became rapid and strongly exothermic. External cooling was used as required in order to avoid a temperature above 75°. After the organic layer became pale yellow or colorless, the reaction mixture was diluted with 150 ml. of water, cooled and the crude 2-bromo-2-nitropentane was extracted with 35–37° petroleum ether. The extract was washed successively with 2% aqueous sodium hydroxide solution and with water, dried and concentrated by distillation of the solvent. The crude bromonitro compound—after evacuating to about 50 mm. to flash out the final traces of solvent—weighed 23 g. (about 0.115 mole).

The 2-bromo-2-nitropentane was debrominated using 22.0 g. (0.58 mole) of sodium borohydride (5 moles per mole of crude bromonitro compound) employing the procedure described by Iffland and Criner.[3b] After completion of the reaction, the mixture was made alkaline with 25% aqueous sodium hydroxide solution and thoroughly extracted with petroleum ether. The nitro compound was isolated from the alkaline solution by acidification with hydroxylamine hydrochloride and extraction in the usual manner.[3b] There was obtained 6.7 g. of 2-nitropentane having the properties listed in Table I.

Preparation of 2-Nitrohexane (NBA Procedure).—A suspension of 17.25 g. (0.15 mole) of 2-hexanone oxime and 9.1 g. (0.11 mole) of zinc oxide was prepared in 150 ml. of water and contained in a 500-ml. three-necked flask. A solution was prepared by dissolving 25 g. (0.18 mole) of N-bromoacetamide in 100 ml. of water and was added to the cooled (5°) and stirred oxime suspension. This addition required *ca.* 30 min. The reaction mixture was stirred an additional 30 min. while warming nearly to room temperature and then filtered. The excess zinc oxide was thoroughly washed with petroleum ether and the blue oil in the filtrate finally collected by extraction with 35–37° petroleum ether. This extract was processed exactly as described for the corresponding extract in the preparation of 2-nitropentane. There was obtained 3.85 g. of 2-nitrohexane having the properties indicated in Table I.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE SAMUEL C. HOOKER LABORATORY OF THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Terpenoids. VII.[1] Experiments in the Glycyrrhetic Acid Series

BY CARL DJERASSI AND C. M. FOLTZ[2]

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The decarboxylation product of 18-dehydroglycyrrhetic acid acetate (IIc) is shown to be $\Delta^{13(18),19}$-30-noroleadien-3β-ol-11-one acetate (III), both double bonds moving out of conjugation with the carbonyl group. Chromium trioxide oxidation of this substance leads to opening of ring E with formation of an unsaturated triketone VI, the structure of which is substantiated by reduction and cyclization experiments. These results confirm the location of the carboxyl group of glycyrrhetic acid as proposed by Ruzicka and Jeger.

Glycyrrhetic acid (Ia)[3] is a pentacyclic triterpene of unusual interest. It occurs in licorice root as the disaccharide glycoside glycyrrhizic acid[4] and it is one of the few triterpenes with pronounced physiological effects.[3a] Particularly noteworthy is the observation of Groen and co-workers[5] that glycyrrhizic acid exhibits qualitatively the same effect on the electrolyte balance in Addison's disease as does the adrenal hormone desoxycorticosterone. From a chemical standpoint, the aglycone glycyrrhetic acid (Ia) is unusual in that it is the only known triterpene with an 11-oxygen function and, furthermore, by virtue of certain decarboxylation reactions described below, it offers a ready means to the opening of ring E and a potentially attractive synthetic entrance into the taraxasterol and α-amyrin series.[6]

