30 ml. of glacial acetic acid for one hour at 20–22°. Absorption of ozone was quantitative during the first 50 minutes and the rate of absorption rapidly decreased during the next ten minutes. The ozonide was decomposed by the addition of 5 g. of zinc dust and 10 ml. of water. After standing 20 minutes, the solution was separated from the zinc by filtration into a 250-ml. flask. The ozone reaction flask was rinsed with 100 ml. of water, which was added to the filtrate. The solution was distilled to approximately one-third of its original volume and the distillate was collected in a suspension of 1.4 g. of 2,4-dinitrophenylhydrazine hydrochloride in 50 ml. of 2 *N* hydrochloric acid. The suspension of dinitrophenylhydrazones was extracted with 500 ml. of benzene, the benzene solution dried over sodium sulfate and concentrated to 150 ml. when it was ready for chromatography.

Chromatography of the Dinitrophenylhydrazones from Ozonized Humulone.—Silicic acid, Mallinckrodt 100 mesh Analytical Reagent[10] was washed on a Buchner funnel successively with 3 vols. of absolute ethanol, 3 vols. of acetone and 3 vols. of petroleum ether 30–60° and dried 18 hours at 110–115° and 25 mm. A column of the silicic acid, 52 mm. × 220 mm., was prepared and prewashed with one bed volume of anhydrous ethyl ether followed by three volumes of hexane.

One-half of the benzene solution (75 ml.) of dinitrophenylhydrazones from ozonized humulone was diluted with two volumes of hexane and adsorbed on the column. Development with hexane–ether (6:1) yielded an intense slow-moving band and a second extremely faint fast-moving zone. The fast zone, on elution, yielded approximately 5 mg. of orange material. This was not isobutyraldehyde dinitrophenylhydrazone as shown by a mixed chromatogram with authentic isobutyraldehyde dinitrophenylhydrazone. From the principal band there was obtained a crystalline product which on recrystallization from 35 ml. of absolute ethanol yielded 638 mg. (126 mole %). The identity of this compound as acetone 2,4-dinitrophenylhydrazone was demonstrated by mixed capillary melting points with the authentic compound, m.p. 124–125°, by microscopic observation of fusion behavior, and comparison of optical and crystallographic properties with the authentic compound. The derivative had the analyses: Found: C, 45.6; H, 4.24; N, 23.3. Calculated for $C_9H_{10}N_4O_4$; C, 45.38; H, 4.23; N, 23.53.

Ozonization of Lupulone.—Lupulone, 1.159 g. (0.0028 equiv.) was ozonized under the same conditions as humulone for one hour. One-half of the dinitrophenylhydrazone solution when chromatographed as above yielded a slow, sharp intense band and a very faint fast-moving zone. The fast band yielded only a trace of yellow resinous material and the main band yielded 885 mg. (198 mole %) of acetone dinitrophenylhydrazone. The absorption of ozone was practically quantitative during the one-hour period. Ozonization of 1.18 g. (0.00285 equiv.) of lupulone for two hours yielded 1.418 g. of acetone dinitrophenylhydrazone (209 mole % yield).

Isolation of Methyl *n*-Propyl Ketone Dinitrophenylhydrazone.—Lupulone, 923 mg. (0.00223 equiv.) in 30 ml. of acetic acid, was ozonized at 20–22° for six hours. The ozonide was decomposed and the dinitrophenylhydrazone of the distillate prepared as previously described. An aliquot of the benzene solution of dinitrophenylhydrazones amounting to 64% of the total was adsorbed on a silicic acid column 52 mm. × 210 mm. Development with hexane–ether (6:1) yielded two slow-moving closely spaced bands in approximately the expected position for acetone dinitrophenylhydrazone and a fast-moving band in the expected position for the isobutyraldehyde derivative. Each of the slow-moving bands yielded traces of unidentifiable crystalline material. The fast band yielded 46 mg. (12 mole %) of the 2,4-dinitrophenylhydrazone of methyl *n*-propyl ketone crystallized from methanol. No other material could be obtained from the mother liquor. The identity of this material was established by mixed melting point with authentic methyl *n*-propyl ketone 2,4-dinitrophenylhydrazone, m.p. 145–147°, microscopic observation of fusion behavior, and by comparison of optical and crystallographic properties.

