotton effect for desmethoxy-β-erythroidine is negative and the deduction using Weiss and Ziffer's arguments about the chirality of the triene lead to an assignment of absolute configuration for desmethoxy-β-erythroidine of 5*S* which then is in agreement with the findings from X-ray crystallography and our present chemical evidence.

It is of interest that the results of the X-ray study also fix the position of the double bond in dihydro-β-erythroidine as being between C-1–C-6 rather than C-6–C-7. In the past there had not been an adequate basis for deciding between these two possibilities although the assignment made to dihydro-β-erythroidine[21] proves to have been correct. The assignments made to the dihydro derivatives in the aromatic series[22,23] probably need to be re-evaluated.

The conversion of α-erythroidine to β-erythroidine establishes that both have the same configuration at C-3 and C-5.[24] Recently, Hill and Schearer have related (+)-O-ethylphenyl 3-tetrahydrofuryl ketone, a degradation product of α-erythroidine,[25] to (+)-methylsuccinic acid.[26] This allows the deduction that C-12 in α-erythroidine has the absolute *S* configuration and allows the formulation of the whole molecule as shown.

In the case of the aromatic erythrina alkaloids, the relative configurations at C-3 and C-5 have been established by chemical interrelationship,[5,23] by X-ray crystallography,[27] and by synthesis.[28] However, the absolute configurations have not been known. In view of the determination of the absolute configuration of the erythroidines and the evidence in the accompanying paper that the configuration at C-5 is the same for both the erythroidines and the aromatic erythrina alkaloids, a total assignment of configuration of the aromatic series can be given as shown. The extension of assignments of absolute configuration from these to the other aromatic erythrina alkaloids is obvious from existing data[5] and requires no further comment.

Experimental[29]

Tetrahydro-β-erythroidinol (V).—A solution of 28.4 g. of tetrahydro-β-erythroidine[21] in a minimum amount of ether was added dropwise to a stirred suspension of 5.75 g. of lithium aluminum hydride in 1.5 l. of anhydrous ether. When addition was complete, the mixture was boiled under reflux for 3 hr. and then stirred at room temperature overnight. The complex was decomposed by the careful addition of a saturated solution of sodium sulfate, causing the separation of a granular precipitate. After removal of the precipitate and concentration of the ether solution, the residual oil was distilled to give 20.7 g. (73%) of a viscous yellow oil, b.p. 180° (0.1 mm.).

Anal. Calcd. for $C_{16}H_{27}NO_3$: C, 68.29; H, 9.67. Found: C, 68.45; H, 9.95.

Anhydrotetrahydro-β-erythroidinol (VI).—A solution of 18.8 g. of tetrahydro-β-erythroidinol (V) in 130 ml. of 85% phosphoric acid was heated under an atmosphere of nitrogen at 115° for 7.5 hr. The mixture was then cooled and poured onto ice giving a total volume of about 300 ml. The phosphoric acid was neutralized with potassium carbonate and the oil that separated was

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[20] (a) M. Y. Chang, Ph.D. thesis, University of Rochester, 1959; (b) U. Weiss and H. Ziffer, *Experientia*, **19**, 108 (1963). In their paper, Weiss and Ziffer assign β-erythroidine the 5*S* configuration but it is evident that this is the result of a mistake in their use of the Cahn-Ingold-Prelog convention and the logic of their argument as well as their illustration is for a 5*R* assignment.

[21] V. Boekelheide, J. Weinstock, M. F. Grundon, G. L. Sauvage, and E. J. Agnello, *J. Am. Chem. Soc.*, **75**, 2550 (1953).

[22] M. Carmack, B. C. McKusick, and V. Prelog, *Helv. Chim. Acta*, **34**, 1601 (1951).

[23] V. Prelog, *Angew. Chem.*, **69**, 33 (1957).

[24] V. Boekelheide and G. C. Morrison, *J. Am. Chem. Soc.*, **80**, 3905 (1958).

[25] J. C. Godfrey, D. S. Tarbell, and V. Boekelheide, *ibid.*, **77**, 3342 (1955).

[26] R. K. Hill and W. R. Schearer, *J. Org. Chem.*, **27**, 921 (1962).

[27] W. Nowacki and G. F. Bonsma, *Z. Kryst.*, **110**, 89 (1958).

[28] V. Prelog, A. Langemann, O. Rodig, and M. Ternbah, *Helv. Chim. Acta*, **42**, 1301 (1959).

[29] Microanalyses were by F. Pascher, W. Man ser, and Micro-Tech Laboratories.

extracted with ether. The ether solution, after washing with water and drying, was concentrated; the residual oil was distilled to give 14.5 g. (84%) of a nearly colorless oil, b.p. 115° (10^{-4} mm.).