The presently accepted structure of glycyrrhetic acid (Ia) is due principally to the outstanding researches of Ruzicka, Jeger and their collaborators and briefly is based on the following facts: The presence of the 11-keto group is demonstrated by the typical ultraviolet absorption maximum at 250 mμ[7] and the catalytic hydrogenolysis[8] of the unreactive keto group to desoxoglycyrrhetic acid. Conversion of the latter's carboxyl function to methyl[9] furnished β-amyrin, thus establishing the entire structure of glycyrrhetic acid with the exception of the position of the carboxyl group. The placement of the carboxyl group at C-20 was based to a large extent on two important experiments by Ruzicka and Jeger.[10,11] The first involved selenium dioxide oxidation of 11-desoxoglycyrrhetic acid to the corresponding $\Delta^{9(11),13(18)}$-dien-12,19-dione and the demonstration of a β-ketoester function in this compound, while the second approach dealt with an examination of the decarboxylation of dehydroglycyrrhetic acid (II). Since we were not completely satisfied with the correctness of the structure assignments in this instance and since these intermediates are of crucial importance for any subsequent conversion to taraxasterol derivatives, we have undertaken a reinvestigation of the decarboxylation of dehydroglycyrrhetic acid. The experiments described below represent additional evidence for the correctness of the Ruzicka–Jeger[10] formulation (Ia) for glycyrrhetic acid.

The glycyrrhetic acid was obtained directly as the methyl ester Ib by methanolic hydrochloric acid hydrolysis[12] of commercially available ammoniated glycyrrhizin rather than *via* the purified po-

(1) Paper VI, C. Djerassi, E. Farkas, A. J. Lemin, J. C. Collins and F. Walls, THIS JOURNAL, **76**, 2969 (1954).

(2) Organon Research Fellow, 1952–1954.

(3) The extensive literature has been reviewed by (a) C. Niemann, *Chem. Weekblad*, **48**, 213 (1952); (b) O. Jeger in L. Zechmeister's "Progress in the Chemistry of Organic Natural Products," **6**, 1 (1950); (c) Elsevier's "Encyclopedia of Organic Chemistry," **14** (Supplement), 1057 (1952).

(4) The structure of the disaccharide moiety has been elucidated by B. Lythgoe and S. Trippett, *J. Chem. Soc.*, 1983 (1950).

(5) J. Groen, H. Pelser, M. Frenke, C. E. Kamminga and A. F. Willebrands, *J. Clin. Invest.*, **31**, 87 (1952), and earlier references.

(6) If the α-amyrins are indeed epimeric at C-17 with the β-amyrins (*cf.* O. Jeger, *Angew. Chem.*, **63**, 196 (1951)) then glycyrrhetic acid would lead to the wrong stereochemical series.

(7) L. Ruzicka and S. L. Cohen, *Helv. Chim. Acta*, **20**, 804 (1937).

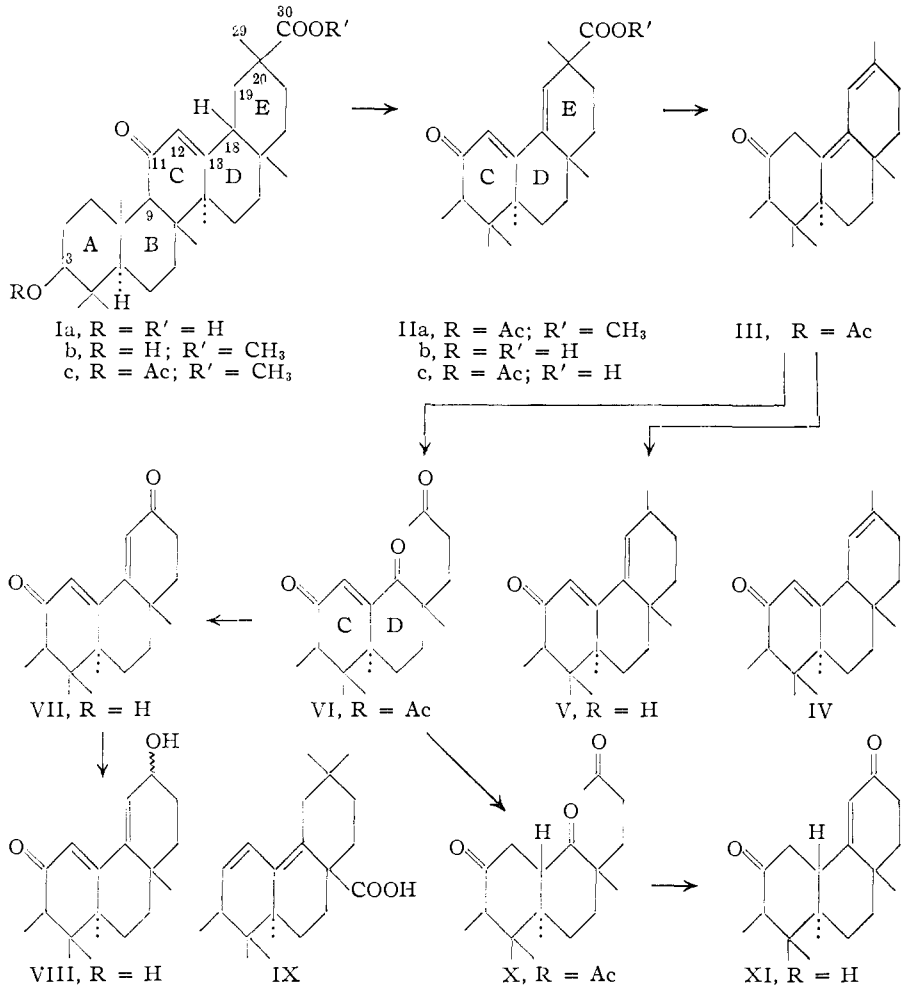
(8) L. Ruzicka, H. Leuenberger and H. Schellenberg, *ibid.*, **20**, 1271 (1937).