Acknowledgment.—The author expresses his appreciation to Mr. L. M. White for analysis, to Mr. Gordon Alderton for a supply of lupulone, to Dr. F. T. Jones for microscopic identifications, and to Dr. T. W. Campbell for the use of an ozone apparatus.

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[10] Mention of this product does not imply that it is endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

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

Steroidal Sapogenins. X.[1a] Unsaturated 22-Isospirosten-3-ones[1b,2]

BY R. YASHIN, G. ROSENKRANZ AND CARL DJERASSI

$\Delta^{5,7}$-22-Isospirostadien-3β-ol (I) on Oppenauer oxidation leads to $\Delta^{4,7}$-22-isospirostadien-3-one (II), only one double bond migrating into conjugation with the carbonyl group. Similar treatment of $\Delta^{5,7,9(11)}$-22-isospirostatrien-3β-ol (IV) affords $\Delta^{4,7,9(11)}$-22-isospirostatrien-3-one (V), which upon catalytic reduction in an alkaline medium yields $\Delta^{7,9(11)}$-22-isospirostadien-3-one (VIII) and thence, by lithium aluminum hydride reduction, $\Delta^{7,9(11)}$-22-isospirostadien-3α-ol (IX). These two dienes (VIII and IX) of the 5-*normal* configuration represent important intermediates for the chemical introduction of an oxygen atom into position C-11. Conversion of $\Delta^{4,7,9(11)}$-22-isospirostrien-3-one (V) to the enol acetate VI followed by acid hydrolysis gives $\Delta^{4,6,8}$-22-isospirostatrien-3-one (VII). Dibromination of Δ^{4}-22-isospirosten-3-one (XI) and dehydrobromination of the resulting 2,6-dibromo-Δ^{4}-3-ketone XII with collidine affords $\Delta^{1,4,6}$-22-isospirostatrien-3-one (XIII). Ultraviolet and infrared spectroscopic data are reported for all products and the infrared band at 1656 cm.$^{-1}$ is shown to be associated with a conjugated trienone system (VII, X, XIII).

As pointed out in earlier communications,[3,4] 7,8;9,11-dienes of the steroid series represent useful intermediates for the chemical introduction of an oxygen atom into position C-11 of ring C unsubstituted starting materials. The preparation of certain 7,8;9,11-dienes of the sapogenin series[3] and thence, by side chain degradation, of the pregnane series[4] was accomplished in a facile manner, since they possessed the *allo* configuration (rings A/B *trans*) which is produced almost exclusively on hydrogenation of 5,6;7,8-dienes (I), the starting materials employed. The synthesis of 7,8;9,11-dienes with the normal configuration (rings A/B *cis*) (*e.g.*, VIII) appeared particularly attractive, since such dienes are closely related to the 9,11-

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[1] (a) IX, A. Sandoval, J. Romo, St. Kaufmann, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 3820 (1951); (b) taken in part from a thesis presented by Srta. Rosa Yashin to the Facultad de Química, Universidad Motolinia.

[2] For nomenclature of steroidal sapogenins, see G. Rosenkranz and C. Djerassi, *Nature*, **166**, 104 (1950).

[3] G. Rosenkranz, J. Romo, E. Batres and C. Djerassi, *J. Org. Chem.*, **16**, 298 (1951).

[4] C. Djerassi, J. Romo and G. Rosenkranz, *ibid.*, **16**, 754 (1951).

unsaturated bile acids employed by Fieser, Heymann and Rajagopalan[5] as starting materials for a novel and successful introduction of a C-11 keto group. The present paper describes certain studies in the sapogenin series designed to furnish dienes of the *normal* configuration, which are suitable substrates for the oxidative introduction of an oxygen function at C-11.