Anal. Calcd. for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32. Found: C, 72.88; H, 9.64; N, 5.12.

The **picrate** of **VI** formed readily in ethanol and, after recrystallization from the same solvent, melted at 215° dec.

Anal. Calcd. for $C_{22}H_{27}N_4O_9$: C, 53.65; H, 5.73; N, 11.38. Found: C, 53.63; H, 5.69; N, 11.12.

Anhydrotetrahydro-β-erythroidinol Methotetraphenylborate.—A solution of 200 mg. of VI in 15 ml. of methanol was treated with 10 ml. of methyl iodide. The mixture was allowed to stand under nitrogen for 12 hr. Removal of the methanol gave a glass which could not be induced to crystallize. Treatment of the glass with sodium tetraphenylborate following the procedure of Crane[30] yielded a solid which, after recrystallization from an acetone–methanol mixture, gave white crystals, m.p. 215–219°.

Anal. Calcd. for $C_{41}H_{48}BNO_2$: C, 82.40; H, 8.09; N, 2.34. Found: C, 82.64; H, 7.95; N, 2.64.

Des-N-methylanhydrotetrahydro-β-erythroidinol (**VII**).—To a solution of 12.0 g. of VI in 50 ml. of anhydrous methanol there was added 70 ml. of methyl iodide and the mixture was allowed to stand overnight under nitrogen. Removal of the solvent followed by two washings with ether and decantation left a glass which was dissolved in methanol and passed over an ion-exchange column (Dowex-2, OH^-). The methanol eluate was concentrated and the residual oil was distilled using a short-path still. The Hofmann decomposition began at 120° and the pressure was gradually lowered leading to distillation at 10^{-4} mm. There was collected 10.84 g. of a colorless oil.

Anal. Calcd. for $C_{17}H_{27}NO_2$: C, 73.60; H, 9.81; N, 5.05. Found: C, 73.64; H, 9.75; N, 5.58.

The **picrate** of **VII** was prepared in ethanol and, after recrystallization from the same solvent, gave yellow crystals, m.p. 155–157°.

Anal. Calcd. for $C_{23}H_{30}N_4O_9$: C, 54.54; H, 5.97; N, 11.06. Found: C, 54.61; H, 5.98; N, 11.03.

The **styphnate** of **VII** was formed in ethanol and, after recrystallization from the same solvent, melted at 135–137°.

Anal. Calcd. for $C_{23}H_{30}N_4O_{10}$: C, 52.87; H, 5.79; N, 10.72. Found: C, 52.84; H, 5.75; N, 10.76.

Des-N-methylanhydrotetrahydro-β-erythroidinol Methotetraphenylborate.—The methotetraphenylborate of VII was prepared in the same manner as that described for the methotetraphenylborate of VI. After recrystallization from an acetone–methanol mixture, it gave white crystals, m.p. 180–182°.

Anal. Calcd. for $C_{42}H_{50}BNO_2$: C, 82.35; H, 8.25; N, 2.29. Found: C, 82.25; H, 8.25; N, 2.62.

Des-N,N-dimethylanhydrotetrahydro-β-erythroidinol (**VIIIa and VIIIb**).—A solution of 4.51 g. of VII in 20 ml. of methanol was treated with 20 ml. of methyl iodide and allowed to stand under a nitrogen atmosphere for 12 hr. Removal of solvent followed by washing with ether left a glass which was dissolved in methanol and passed over an ion-exchange column (Dowex-2, OH^-). Concentration of the methanol eluate followed by distillation of the residue gave 4.1 g. (86%) of a nearly colorless oil, b.p. 120° (10^{-4} mm.).

Anal. Calcd. for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 73.84; H, 9.75; N, 4.80.

Microhydrogenation of the mixture of VIIIa and VIIIb showed a rapid uptake of 1 mole of hydrogen followed by slower uptake of a further 1.4 moles.

Des-N-methylanhydrohexahydro-β-erythroidinol (**IX**).—A solution of 822 mg. of VII in 25 ml. of ethanol containing 200 mg. of a pre-reduced Raney nickel catalyst was subjected to hydrogenation at room temperature and atmospheric pressure. There was a rapid uptake of hydrogen corresponding to 90% of theoretical for 1 mole. After removal of the catalyst, the ethanol solution was treated directly with picric acid to give, after recrystallization from ethanol, 800 mg. of yellow crystals, m.p. 173–175°.