(9) L. Ruzicka and A. Marxer, *ibid.*, **22**, 195 (1939).

(10) L. Ruzicka and O. Jeger, *ibid.*, **25**, 775 (1942).

(11) L. Ruzicka, O. Jeger and M. Winter, *ibid.*, **26**, 265 (1943).

(12) *Cf.* P. Bilham, G. A. R. Kon and W. C. J. Ross, *J. Chem. Soc.*, 535 (1942).



tassium or ammonium glycyrrhizinate.[13] The corresponding 3-acetate Ic was brominated at 80° resulting in concomitant dehydrobromination of the intermediate[14] (presumably 18) bromo derivative and the direct formation of methyl dehydroglycyrrhetate acetate (IIa) with $\lambda_{max.}^{EtOH}$ 280 mμ[15] and $[\alpha]^{23}D$ + 329°.[16] Transformation of IIa to the corresponding 3-acetoxy acid IIc was accomplished in the standard manner and the decarboxylation of this acid—a crucial experiment in the structure proof of glycyrrhetic acid—proceeded smoothly at 210° exactly as indicated by Ruzicka and Jeger.[10] The physical constants (λ_{max}^{EtOH} 250 mμ, log ε 4.42, $[\alpha]^{19}D$ −138°) were in excellent agreement with the values reported in the literature for the decarboxylation product to which had been assigned the structure of $\Delta^{12,19}$-30-noroleadien-3β-ol-11-one acetate (IV) principally on the basis of the *position* of the ultraviolet absorption maximum which is now again identical with that of glycyrrhetic acid (I). It is clear, however, that the high *extinction* coefficient, confirmed in the present work, is incompatible with structure IV but is typical of *transoid* dienes.[17] The isomeric $\Delta^{13(18),19}$-diene III would fulfill this requirement and the calculated position of the ultraviolet absorption maximum (250 mμ) coincides exactly with the observed value. The strongly negative rotation is indicative of triterpenes with a 13–18 double bond[18] and structure III was confirmed by the infrared spectrum, which exhibited only carbonyl bands corresponding to acetate and *saturated* carbonyl groups, and by the red coloration produced with tetranitromethane. As was to be expected, treatment of the non-conjugated $\Delta^{13(18),19}$-11-ketone III with base resulted in a shift of the double bonds to afford the completely conjugated dienone system. The product V of this alkaline isomerization could not be obtained in crystalline form but the nature of the chromophoric system was substantiated by the ultraviolet and infrared spectra. The 30-nordienone III should prove to be an interesting starting material for the introduction of a methyl group into position 19.

The shift of a double bond to the position originally occupied by the carboxyl group in the decarboxylation of β,γ-unsaturated acids is well substantiated.[19] It is interesting to note that the present case (IIc → III) is an example of the decarboxylation of a β,γ,δ,ε-di-unsaturated acid in which

(13) *Cf.* L. Ruzicka and H. Leuenberger, *Helv. Chim. Acta*, **19**, 1402 (1936); L. Ruzicka, M. Furter and H. Leuenberger, *ibid.*, **20**, 312 (1937).