While hydrogenation of Δ^{5}-3-hydroxysteroids affords almost exclusively saturated *allo*-3-hydroxy derivatives, there are recorded in the literature[6] a number of examples where a Δ^{4}-3-ketone furnishes the corresponding *normal* ketones, the yield varying with the specific substance at hand. We have, therefore, prepared a number of Δ^{4}-3-ketones of the sapogenin series with one or more additional double bonds, to serve as models for hydrogenation studies. The feasibility of using such Δ^{4}-22-isospirosten-3-ones for the preparation of the corresponding 5-*normal* isomers will be demonstrated below for the most important case (V→ VIII).

Oppenauer oxidation of the readily available $\Delta^{5,7}$-22-isospirostadien-3β-ol (I)[7] proceeded as in other series[8] with migration of only one double bond and furnished $\Delta^{4,7}$-22-isospirosten-3-one (II). The structure of the ketone II was proved by its ultraviolet absorption spectrum at 238 mμ (log ε 4.29) and infrared band at 1676 cm.$^{-1}$, typical of Δ^{4}-3-ketosteroids.[9] Conversion to the enol acetate afforded the fully conjugated $\Delta^{3,5,7}$-22-isospirostatrien-3-ol 3-acetate (III), whose ultraviolet absorption spectrum was practically identical with that of the corresponding ergosterol derivative.[10] In agreement with the observation made with dehydroergosterol,[10] $\Delta^{5,7,9(11)}$-22-isospirostatrien-3β-ol (IV)[3] underwent Oppenauer oxidation with migration of only the 5,6-double bond yielding the required $\Delta^{4,7,9(11)}$-22-isospirostatrien-3-one (V). The infrared band at 1674 cm.$^{-1}$, characteristic[9] of an isolated Δ^{4}-3-ketone system, on the one hand, and the high extinction coefficient (ultraviolet maximum at 242 mμ, log ε 4.51) indicative of two, isolated chromophoric systems absorbing in the same region, on the other hand fully substantiate the assigned structure (V). Hydrogenation of this trien-3-one V with palladium-on-charcoal catalyst in ethanol solution in the presence of potassium hydroxide[11,12] led to $\Delta^{7,9(11)}$-22-isospirostadien-3-one (VIII), the desired diene of the *normal* series. The spectroscopic results were fully consistent with this formulation: the infrared band at 1716 cm.$^{-1}$ demonstrated the presence of the *un*conjugated 3-keto group[9] while the double maximum at 236 and 244 mμ, typical of the 7,8;9,11-diene moiety,[3,4,13] confirmed the presence of that grouping. The 5-*normal* configuration of the hydrogenation product VIII was established by the course of the lithium aluminum hydride reduction, which led to a dienol, isomeric but *not* identical (physical constants and infrared spectrum) with $\Delta^{7,9(11)}$-22-iso*allo*spirostadien-3β-ol.[3] The substance gave no precipitate with digitonin and hence is best formulated as $\Delta^{7,9(11)}$-22-isospirostadien-3α-ol (IX). Shoppee and Summers[14] have demonstrated recently that 3-ketosteroids of the 5-*normal* configuration on treatment with lithium aluminum hydride yield the 3α-alcohols, while the 5-*allo* isomers led to the 3β-hydroxy epimers.

