[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Structure of Monocrotaline. XV

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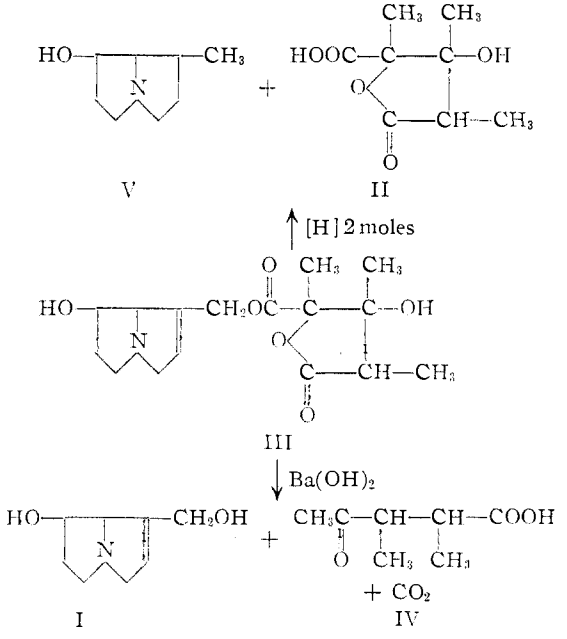
RECEIVED JULY 18, 1952

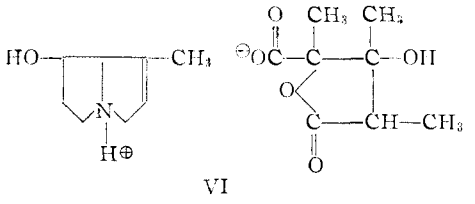
It is shown that the alkaloid monocrotaline has two ester groups but no five-membered lactone ring and that the two free hydroxyl groups are vicinal and alpha–beta to the carboxyl group which is joined to the nucleus through an allylic ester link. These facts, taken with the previously demonstrated structures of retronecine and monocrotalic acid, establish the proposed bridged ring diester structure (VII) for monocrotaline.

The establishment of the structures of the two moieties derived from the alkaloid monocrotaline by degradation; namely, retronecine[1] (I) and monocrotalic acid[2] (II), led to the deduction that the alkaloid must have the lactone ester structure (III).[2b] Retronecine (I) is obtained from the alkaloid by alkaline hydrolysis with concomitant degradation of the monocrotalic acid to monocrotic acid (IV) (α,β-dimethyllevulinic acid). Monocrotalic acid is produced when the alkaloid is



reduced catalytically with two moles of hydrogen; one molecule is consumed for hydrogenolysis of the allyl ester link and the second for reduction of the double bond in the retronecine with the formation of retronecanol (V), the other product of the reaction. Similarly, when monocrotaline was quantitatively hydrogenolyzed at room temperature and atmospheric pressure over 6% palladium-on-strontium carbonate, only one molecule of hydrogen was absorbed and the product was the salt (VI) of desoxyretronecine and monocrotalic acid. This experiment tended to confirm the structure (III) previously proposed for the alkaloid.

The infrared spectrum of monocrotaline, however, has only a single broad ester carbonyl band at 1725 cm.$^{-1}$ with a shoulder at 1737 cm.$^{-1}$ and does not have any band in the five-membered lactone carbonyl region from 1760 to 1800 cm.$^{-1}$. The methyl ester of monocrotalic acid, the simplest analog of the lactone ester structure (III), has a lactone carbonyl band at 1780 cm.$^{-1}$ and an ester carbonyl band at 1705 cm.$^{-1}$ in nujol mull or 1733 cm.$^{-1}$ in chloroform solution. The salt VI has a lactone carbonyl band at 1764 cm.$^{-1}$, a carboxyl (zwitterion) band at 1613 cm.$^{-1}$, but no normal ester carbonyl absorption. The infrared spectrum of monocrotaline could be more satisfactorily explained if the structure of the alkaloid were represented as a bridged ring diester structure (VII), characteristic of the *Senecio* alkaloids derived from retronecine.[3] Chemical evidence has now been supplied which indicates that such a structure is correct and that the previously proposed formula (III) should be rejected.