(14) G. A. R. Kon and W. C. J. Ross (*J. Chem. Soc.*, 741 (1942)) state that an intermediate dibromo (presumably 12,13-dibromide) derivative precipitates which has to be dehydrobrominated with pyridine. Our experiments, patterned after those of Ruzicka and Jeger (ref. 10) and the original basic procedure of C. W. Picard and F. S. Spring (*J. Chem. Soc.*, 35 (1941)) always resulted in the direct formation of dehydroglycyrrhetic acid (II) and are thus in agreement with the observations of the two latter groups of investigators.

(15) The position of this maximum, though typical of linearly conjugated dienones (*e.g.*, $\Delta^{4,6}$-3-ketosteroids), is low if compared to the value (303 mμ) calculated on the basis of the empirical rules established for steroids (L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1949, p. 192) but his method of calculation may not necessarily be applicable to such *cisoid* dienones since no model of unequivocally proved structure is available (L. Dorfman, *Chem. Revs.*, **53**, 47 (1953)).

(16) This high positive rotation appears to be characteristic of triterpenes possessing the 12,18-diene system such as isodehydroöleanolic acid (D. H. R. Barton and C. J. W. Brooks, *J. Chem. Soc.*, 257 (1951)).

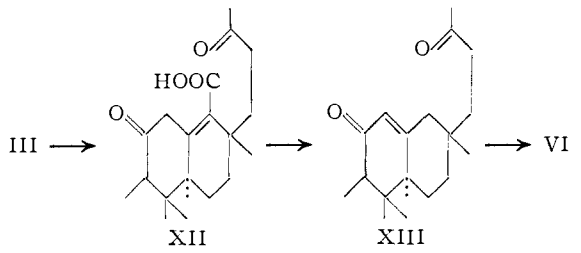
(17) *Cf.* E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *ibid.*, 1890 (1949); G. D. Laubach, E. C. Schreiber, E. J. Agnello, E. N. Lightfoot and K. J. Brunings, THIS JOURNAL, **75**, 1514 (1953).

(18) *Cf.* F. A. Alves and C. R. Noller, *ibid.*, **74**, 4043 (1952).

(19) R. T. Arnold, O. C. Elmer and R. M. Dodson, *ibid.*, **72**, 4359 (1950).

both double bonds migrate in spite of the fact that as a consequence the second double bond moves out of conjugation with the keto group. Barton and Brooks,[16] in an attempt to differentiate between two possible mechanisms (cyclic[19] or β-carbonium ion intermediate) in the decarboxylation of β,γ-unsaturated acids, have used the reported[10] decarboxylation of dehydroglycyrrhetic acid acetate (IIc) to IV as a test case in favor of the cyclic mechanism. In view of the presently revised structure III for the decarboxylation product their reasoning is invalid, but any proposed mechanism will have to take into account the apparent anomaly that the thermal decarboxylation of dehydroöleanolic acid (IX) involves the shift of only one double bond.[12,19a]

In a later paper, Ruzicka, Jeger and Winter[11] investigated the chromium trioxide oxidation of the decarboxylation product (III, at that time believed to be IV) and isolated a ketone to which was assigned the ring E-opened formulation VI, principally on the basis of the ultraviolet absorption maximum at 257 mμ; no further transformations were reported. The formation of this substance could be rationalized on the basis of either structure III or IV for the starting material by assuming initial oxidation of the 19–20 double bond to the acid XII followed by decarboxylation to XIII and subsequent allylic oxidation.