As was to be anticipated on the basis of the results recorded in the ergosterol and lumisterol series,[10] the trienone V on treatment with acetic anhydride–pyridine afforded in nearly quantitative yield the fully conjugated enol acetate, $\Delta^{3,5,7,9(11)}$-22-isospirostatetraen-3-ol 3-acetate (VI) with ultraviolet absorption maxima at 336, 354 and 372 mμ. This enol acetate as well as its 9,11-dihydro analog III exhibited a carbonyl band at 1760 cm.$^{-1}$, thus representing a very slight shift with respect to the maximum at 1754 cm.$^{-1}$ observed[9] with $\Delta^{3,5}$-dien-3-ol 3-acetates. Acid hydrolysis of the enol acetate VI ($[\alpha]^{20}_{\mathrm{D}}$ −223°) produced an unsaturated ketone with $[\alpha]^{20}_{\mathrm{D}}$ + 627°, ultraviolet absorption maxima at 244, 284 and 388 mμ, infrared band at 1656 cm.$^{-1}$, to which can almost certainly be assigned the $\Delta^{4,6,8}$-22-isospirostatrien-3-one (VII) structure. At one time such a chromophoric system has been assumed[15] to exist in certain polybrominated derivatives of Δ^{4}-cholesten-3-one, an interpretation which has since been shown to be untenable.[16] However, pertinent to the structure assignment of the ketone VII is the observation that $\Delta^{1,3,5}$-cholestatrien-7-one (X) shows ultraviolet absorption maxima[17] at 230, 278 and 348 mμ. The maxima at 244, 284 and 388 mμ of our trienone VII are thus in excellent agreement with expectation, since the substance contains the same chromophoric system as the cholestatrienone X, but is substituted by additional alkyl groups which are known to produce a bathochromic shift. It is of interest to note that the cholestatrienone X has $[\alpha]^{20}_{\mathrm{D}}$ −784° and our spirostatrienone VII, $[\alpha]^{20}_{\mathrm{D}}$ +627°. Apparently, the linearly conjugated trienone grouping produces very large rotation changes as compared with the corresponding dienone or enone.

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(5) L. F. Fieser, H. Heymann and S. Rajagopalan, THIS JOURNAL, **72**, 2306 (1950).

(6) *Cf.* H. Grasshof, *Z. physiol. Chem.*, **223**, 249 (1934); A. Butenandt, K. Tscherning and G. Hanisch, *Ber.*, **68**, 2097 (1935); R. E. Marker, T. Tsukamoto and D. L. Turner, THIS JOURNAL, **62**, 2525 (1940).

(7) G. Rosenkranz, J. Romo and J. Berlin, *J. Org. Chem.*, **16**, 290 (1951).

(8) C. Djerassi in R. Adams "Organic Reactions," Vol. VI, Chapter V, John Wiley and Sons, Inc., New York, N. Y., 1951.

(9) R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950).

(10) I. M. Heilbron, T. Kennedy, F. S. Spring and G. Swain, *J. Chem. Soc.*, 869 (1938).

(11) Model experiments with $\Delta^{7,9(11)}$-22-iso*allo*spirostadien-3β-ol demonstrated that the diene system was not affected under those conditions.

(12) The addition of alkali favors formation of the *cis*-isomer (*cf.* A. L. Wilds, J. A. Johnson and R. E. Sutton, THIS JOURNAL, **72**, 5524 (1950) and references cited therein).