VI

Monocrotaline reacts rapidly and exothermally with thionyl chloride to evolve hydrogen chloride and affords a crystalline compound in essentially quantitative yield. This reaction is summarized in the scheme

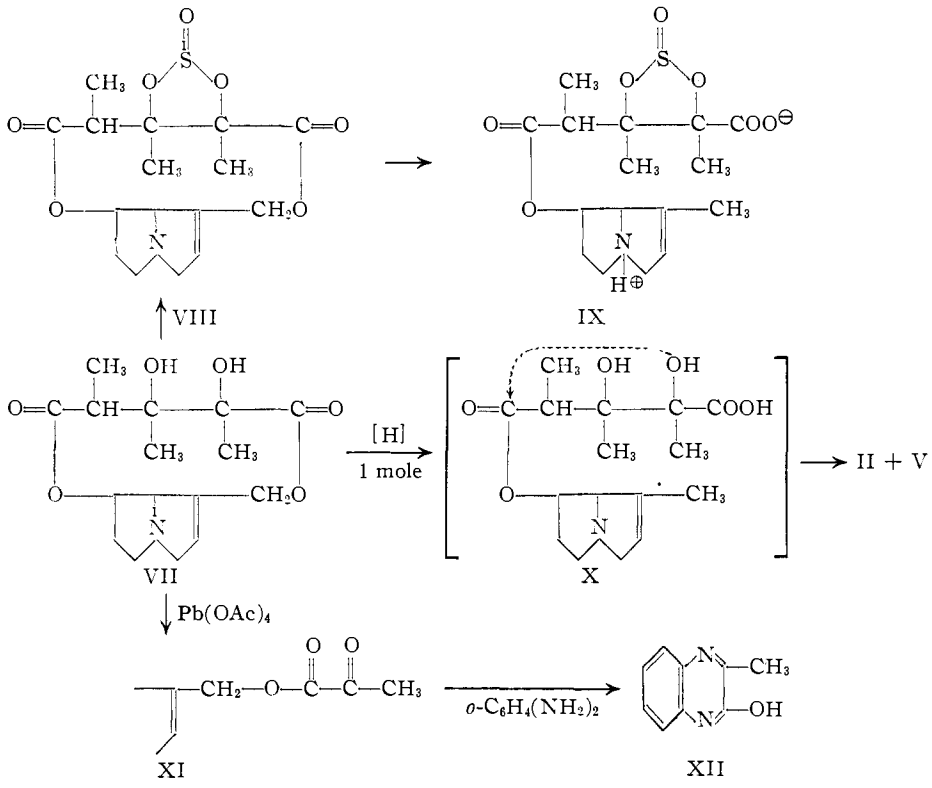
$$C_{16}H_{23}NO_6 + SOCl_2 \longrightarrow \underset{\text{VIII}}{C_{16}H_{21}NO_7S\cdot HCl} + HCl$$

The product is clearly an amine hydrochloride since it is water soluble, gives an immediate precipitate with aqueous silver nitrate, and is converted to the water-insoluble free base, $C_{16}H_{21}NO_7S$ (VIII) when treated with one equivalent of cold aqueous sodium hydroxide. The infrared spectrum of the hydrochloride has an ester carbonyl band at 1740 cm.$^{-1}$ with a shoulder at 1747 cm.$^{-1}$ while that of the free base has two peaks, one at 1728 cm.$^{-1}$ and the other at 1738 cm.$^{-1}$. Neither compound gives any absorption in the five-membered lactone carbonyl region or in the hydroxyl stretching region from 3100 to 3700 cm.$^{-1}$. Monocrotaline shows one hydroxyl band at 3540 cm.$^{-1}$ (shoulder, 3580 cm.$^{-1}$). The absence of hydroxyl bands in these derivatives of monocrotaline suggests that the two free hydroxyl groups known to have originally been

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

(2) (a) R. Adams and T. R. Govindachari, *ibid.*, **72**, 158 (1950); (b) R. Adams and F. B. Hauserman, *ibid.*, **74**, 694 (1952); (c) R. Adams, B. L. van Duuren and B. H. Braun, *ibid.*, **74**, 5608 (1952).