If structure VI were indeed correct, then the hitherto resistant 12–13 double bond should be reducible by zinc dust, a behavior typical of ene-diones. Furthermore, cyclization with reformation of ring E (now lacking both *gem*-dimethyl groups) should be possible. We have repeated the oxidation of the decarboxylation product III and were able to isolate in approximately 15% yield the previously reported[11] yellowish triketone VI with the expected infrared and ultraviolet spectral properties. Reduction with zinc dust yielded a colorless dihydro derivative, formulated[20] as the saturated acetoxy triketone X, since it did not show high selective ultraviolet absorption or infrared carbonyl bonds compatible with the presence of an unsaturated ketone system. Treatment of the saturated triketone X with sodium methoxide resulted in cyclization and formation of an unsaturated diketone to which we assign structure XI on the basis of its analytical composition and spectral properties, λ_{max}^{EtOH} 240 mμ, log ϵ 4.12 and infrared carbonyl bands at 5.90 (saturated 11-ketone) and 6.06 μ (α, β-unsaturated ketone).

(19a) We have confirmed the earlier report (ref. 12) that only one double bond shifts in the decarboxylation of IX.

(20) The *trans* C/D juncture has not been proved but is assumed to have been produced during the zinc–acetic acid treatment in preference to the *cis* juncture.

It is pertinent to mention that this cyclization proceeded even more readily with the unsaturated triketone VI where 1% methanolic potassium hydroxide sufficed instead of sodium methoxide. The faintly yellowish cyclization product VII showed the typical[16] strongly positive rotation and exhibited only a single infrared carbonyl band at 6.01 mμ, consistent with the presence of the unsaturated carbonyl system, and an ultraviolet absorption maximum at 286 mμ. No proper cyclic models appear to be available for ultraviolet comparison with the *cisoid* diene-dione VII, but the open chain analog, diacetylbutadiene[21] possesses a maximum at 278 mμ. Some support for the diene-dione chromophore in VII was adduced as follows. As was to be expected from the comparative resistance of 11-keto steroids toward sodium borohydride,[22] similar reduction of the diene-dione VII afforded an amorphous product, believed to be the $\Delta^{12,18}$-dien-3β,20-diol-11-one VIII, since the position of its ultraviolet absorption maximum (278 mμ) was nearly identical with that of dehydroglycyrrhetic acid (II) and the infrared spectrum still showed the presence of an unsaturated carbonyl group (6.05 μ).

All of the above results can be explained in terms of the Ruzicka–Jeger[10] structure Ia for glycyrrhetic acid and, in particular, they confirm the location of the carboxyl group at C-20.

Acknowledgment.—We are greatly indebted to Organon, Inc., for financial assistance and to Dr. D. A. van Dorp of N. V. Organon, Oss, for interesting correspondence.

Experimental[23]

Methyl Glycyrrhetate 3-Acetate (Ic).—A mixture of 400 g. of ammoniated glycyrrhizin scales (S. B. Penick & Co.), 200 cc. of concd. hydrochloric acid and 2 l. of methanol was refluxed with stirring for 24 hours. The reddish-brown precipitate (182 g.), obtained on dilution with water and filtration was extracted continuously for 48 hours with chloroform in a Soxhlet apparatus. The extract (750 cc.) was passed through a column of 750 g. of activated alumina (AlCOA, grade F-20) and eluted with a total of 9 l. of chloroform. Recrystallization from methanol–methylene chloride afforded 12.4 g. (from the first 2 l. of eluate) of pale yellowish crystals with m.p. 220–227° and 19.4 g. (from the remaining 7 l. of eluate) of colorless needles with m.p. 237–240°. Both crops were combined and refluxed for four hours with 100 cc. of acetic anhydride. After processing in the usual manner and recrystallizing twice from methanol–methylene chloride, there was obtained 23.6 g. of colorless crystals with m.p. 294–297°, $[\alpha]^{19}D$ +133°; λ_{max}^{EtOH} 249 mμ, log ϵ 4.10; $\lambda_{max}^{CHCl_3}$ 5.82, 6.05 and 8.0 μ (type A band)[24]; lit.[13] m.p. 299–300°, $[\alpha]^{19}D$ +145°.

Methyl 18-Dehydroglycyrrhetate 3-Acetate (IIa).—Reproducible results could be obtained only on a small scale. In a representative experiment, 2.64 g. of Ic in 100 cc. of glacial acetic acid was treated dropwise at 80° over a period of 20 minutes with 17.6 cc. of a 5% solution of bromine in acetic acid. After heating for an additional one-half hour at 80°, water was added and the product was collected,

(21) A. L. Nussbaum, O. Mancera, R. Daniels, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 3263 (1951).