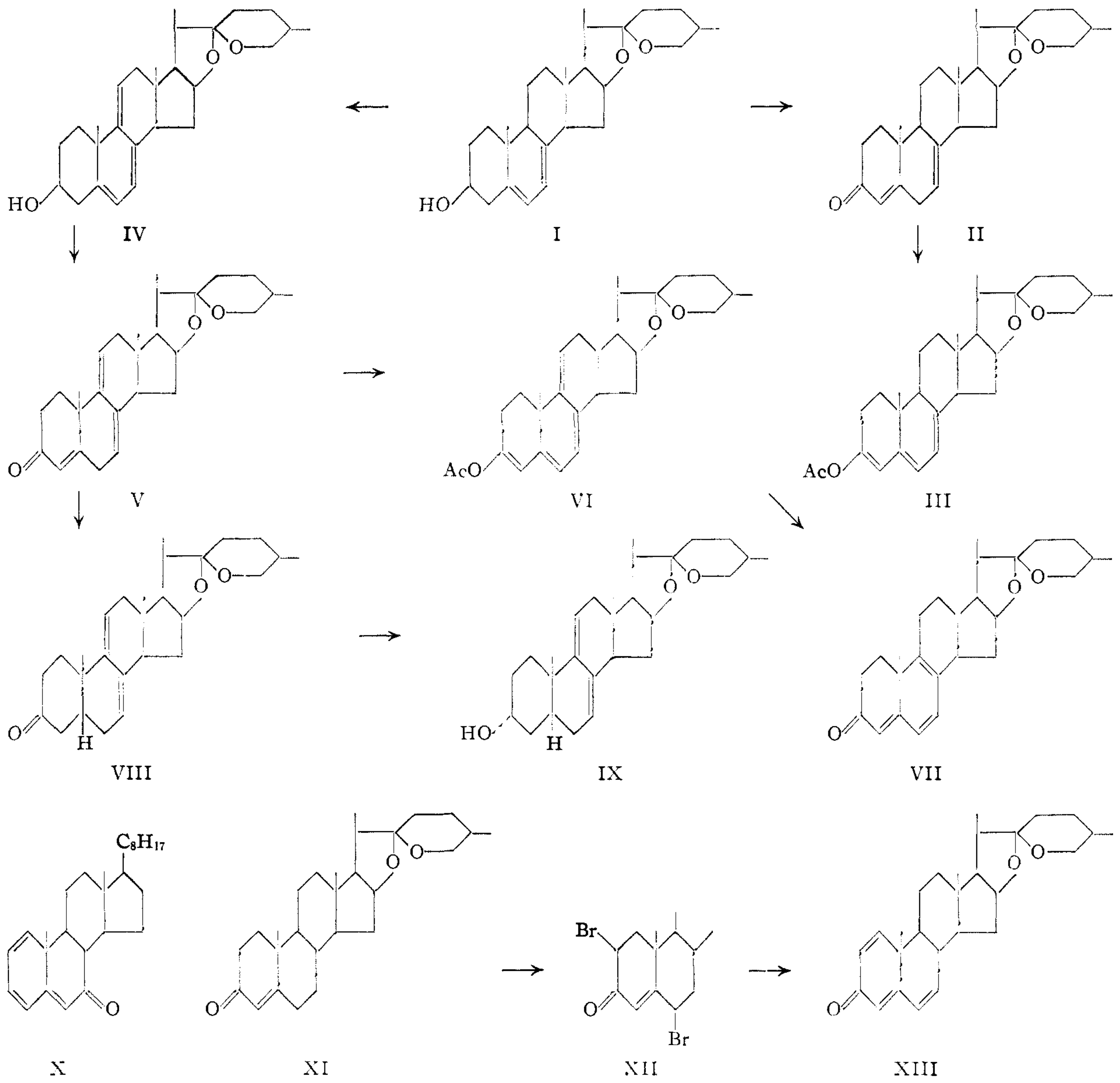
(13) D. H. R. Barton and J. D. Cox, *J. Chem. Soc.*, 219 (1949).

(14) C. W. Shoppee and G. H. R. Summers, *ibid.*, 687 (1950).

(15) A. Butenandt, G. Schramm and H. Kudszus, *Ann.*, **531**, 176 (1937).

(16) C. Djerassi, G. Rosenkranz, J. Romo, St. Kaufmann and J. Pataki, THIS JOURNAL, **72**, 4534 (1950).

(17) P. Karrer and A. R. Naik (*Helv. Chim. Acta*, **32**, 2392 (1949)) report maxima at 230 and 350 mμ (ethanol) without extinction coefficients. Sr. H. J. Flores of our laboratory repeated the Karrer–Naik synthesis and observed the following ultraviolet absorption maxima for the trienone X: 230 mμ (log ε 4.15), 278 mμ (log ε 3.95) and 348 mμ (log ε 3.83).