(3) Although the two –COO– linkages in monocrotaline (VII) and its sulfite derivative (VIII) are by definition actually lactones, they are present in an eleven-membered ring containing the pyrrolizidine nucleus in which the fused rings are angular in form. Such linkages were expected to exhibit absorption similar to normal ester linkages and the facts have verified this postulation. They are therefore for the purposes of the discussion that follows called *ester* linkages.



present are incorporated in a cyclic sulfite ester. Examination of some typical cyclic sulfite esters derived from vicinal glycols[3a] has led to the tentative assignment of a band in the 1200 to 1230 cm.$^{-1}$ region to the sulfur–oxygen double bond.[4] Monocrotaline sulfite hydrochloride has a strong band at 1212 cm.$^{-1}$ while the free base has two bands, one at 1207 cm.$^{-1}$ and the other at 1222 cm.$^{-1}$, either or both of which may be due to the sulfite ester group.

Both monocrotaline sulfite hydrochloride and the free base were hydrogenolyzed over palladium on strontium carbonate. In each case, exactly one mole equivalent of hydrogen was required and the products were the corresponding amino acid hydrochloride and the free amino acid (IX). The infrared spectra of these compounds have one significant band in common, an ester carbonyl absorption at 1748 cm.$^{-1}$ (the hydrochloride) and at 1736 cm.$^{-1}$ (the free base). In addition, the shift of the carboxyl band from 1713 cm.$^{-1}$ (for the free acid function) to 1636 cm.$^{-1}$ (for the carboxylate ion) may be noted, corresponding to the change from an amino acid hydrochloride to the amino acid zwitterion.[5] The sulfite band (provisional assignment) appears at 1210 cm.$^{-1}$ (shoulder) and 1227 cm.$^{-1}$ in the hydrochloride, while the free amino acid has only a shoulder at 1207 cm.$^{-1}$. The infrared absorption spectra of the pertinent compounds are shown in Chart I.

The presence of an ester band in each of the dihydro compounds containing the sulfite ester group is in distinct contrast to the spectrum of the salt (VI) derived from monocrotaline by hydrogenolysis which has no normal ester carbonyl absorption. This clearly indicates that the necic acid was originally joined to the pyrrolizidine nucleus by two ester links, one of which is easily cleaved by hydrogenolysis while the other survives only when the hydroxyl alpha to the carboxylic acid group is blocked, in the above case by the sulfite ester group. Therefore, when monocrotaline is hydrogenolyzed, the allylic ester is first cleaved (X), then an intramolecular transesterification takes place between the hydroxyl alpha to the carboxyl group and the ester group at the C-7 position of the retronecine nucleus with the formation of the lactone ring of monocrotalic acid.

The establishment of the location of the free hydroxyl group in monocrotalic acid,[2] adjacent to the oxygen of the lactone, the formation of a cyclic sulfite ester (which occurs readily only with 1,2-glycols)[6] from monocrotaline, and the failure of this sulfite, in contrast to monocrotaline, to form a product containing a lactone linkage upon hydrogenolysis make it apparent that the two hydroxyls are vicinal and alpha–beta to the allylic ester carboxyl group. This was further demonstrated by lead tetraacetate oxidation of monocrotaline. The reaction proceeds rapidly and exothermally and consumes in excess of one mole of reagent. The lead was removed as the sulfate and an aqueous solution of *o*-phenylenediamine dihydrochloride was added. The crystalline product thus obtained was identified as 2-hydroxy-3-methylquinoxaline (XII). The hydroxyl groups are, therefore, alpha–beta to an ester group and upon oxidation the necic acid bridge opens to give a pyruvic ester moiety (XI) which then reacts with the diamine to give the quinoxaline derivative (XII).

The carbonyl absorption frequencies[7] of the epimeric monocrotalic acids,[2c] the epimeric anhydrodihydromonocrotalic acids,[2b] and certain of their derivatives are summarized in Table I. These data show that the five-membered lactone carbonyl frequency may be abnormally low (1740–1750 cm.$^{-1}$) in nujol mull but, in all cases examined, was in the normal range (1760–1800 cm.$^{-1}$) for the solution spectra. It is interesting to note that,

(3a) This work will be described in a subsequent communication.