(22) O. Mancera, H. J. Ringold, C. Djerassi, G. Rosenkranz and F. Sondheimer, *ibid.*, **75**, 1286 (1953).

(23) Melting points of analytical samples were determined on the Kofler block. Rotations were measured in chloroform, ultraviolet absorption spectra in 95% ethanol and infrared spectra in chloroform solution (Baird double beam recording spectrophotometer with 0.1-mm. cells). The microanalyses were carried out by Geller Laboratories, Hackensack, N. J., and Mr. J. F. Alicino, Metuchen, N. J.

(24) R. N. Jones, P. Humphries, F. Herling and K. Dobriner, THIS JOURNAL, **73**, 3215 (1951).

dried and recrystallized from methanol–methylene chloride. In this manner, 23.6 g. of Ic yielded 17.80 g. of colorless crystals with m.p. 244–247°, $[\alpha]^{23}D$ +329°, yellow color with tetranitromethane, λ_{max}^{EtOH} 280 mμ, log ε 4.11; $\lambda_{max}^{CHCl_3}$ 5.80 and 6.05 μ; lit.[10] m.p. 247–248°, $[\alpha]D$ +282°.

18-Dehydroglycyrrhetic Acid 3-Acetate (IIc).—The above acetate methyl ester (20.7 g.) was refluxed for 15 hr. in an atmosphere of nitrogen with 750 cc. of 10% methanolic potassium hydroxide. The crude acid IIb (m.p. 160–170° dec., 19.6 g.), obtained after ether extraction of the acidified reaction mixture, was acetylated by heating at 80° with acetic anhydride–pyridine (1:2) for three hours. Crystallization from aqueous methanol afforded 15.2 g. of the acetoxy acid IIc with m.p. 215–220° dec., $[\alpha]D$ +312°; λ_{max}^{EtOH} 282 mμ, log ε 4.08; $\lambda_{max}^{CHCl_3}$ 5.82 and 6.05 μ, yellow color with tetranitromethane; lit.[10] m.p. 215–220° dec., $[\alpha]D$ +300°.

$\Delta^{13(18),19}$-30-Noroleadien-3β-ol-11-one Acetate (III).—The acetoxy acid (0.5 g., m.p. 215–220°) was sublimed at 205–210° and 0.01 mm. yielding 0.42 g. of sublimate with m.p. 155–160°. Recrystallization from methanol–methylene chloride led to 0.28 g. of colorless needles with m.p. 163–165°, $[\alpha]^{19}D$ −138°; λ_{max}^{EtOH} 250 mμ, log ε 4.42; $\lambda_{max}^{CHCl_3}$ 5.82 and 5.90 μ, red color with tetranitromethane; lit.[10] m.p. 164–165°, $[\alpha]D$ −139°; λ_{max}^{EtOH} 250 mμ, log ε 4.4, yellow (!) color with tetranitromethane.

Treatment of a sample of the decarboxylation product with 5% methanolic potassium hydroxide for 24 hours at room temperature furnished a yellowish, resinous solid (m.p. 93–99°) which could not be crystallized. On the basis of its ultraviolet absorption maximum at 278 mμ, the yellow color with tetranitromethane and the single infrared carbonyl band at 6.03 μ, the substance is assigned the **$\Delta^{12,18}$-30-noroleadien-3β-ol-11-one (V)** structure.

Δ^{12}-19,30-Bisnoroleanene-11,18,20-trione-3β-ol Acetate (VI).—A sample (1.28 g.) of the decarboxylation product III (m.p. 155–160°) in 40 cc. of acetic acid was treated slowly with a solution of 0.88 g. of chromium trioxide in 40 cc. of 90% acetic acid. After 24 hours at room temperature, methanol was added, the bulk of the solvent was removed *in vacuo* and the product was extracted with ether. After washing with carbonate solution and water, drying, evaporating and crystallizing from methanol–methylene chloride there was obtained 0.2 g. of pale yellowish crystals with m.p. 245–248°, $[\alpha]D$ +37.7°; λ_{max}^{EtOH} 255 mμ, log ε 3.89; $\lambda_{max}^{CHCl_3}$ 5.81 and 5.98 μ, no color with tetranitromethane; lit.[11] m.p. 246–248°. A sample was sublimed *in vacuo* at 210° before analysis.