To complete the preparation and characterization of the isomeric 22-isospirostatrien-3-ones, we have applied the recently described[16] dibromination–dehydrobromination procedure of Δ^4-3-ketosteroids to Δ^4-22-isospirosten-3-one (XI).[18] The resulting $\Delta^{1,4,6}$-22-isospirostatrien-3-one (XIII) exhibited ultraviolet absorption maxima at 222, 256 and 296 mμ, in excellent agreement with the values reported[16] for other steroidal 1,4,6-trien-3-ones, and an infrared carbonyl band at 1656 cm.$^{-1}$. This band, which occurs at lower frequency than any other carbonyl band so far reported for steroids[9] appears to be typical for trienones (VII, X[19] and XIII[20]).

Experimental[21]

$\Delta^{4,7}$-22-Isospirostadien-3-one (II).—A solution of 20 g. of $\Delta^{5,7}$-22-isospirostadien-3β-ol (I)[7] in 700 cc. of toluene and 100 cc. of cyclohexanone was concentrated to a volume of 650 cc., 10 g. of aluminum t-butoxide in 50 cc. of dry toluene was added and the mixture was refluxed for one hour. After addition of a solution of 20 g. of Rochelle salt in 100 cc. of water, the volatile components were removed by steam distillation (1.5 hours) and the residue extracted with ethyl acetate. Evaporation to dryness and recrystallization from methanol afforded 13.8 g. (69%) of nearly colorless crystals with m.p. 183–186°, $[\alpha]^{20}\text{D}$ −62°. The analytical sample of the dienone II was obtained from pentane–ethyl acetate as colorless needles with m.p. 188–190° (Kofler), $[\alpha]^{20}\text{D}$ −65°, ultraviolet absorption maximum at 238 mμ (log ϵ 4.29) and infrared band at 1676 cm.$^{-1}$.

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[18] R. E. Marker, T. Tsukamoto and D. L. Turner, THIS JOURNAL, **62**, 2525 (1940).

[19] $\Delta^{1,3,5}$-Cholestatrien-7-one (X) showed a single carbonyl maximum at 1656 cm.$^{-1}$.

[20] Two additional trienones of this type, $\Delta^{1,4,6}$-androstatrien-17β-ol-3-one 17-acetate (ref. 16) and 9-methyl-3-keto-$\Delta^{1,2;4,10;5,6}$-tetrahydronaphthalene (A. Sandoval, L. Miramontes, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 990 (1951)) also possessed a carbonyl maximum at 1656 cm.$^{-1}$.

[21] Melting points are uncorrected unless marked "Kofler," which were determined on the Kofler block. Rotations were determined in chloroform, ultraviolet absorption spectra (Beckman D. U. spectrophotometer) in 95% ethanol, and infrared spectra (Perkin–Elmer Model 12C spectrometer with sodium chloride prism) in carbon disulfide solution. We are indebted to Srta. Paquita Revaque and staff for all physical measurements and to the Srtas. Amparo Barba and Rachel Cervera for the microanalyses. We are also grateful to Srta. Mercedes Velasco for assistance in certain experiments.

Anal. Calcd. for $C_{27}H_{38}O_3$: C, 78.98; H, 9.33. Found: C, 79.02; H, 9.34.

$\Delta^{3,5,7}$-22-Isospirostatrien-3-ol 3-Acetate (III).—Conversion to the enol acetate was accomplished in nearly quantitative yield by refluxing 0.5 g. of the dienone II with 2 cc. of acetic anhydride and 2 cc. of pyridine for 3 hours and then diluting with water. The precipitated solid was recrystallized from ethyl acetate–methanol; m.p. 188–190°(Kofler), $[\alpha]^{20}\text{D}$ −163°, ultraviolet absorption maxima at 302 mμ (log ε 4.30), 314 mμ (log ε 4.37) and 330 mμ (log ε 4.42), and infrared carbonyl maximum at 1760 cm.$^{-1}$.

Anal. Calcd. for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91. Found: C, 77.29; H, 8.67.