(4) J. Cymermann and J. B. Willis, *J. Chem. Soc.*, 1332 (1951).

(5) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 15.

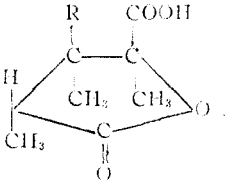
(6) See, however, C. Th. Herzig and M. Ehrenstein, *J. Org. Chem.*, **17**, 724 (1952).

(7) All of the curves reported for the first time in this paper were taken on a Perkin-Elmer Model 21 spectrophotometer.

compared in the mull, the stereochemistry of a molecule may have a pronounced effect on the location of this band; thus natural, −5.0°, monocrotalic acid has an abnormally low absorption at 1740 cm.$^{-1}$ while the epimer, −60.0°, absorbs normally at 1780 cm.$^{-1}$. In all cases the derivatives of these lactone acids exhibited normal lactone carbonyl absorption even in the mull. In one case, however, *viz.*, methyl monocrotalate, the ester carbonyl absorption in the mull is abnormally low (1705 cm.$^{-1}$) and shifts to the normal range (1733 cm.$^{-1}$) in solution.

TABLE I

CARBONYL ABSORPTION FREQUENCIES



R = H	Lactone Nujol	Lactone Soln.	Carboxyl, Nujol	Ester or amide soln.
Acid +5.6°	1740	1774[a,c]	1715	1736[a,c]
Acid −60.0°	1745	1782[a,c]	1720	1720[a,c]
Amide *rac.*	1774	1777[a]	1685	1695[a,c]
Acid +5.6°, *p*-bromophenacyl ester	..	1778[a,c]	..	1755[a,c,g]
Acid −60.0°, *p*-bromophenacyl ester	..	1780[a,c]	..	1750[a,c,g]
R = OH				
Acid[e] −5.0°	1740	1780[b]	1705	1755[b] and 1730 ?
Acid[e] −60.0°	1780	..	1710	..
Acid −5.0°, methyl ester	1780[d]	1777[a]	1705[d]	1733[a]
Acid −5.0°, desoxyretronecine salt	1774[d]	..	1620[d]	..
Acid −5.0°, brucine salt	1765		1605[f]	

[a] $CHCl_3$ solution. [b] Dioxane solution. [c] Ref. 2c. [d] This communication. [e] Ref. 2c. [f] A band at 1640 cm.$^{-1}$ is probably due to the lactam function of the brucine molecule. [g] The isolated ketone band appears at 1710 cm.$^{-1}$ in the −5.0° acid derivative and at 1705 cm.$^{-1}$ in the −60.0° acid derivative.

Acknowledgment.—The authors are indebted to Mr. J. Nemeth, Mrs. Esther Fett and Mrs. Katherine Pih for the microanalyses and to Miss Helen Miklas for the infrared spectra.

Experimental[8]

Monocrotaline (VII).—The monocrotaline used in these investigations were obtained from *Crotalaria spectabilis*,[9] m.p. 196–197°. Two derivatives not previously reported were prepared, the picrate, m.p. 231–231.5° (dec.), and the methobromide, m.p. 216–216.5° (dec.).

Anal. (Picrate) Calcd. for $C_{16}H_{23}NO_6 \cdot C_6H_3N_3O_7$: C, 47.66; H, 4.73; N, 10.10. Found: C, 47.87; H, 5.03; N, 10.36. (Methobromide) Calcd. for $C_{16}H_{23}NO_6 \cdot CH_3Br$: C, 48.58; H, 6.24; N, 3.33. Found: C, 48.76; H, 6.23; N, 3.37.

Catalytic Hydrogenolysis. (a) Catalyst.—The 6% palladium-on-strontium carbonate was prepared according to the procedure of Mozingo[10] for the palladium-on-barium carbonate with only minor modifications. The strontium carbonate (Eimer and Amend, C.P.) was suspended in water at 60° and this temperature was maintained throughout the preparation. At the end of the reduction the *p*H was adjusted to about 9 (Hydrion paper), the jet black slurry digested for 5 minutes, and then washed by decantation until the wash water was neutral to litmus and gave no precipitate with aqueous silver nitrate. The catalyst was dried for 24 hours at 100°.