Anal. Calcd. for $C_{30}H_{44}O_5$: C, 74.34; H, 9.15. Found: C, 74.25; H, 8.95.

19,30-Bisnoroleanane-11,18,20-trione-3β-ol Acetate (X).—A mixture of 0.6 g. of the above unsaturated triketone VI and 0.5 g. of zinc dust in 50 cc. of acetic acid was refluxed for 30 minutes followed three times at 30-minute intervals by the addition of 0.2-g. portions of zinc. Filtration, evaporation of the solvent, extraction with ether and recrystallization of the ether residue from methanol–methylene chloride furnished 0.31 g. of colorless needles with m.p. 237–240°, $[\alpha]^{19}D$ +38.4°, no selective absorption in the ultraviolet, $\lambda_{max}^{CHCl_3}$ 5.83 and 5.88 μ. The analytical sample was sublimed at 215° and 0.05 mm.

Anal. Calcd. for $C_{30}H_{46}O_5$: C, 74.03; H, 9.53. Found: C, 74.25; H, 9.14.

$\Delta^{12,18}$-29,30-Bisnoroleadien-3β-ol-11,20-dione (VII).—A solution of 0.1 g. of the unsaturated triketone VI in 300 cc. of 1% methanolic potassium hydroxide was allowed to stand at room temperature for three days. Concentration *in vacuo*, dilution with water, extraction with ether and crystallization of the ether residue from hexane–acetone gave 0.023 g. of faintly yellowish needles with m.p. 270–272°, $[\alpha]^{19}D$ +465°; λ_{max}^{EtOH} 286 mμ, log ε 4.18; $\lambda_{max}^{CHCl_3}$ 6.01 mμ. A sample was sublimed at 210° before analysis.

Anal. Calcd. for $C_{28}H_{40}O_3$: C, 79.20; H, 9.50. Found: C, 79.28; H, 9.50.

A portion of the above cyclization product was allowed to stand at room temperature for 12 hr. in 80% dioxane solution with one-fifth its weight of sodium borohydride. After acidification to *p*H 2, extraction with ether and evaporation to dryness there was obtained in quantitative yield an amorphous residue with ultraviolet absorption maximum at 278 mμ and an infrared band at 6.05 μ of approximately one-half the intensity found in the starting material. Both the reduced intensity and the slight bathochromic shift of the infrared band are in accordance with structure VII.

Δ^{18}-29,30-Bisnoroleanen-3β-ol-11,20-dione (XI).—When the saturated triketone X was subjected to exactly the same cyclization conditions as described above for VI, there was obtained a colorless solid with m.p. 228–230°, no selective absorption in the ultraviolet, $\lambda_{max}^{CHCl_3}$ 5.90 μ which was the saponified, uncyclized trione X (R = H) as demonstrated by reacetylation to the starting acetate (X, R = Ac).

Anal. Calcd. for $C_{28}H_{44}O_4$: C, 75.63; H, 9.97. Found: C, 75.65; H, 10.12.

Consequently, the following more drastic conditions were adopted for the cyclization. The saturated acetoxy triketone (X) (100 mg.) was refluxed for 24 hours in an atmosphere of nitrogen with 30 cc. of a 5% solution of sodium methoxide in anhydrous methanol. After working up in the usual manner and crystallizing from acetone–hexane, there was isolated 52 mg. of needles with m.p. 287–291°. The analytical sample (21 mg.) was obtained from methanol–chloroform, m.p. 304–308°, $[\alpha]^{19}D$ +98°, λ_{max}^{EtOH} 240 mμ, log ε 4.12; $\lambda_{max}^{CHCl_3}$ 5.90 and 6.05 μ; a fairly strong band at 6.25 μ is presumably due to the 18,19-double bond.

Anal. Calcd. for $C_{28}H_{42}O_3$: C, 78.82; H, 9.92. Found: C, 78.75; H, 10.11.

DETROIT, MICHIGAN