$\Delta^{4,7,9(11)}$-22-Isospirostatrien-3-one (V).—The Oppenauer oxidation of 44 g. of $\Delta^{5,7,9(11)}$-22-isospirostatrien-3β-ol (IV)[3] was carried out exactly as described above with 2 l. of toluene, 400 cc. of cyclohexanone and 22 g. of aluminum *t*-butoxide. Direct crystallization from methanol yielded 8.3 g. of light yellowish crystals with m.p. 163–165°, and chromatography of the mother liquors on 350 g. of ethyl acetate-washed alumina followed by elution with hexane gave an additional 8.1 g. of ketone of the same degree of purity, thus raising the yield to 37%. The analytical sample crystallized from hexane as pale yellowish crystals with m.p. 169–171°, $[\alpha]^{20}\text{D}$ + 210°, ultraviolet absorption maximum at 242 mμ (log ε 4.51), infrared carbonyl band at 1674 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88. Found: C, 79.21; H, 8.82.

$\Delta^{3,5,7,9(11)}$-22-Isospirostatetraen-3-ol 3-Acetate (VI).—After refluxing for 3 hours, a solution of 5.0 g. of the trienone V in 20 cc. of pyridine and 20 cc. of acetic anhydride was poured into 1 l. of water and the yellowish-brown solid collected; yield 5.3 g., m.p. 172–175°. Filtration of this material in hexane–benzene (8:2) solution through a short column of ethyl acetate-washed alumina followed by recrystallization from ethyl acetate–methanol led in 80% yield to nearly colorless crystals of the enol acetate VI with m.p. 175–176° (Kofler), $[\alpha]^{20}\text{D}$ −223°, ultraviolet absorption maxima at 336 mμ (log ε 4.25), 354 mμ (log ε 4.34) and 372 mμ (log ε 4.21) and infrared carbonyl maximum at 1760 cm.$^{-1}$.

Anal. Calcd. for $C_{29}H_{38}O_4$: C, 77.30; H, 8.50. Found: C, 77.60; H, 8.51.

$\Delta^{4,6,8}$-22-Isospirostatrien-3-one (VII).—The above crude enol acetate VI (2.5 g.) was refluxed for one hour with 500 cc. of methanol, 4 cc. of concd. hydrochloric acid and 4 cc. of water, the product precipitated with water and purified by chromatography on 80 g. of alumina. Elution with hexane–benzene (4:6) and recrystallization from methanol–ethyl acetate afforded 1.16 g. (51%) of the trienone VII with m.p. 163–165° (Kofler), $[\alpha]^{20}\text{D}$ +627°, ultraviolet absorption maxima at 244 mμ (log ε 4.25), 284 mμ (log ε 3.34) and 388 mμ (log ε 4.09), and infrared carbonyl band at 1656 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88. Found: C, 79.04; H, 8.81.

The hydrolysis of the enol acetate VI was also studied polarimetrically. A solution of 20 mg. of enol acetate in 1.5 cc. of chloroform, 3.1 cc. of ethanol, 0.15 cc. of water and 0.25 cc. of concd. hydrochloric acid at 20° gave the following values:

Time (hr.)	$[\alpha]^{20}\text{D}$	Time (hr.)	$[\alpha]^{20}\text{D}$
0.05	−111	3	+ 54
.2	−105	4	+108
.5	− 79	6	+231
1	− 36	22	+527
2	− 10	30	+561

$\Delta^{7,9(11)}$-22-Isospirosten-3-one (VIII).—A cooled solution of 2.0 g. of $\Delta^{4,7,9(11)}$-22-isospirostatrien-3-one (V) in 60 cc. of ethanol (distilled over Raney nickel) was treated with a solution of 0.6 g. of potassium hydroxide in 10 cc. of ethanol followed by the addition of 0.15 g. of 10% palladium-on-charcoal catalyst (American Platinum Works, Newark, N. J.). After shaking at room temperature and atmospheric pressure in an atmosphere of hydrogen until no more gas up-take was observed, the catalyst was filtered, the filtrate was acidified and diluted with water, extracted with ether, dried and evaporated. Crystallization from methanol gave 1.06 g. of colorless crystals with m.p. 189–192°, $[\alpha]^{20}\text{D}$ +6°. Further recrystallization raised the m.p. of the dienone VIII to 191–193°, $[\alpha]^{20}\text{D}$ 0°, ultraviolet absorption maxima at 236 mμ (log ε 4.08) and 244 mμ (log ε 4.06). The infrared spectrum showed a carbonyl maximum at 1716 cm.$^{-1}$ (unconjugated 3-ketosteroid[9]) but no hydroxyl band.