(b) **Procedure.**—All of the hydrogenations were conducted at room temperature in a semi-micro atmospheric pressure apparatus of conventional design. The system, including the flask containing a solution of the compound and suspended catalyst, was alternately evacuated and then refilled with hydrogen that had been presaturated with the solvent. After the system had come to equilibrium, the magnetic stirrer was started and the course of the hydrogenation followed by the change of volume measured in the associated gas buret. Appropriate corrections for the temperature and partial pressure of hydrogen above the solvent were applied to calculate the STP volume of hydrogen consumed. The catalyst was finally removed by filtration and the product recovered by removing the solvent under reduced pressure.

Desoxyretronecine Monocrotalate (VI).—A solution of 0.650 g. of monocrotaline in 20 ml. of ethanol (distilled from magnesium ethoxide) over 0.050 g. of catalyst consumed 45.2 ml. (S.T.P.) of hydrogen and the reduction then stopped completely: required for one mole equivalent of hydrogen, 44.8 ml. (S.T.P.). The product precipitated during the reduction and it was necessary to extract the catalyst three times with 25-ml. portions of boiling ethanol to ensure complete recovery. The yield of crystalline material was essentially quantitative (0.65 g.). After recrystallization from a large volume of acetone the melting point was 172.5–172.8° (dec.).

Anal. Calcd. for $C_{16}H_{25}NO_6$: C, 58.70; H, 7.69; N, 4.28. Found: C, 58.75; H, 7.71; N, 4.34.

Rotation.—0.0401 g. made up to 2.0 ml. with 95% ethanol at 32.5°: $\alpha^{32.5}D$ +0.1945°, *l* 1, $[\alpha]^{32.5°}D$ +9.70°.

A solution of 0.5 g. of desoxyretronecine monocrotalate, 0.9 ml. of concentrated hydrochloric acid and 2.0 ml. of water was extracted 15 times with 2-ml. portions of ether, the combined extracts dried over magnesium sulfate and the solvent removed under reduced pressure. There was obtained 0.25 g. (86%) of monocrotalic acid, m.p. 181–182°, not depressed upon admixture with an authentic specimen, m.p. 181–182°.

The aqueous layer was made strongly basic with aqueous sodium hydroxide and extracted 3 times with 10-ml. portions of chloroform. The solvent was removed under reduced pressure and the residual oil solidified after one hour *in vacuo* (15 mm.). After one recrystallization from petroleum ether (b.p. 40–60°) it melted at 77–78°, not depressed upon admixture with an authentic sample, m.p. 77–78°, of desoxyretronecine.

Monocrotaline Sulfite Hydrochloride.—This compound was prepared by a modification of the original procedure.[11] Ten grams of monocrotaline was added slowly to 25 ml. of thionyl chloride with external cooling. There was an immediate exothermic reaction and a vigorous evolution of hydrogen chloride. After 30 minutes the excess thionyl chloride was removed under reduced pressure and the crystalline residue was washed with anhydrous benzene and dried. The crude product weighed 12.5 g. (99%). After recrystallization from ethanol it melted at 226–226.5° (dec.).

Anal. Calcd. for $C_{16}H_{21}NO_7S \cdot HCl$: C, 47.11; H, 5.44; N, 3.43; S, 7.86. Found: C, 47.38; H, 5.65; N, 3.42; S, 7.66.

Rotation.—0.2501 g. made up to 5.0 ml. with water at 32°: $\alpha^{32}D$ +0.7629°, *l* 1, $[\alpha]^{32}D$ +15.26°.

Monocrotaline Sulfite (VIII).—A solution of 2.70 g. of the hydrochloride in 15 ml. of water was treated with 50 ml. of cold 0.132 *N* aqueous sodium hydroxide and 1.6 g. (65%) of the free base was obtained as a precipitate of very fine matted white needles. After recrystallization from ethanol it formed elongated prisms, m.p. 155.4–155.8° (dec.).

Anal. Calcd. for $C_{16}H_{21}NO_7S$: C, 51.74; H, 5.70; N, 3.77; S, 8.63. Found: C, 51.66; H, 5.76; N, 3.78; S, 8.64.