Anal. Calcd. for $C_{23}H_{32}N_4O_9$: C, 54.32; H, 6.34; N, 11.02. Found: C, 54.23; H, 6.56; N, 10.47.

Des-N,N-dimethylanhydrohexahydro-β-erythroidinol (**Xa and Xb**).—A solution of 11.0 g. of IX (regenerated from the picrate) in 30 ml. of methanol was treated with 60 ml. of methyl iodide and the mixture was allowed to stand overnight under a nitrogen atmosphere. After removal of the solvent, the glassy methiodide was washed twice with ether, dissolved in methanol, and passed over an ion-exchange column (Dowex-2, OH^-). The methanol eluate was concentrated and the residual oil was subjected to thermal decomposition using a short-path still. There was collected 10.2 g. (87%) of a nearly colorless oil, b.p. 110–130° (10^{-4} mm.). Microhydrogenation of this oil over Raney nickel showed the uptake of 99% of theoretical for 1 mole of hydrogen.

Anal. Calcd. for $C_{18}H_{31}NO_2$: C, 73.67; H, 10.65. Found: C, 73.62; H, 10.65.

Desazaanhydrooctahydro-β-erythroidinol (**XIIa and XIIb**).—A solution of 11.1 g. of the mixture of Xa and Xb in 30 ml. of methanol was treated with 60 ml. of methyl iodide and allowed to stand overnight under nitrogen. The mixture was concentrated, washed twice with ether, and then redissolved in 50 ml. of methanol. To the solution was then added 30 mg. of Adams catalyst and it was subjected to hydrogenation at room temperature and atmospheric pressure until 1 mole of hydrogen was absorbed. The catalyst was removed and the solution was passed over an ion-exchange column (Dowex-2, OH^-). Concentration of the eluate followed by distillation of the residue using a short-path still gave 7.9 g. (86%) of a colorless oil, b.p. 100–120° (10^{-4} mm.), λ_{max} 240 mμ (log ε 3.91). Microhydrogenation over Adams catalyst gave an uptake of hydrogen corresponding to 96% of theoretical for one double bond. The hydrogenation product was transparent in the ultraviolet and showed no vinyl hydrogens in the n.m.r.

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.90; H, 10.59.

Permanganate Oxidation of Desazaanhydrooctahydro-β-erythroidinol (XIIa and XIIb) to Give (3*S*)-3-Methoxyadipic Acid.—A solution of 4.0 g. of the mixture of XIIa and XIIb in 30 ml. of *t*-butyl alcohol was diluted with 40 ml. of water and then cooled to 0°. To this was added dropwise with stirring a solution of 4.0 g. of potassium permanganate in a minimum amount of water. The addition required about 2 hr. The manganese dioxide formed was destroyed by adding concentrated sulfuric acid until the pH was below 7 followed by careful addition of solid sodium bisulfite. The resulting clear solution was concentrated to 150 ml. and then acidified by addition of 30 ml. of glacial acetic acid and 10 ml. of concentrated sulfuric acid. This solution was then cooled to 0° and treated with 10 g. of potassium permanganate over a period of 1.5 hr. with stirring. The manganese dioxide was destroyed by adding sodium bisulfite while the solution was maintained at 0°. The resulting solution was evaporated at room temperature until dry. The solid residue was extracted with five 100-ml. portions of ether. The ether extracts were filtered and then concentrated to give 1.88 g. of a brown oil. The separation of the resulting mixture of acids was carried out by countercurrent distribution using the buffer system of Bergstrom, *et al.*[10] From a forty-tube distribution, tubes 10–19 were found to contain β-methoxyadipic acid, as identified by paper chromatography. The aqueous phase in these tubes was saturated with sodium sulfate and the ether layers were combined. Concentration of the ether gave 580 mg. of an oil. This was converted to the barium salt following Bergstrom, *et al.*,[10] and the barium salt was then treated with (*S*)-benzylthiuronium sulfate. The resulting sticky product was recrystallized three times from acetone containing a drop of methanol to give 45 mg. of crystals, m.p. 136–141°, $[\alpha]^{20}D$ −0.64 ± 0.25° (58 mg. in 0.747 ml. of methanol).[31]

The infrared spectrum of these crystals in chloroform was essentially identical with that of a similar spectrum of an authentic specimen of the (*S*)-benzylthiuronium derivative of racemic 3-methoxyadipic acid.

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(30) F. J. Crane, *Anal. Chem.*, **28**, 1794 (1956).

(31) The pure (*S*)-benzylthiuronium derivative of (−)-3-methoxyadipic acid shows a rotation, $[\alpha]^{18}D$ −1.1 ± 0.3 (*c* 0.5, methanol).