Anal. Calcd. for $C_{27}H_{38}O_3$: C, 78.98; H, 9.33. Found: C, 79.11; H, 9.61.

$\Delta^{7,9(11)}$-22-Isospirostadien-3α-ol (IX).—A mixture of 0.8 g. of lithium aluminum hydride in 100 cc. of dry ether was treated dropwise with a solution of 0.8 g. of $\Delta^{7,9(11)}$-22-isospirostadien-3-one (VIII) in 100 cc. of ether. After refluxing for one-half hour, followed by the addition of water and acid, the layers were separated, the ether solution was washed until neutral, dried and evaporated. Recrystallization from methanol yielded 0.55 g. of colorless crystals of the dienol IX with m.p. 208–211° (capillary), 195–197° (Kofler),[22] $[\alpha]^{20}$b +23.4°, ultraviolet absorption maxima at 236 mμ (log ε 4.14) and 244 mμ (log ε 4.17). No carbonyl band was observed in the infrared and an alcoholic solution of the substance gave no precipitate with digitonin, indicating that the hydroxyl group possessed the α-configuration.

Anal. Calcd. for $C_{27}H_{40}O_3$: C, 78.59; H, 9.77. Found: C, 78.48; H, 10.00.

The acetate showed m.p. 154–155° (Kofler), $[\alpha]^{20}\text{D}$ +45°.

Anal. Calcd. for $C_{29}H_{42}O_4$: C, 76.61; H, 9.31. Found: C, 76.35; H, 9.26.

Δ^{4}-2,6-Dibromo-22-isospirosten-3-one (XII).—A solution of 50 g. of Δ^{4}-22-isospirosten-3-one (XI)[18] in 1.2 l. of dry, ice-cold ether containing a few drops of hydrogen bromide–acetic acid was treated dropwise with a solution of 38.8 g. of bromine in 250 cc. of acetic acid. After standing in ice for one-half hour, the colorless crystals of the 2,6-dibromo derivative were filtered, washed with ether and recrystallized from methylene chloride–methanol; yield 55 g., m.p. 205–207° (dec.), $[\alpha]^{20}\text{D}$ −13.9°, ultraviolet absorption maximum at 250 mμ (log ε 4.22).

Anal. Calcd. for $C_{27}H_{38}O_3Br_2$: C, 56.84; H, 6.71; Br, 28.02. Found: C, 56.72; H, 6.98; Br, 28.14.

$\Delta^{1,4,6}$-22-Isospirostatrien-3-one (XIII).—Fifty grams of the 2,6-dibromo ketone XII was refluxed for one hour with mechanical stirring with 300 cc. of re-distilled γ-collidine. After adding ether, the collidine was removed by washing well with dilute acid, and the ether solution was washed until neutral, dried and evaporated to dryness. Several recrystallizations of the residue from acetone led to 15.5 g. (42%) of colorless crystals of the 1,4,6-trien-3-one with m.p. 208–210° (Kofler), $[\alpha]^{20}\text{D}$ −105°, ultraviolet maxima at 222 mμ (log ε 4.13), 256 mμ (log ε 4.09) and 296 mμ (log ε 4.15), typical of 1,4,6-trien-3-ones,[16] and infrared carbonyl band at 1656 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88. Found: C, 79.50; H, 8.45.

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(22) A similar difference in melting points, depending upon the method of determination, has been noticed before in the sapogenin series (ref. 7).