(8) All melting points were taken with calibrated total immersion Anschütz thermometers.

(9) R. Adams and E. F. Rogers, THIS JOURNAL, **61**, 2815 (1939).

(10) R. Mozingo, *Org. Syntheses*, **26**, 77 (1946).

(11) J. E. Mahan, these Laboratories, unpublished work.

Rotation.—0.0702 g. made up to 2.0 ml. with 95% ethanol at 35°: $\alpha^{35}D$ +1.3246°, *l* 1, $[\alpha]^{35}D$ +37.74°.

Dihydromonocrotaline Sulfite Hydrochloride (IX, as Hydrochloride).—A solution of 2.040 g. of monocrotaline sulfite hydrochloride in 65 ml. of 95% ethanol (distilled from Raney nickel) over 0.350 g. of catalyst consumed 108.6 ml. (S.T.P.) of hydrogen at an essentially constant rate of about 10 ml. (S.T.P.) per minute until the reduction stopped completely; required for one mole equivalent of hydrogen, 112.0 ml. (S.T.P.). The product was obtained in essentially quantitative yield as an oil which solidified upon trituration with anhydrous ether. After recrystallization from ethanol–ether it formed colorless needles, m.p. 185.8–186.2° (dec.).

Anal. Calcd. for $C_{16}H_{23}NO_7S \cdot HCl$: C, 46.88; H, 5.90; N, 3.42; S, 7.82. Found: C, 46.94; H, 5.88; N, 3.49; S, 7.64.

Rotation.—0.0701 g. made up to 2.0 ml. with 95% ethanol at 35°: $\alpha^{35}D$ −1.1125°, *l* 1; $[\alpha]^{35}D$ −31.74°.

Dihydromonocrotaline Sulfite (IX).—The reduction of a solution of 1.000 g. of monocrotaline sulfite in 25 ml. of ethanol over 0.150 g. of catalyst was stopped after one mole equivalent (60.3 ml., S.T.P.) had been consumed. The rate had decreased from about 5 ml./minute to less than 0.2 ml./minute and a trial run had shown that hydrogen would be absorbed at a decreasing rate until about two and one-half equivalents had been consumed. At this point the catalyst is apparently poisoned by traces of hydrogen sulfide arising from reduction of the sulfite ester group. The reduction product after one mole equivalent of hydrogen was absorbed was obtained as a crystalline solid after trituration with acetone. Upon recrystallization from ethanol–ether it formed long felted needles, m.p. 169.5–170° (dec.).

Anal. Calcd. for $C_{16}H_{23}NO_7S$: C, 51.46; H, 6.21; N, 3.75; S, 8.59. Found: C, 51.41; H, 6.39; N, 3.77; S, 8.86.

Rotation.—0.0713 g. made up to 2 ml. with water at 26°: $\alpha^{26}D$ +0.8450, *l* 1; $[\alpha]^{26}D$ +23.73°.

Lead Tetraacetate Oxidation of Monocrotaline.—A slurry of 3.25 g. of monocrotaline in 8 ml. of glacial acetic acid was treated with 4.35 g. (10% excess) of lead tetraacetate over a 5-minute period with external cooling to maintain the temperature below 15°. After standing at room temperature for 2 hours the reaction mixture was diluted with a solution of 1.5 g. of ammonium sulfate in 15 ml. of water and the precipitated lead sulfate removed by filtration. A solution of 1.81 g. of *o*-phenylenediamine dihydrochloride in 4 ml. of water was added to the filtrate and after about one minute 2-hydroxy-3-methylquinoxaline precipitated as fine matted needles; yield 1.3 g. (80%). The derivative was recrystallized from dilute acetic acid after preliminary treatment with Darco, m.p. 250.4–251.4°, not depressed upon admixture with an authentic sample, m.p. 250.8–251.4°, prepared from methyl pyruvate and *o*-phenylenediamine dihydrochloride in dilute aqueous acetic acid (reported m.p. 245°).[12]

Anal. Calcd. for $C_9H_8N_2O$: C, 67.49; H, 5.04; N, 17.49. Found: C, 67.24; H, 4.99; N, 17.55.

(12) O. Hinsberg, *Ann.*, **292**, 245 (1896).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF SYNTEX, S.A.]

Steroids. XXXVIII.[1] Synthesis of Allopregnane-3,11,20-trione-17α,21-diol (Dihydroallocortisone) from Allopregnan-3β-ol-11,20-dione

BY J. PATAKI, G. ROSENKRANZ AND CARL DJERASSI[2]

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Allopregnan-3β-ol-11,20-dione (Ia), the key intermediate of all the hitherto described C-11 oxygen introduction methods of plant steroids, was converted into allopregnane-3β,17α-diol-11,20-dione (Ib), by formation of the enol acetate followed by perbenzoic acid oxidation and saponification. Alternately, Δ16-allopregnen-3β-ol-11,20-dione acetate (III) was transformed into the epoxide IV and thence by hydrogen bromide opening and debromination of the intermediate bromohydrin to the 17α-hydroxy derivative Ib. Bromination of Ib produced the 21-bromo compound Ic which upon treatment with potassium acetate led to allopregnane-3β,17α,21-triol-11,20-dione 21-acetate (Id) (Reichstein's Compound D monoacetate). Oxidation with N-bromoacetamide furnished the desired "dihydroallocortisone acetate (II)."

All of the recently described syntheses of cortisone from plant steroids (diosgenin,[3,4] ergosterol,[3] stigmasterol[3,4] and hecogenin[5]) proceed through allopregnan-3β-ol-11,20-dione (Ia). The further transformations of this substance to allopregnane-3,11,20-trione-17α,21-diol acetate (II) (dihydroallocortisone acetate) have been recorded in two recent Communications to the Editor[6,7] and the present paper is concerned with the description of the experimental details of this reaction sequence.

The introduction of the requisite 17α-hydroxy group into Ia was accomplished by two procedures. In the first, the 11,20-dione (Ia) was converted into the enol acetate which without isolation was oxidized with perbenzoic acid and saponified according to the general procedure of Kritchevsky and Gallagher[8] yielding allopregnane-3β,17α-diol-11,20-dione (Ib) without isolation of intermediates. The same reaction with isolation of intermediates has recently been recorded[9] in the case of pregnan-3α-ol-11,20-dione. The second synthesis of Ib involved an adaptation of Julian's method[10] to Δ16-allopregnen-3β-ol-11,20-dione acetate (IIIb) which is the immediate degradation product[3,11] of 22a-5α-spirostan-3β-ol-11-one. Oxidation with alkaline hydrogen peroxide and reacetylation led to the oxide IV which was transformed with hydrogen bromide to the bromohydrin and directly debrominated with Raney nickel to afford after saponification allopregnane-3β,17α-diol-11,20-dione (Ib) identical

(1) Paper XXXVII, O. Mancera, A. Zaffaroni, B. A. Rubin, F. Sondheimer, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **74**, 3711 (1952).

(2) Department of Chemistry, Wayne University, Detroit, Michigan.

(3) E. M. Chamberlain, W. V. Ruyle, A. E. Erickson, J. M. Chemerda, L. M. Aliminosa, R. L. Erickson, G. E. Sita and M. Tishler, THIS JOURNAL, **73**, 2396 (1951).

(4) G. Stork, J. Romo, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 3546 (1951).

(5) C. Djerassi, H. J. Ringold and G. Rosenkranz, *ibid.*, **73**, 5513 (1951).

(6) J. M. Chemerda, E. M. Chamberlain, E. H. Wilson and M. Tishler, *ibid.*, **73**, 4052 (1951).

(7) G. Rosenkranz, J. Pataki and C. Djerassi, *ibid.*, **73**, 4055 (1951).

(8) T. H. Kritchevsky and T. F. Gallagher, *ibid.*, **73**, 184 (1951).

(9) T. H. Kritchevsky, D. L. Garmaise and T. F. Gallagher, *ibid.*, **74**, 483 (1952).

(10) P. L. Julian, E. W. Meyer, W. J. Karpel and I. R. Waller, *ibid.*, **72**, 5145 (1950).

(11) C. Djerassi, E. Batres, J. Romo and G. Rosenkranz, *ibid.*, **74**, 3634 (1952).