lytical data. They also appreciate the Grant-in-Aid for Scientific Research from the Ministry of Education.

Summary

As a substrate for ATPase action of actomyosin, 6-amino-9-purineëthanol triphosphate was synthesized. 4,6-Dichloro-5-aminopyrimidine was derived to monoethanolamino compound followed by successive cyclization in acetic anhydride-ethyl orthoformate and amination in ammonia. Resulting 6-amino-9-purineëthanol was phosphorylated by polyphosphoric acid method to afford a monophosphate, which was tested as a substrate for 5′-nucleotidase. Di- and triphosphates were prepared by phosphorylation with DCC and phosphoric acid in respective yields of 20.3% and 42.4%.

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Kaname Hamamoto: Studies on the Steroidal Components of Domestic Plants. XXIV. Structure of Metagenin. (4).[1]

(*Research Laboratory, Shionogi & Co., Ltd.*[*1])

As described in the previous paper,[1] metagenin was assigned 5β,25D-spirostane-2β,3β,11α-triol (I), but some doubtful points remained for the final conclusion. One is the Huang-Minlon reduction[2] of metagenone (IIa) or its acetate (IIb), which proceeded easily to afford samogenin diacetate[3] as a reduction product, and this is one of the most important reactions to determine the structure of metagenin. It is well known that the Huang-Minlon reduction does not occur at C-11 ketone of steroids under normal conditions and only proceeds in more drastic conditions, such as at 210°, in completely anhydrous medium.[4] Another question is the datum[*2] of the rotatory dispersion curve of metagenone (IIa) (peak at $[\alpha]_{330}$ +112°, trough at $[\alpha]_{262.5}$ −72°), which is very similar to that of 7-oxocholanic acid derivatives,[5] although this could also be compatible with an 11-oxosapogenin[6] because of the strong negative background rotation of the spiroketal side-chain (cf. Fig. 1). For further elucidation of these problems, elimination reaction of the vicinal two hydroxyl groups in metagenin and metagenone was examined. The elimination reactions of 2,3-dihydroxyl groups in steroidal compounds having C-2 equatorial hydroxyl group were already reported for 5α-[7] and 5β-steroids,[8] and for the present case, the method of Djerassi and Fishman in their studies on samogenin[8] was applied.

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*1 Imafuku, Amagasaki, Hyogo-ken (浜元 要).

*2 This was kindly measured by Dr. C. Djerassi of Stanford University, U. S. A.

1) Part XXIII, Part (3): This Bulletin, 8, 1099 (1960).
2) Huang-Minlon: J. Am. Chem. Soc., **68**, 2487 (1946).
3) Part (2). K. Takeda, H. Hamamoto: This Bulletin, 8, 1004 (1960).
4) (*a*) E. B. Hershberg, E. P. Oliveto, R. Rausser: Chem. & Ind. (London), **1958**, 1477; (*b*) D. H. R. Barton, D. A. J. Ives, B. R. Thomas: J. Chem. Soc., **1955**, 2056.
5) C. Djerassi, W. Clossen: J. Am. Chem. Soc., **78**, 3761 (1956).
6) C. Djerassi, R. Ehrlich: *Ibid.*, **78**, 440 (1956).
7) (*a*) N. L. Wendler, H. L. Slates, M. Tischler: *Ibid.*, **74**, 4894 (1952); (*b*) H. L. Slates, N. L. Wendler: *Ibid.*, **78**, 3749 (1956), Chem. & Ind. (London), **1955**, 167.
8) (*a*) C. Djerassi, J. Fishman: J. Am. Chem. Soc., **77**, 4291 (1955); (*b*) C. Djerassi, J. Fishman, J. A. Moore: Chem. & Ind. (London), **1954**, 1320.

2,3-Bis(methanesulfonyloxy)-x-acetoxymetagenin (IIIb), m.p. 225°(decomp.), obtained from the x-monoacetate[3] (IIIa) by the usual manner, was converted into Δ^2-derivative (IVa), m.p. 165°, with sodium iodide and acetone at 120°, and further saponified to a spirost-2-enol (IVb), m.p. 172°. Catalytic hydrogenation of Δ^2-compound (IVa) afforded a saturated acetoxyl derivative (Va), m.p. 187~188°, and its free alcohol (Vb), m.p. 183°.

A similar reaction was carried out on metagenone (IIa) and a saturated spirostanone (VII), m.p. 172~173°, was obtained through metagenone bismethanesulfonate (IIc), m.p. 208° (decomp.), and Δ^2-derivative (VI), m.p. 178°. This ketone (VII) gave the above-mentioned spirostanol (Vb) with sodium and isopropanol, and also an epimeric alcohol (VIII) with lithium aluminium hydride, but was resistant to the usual carbonyl reagents and to Huang-Minlon reduction.

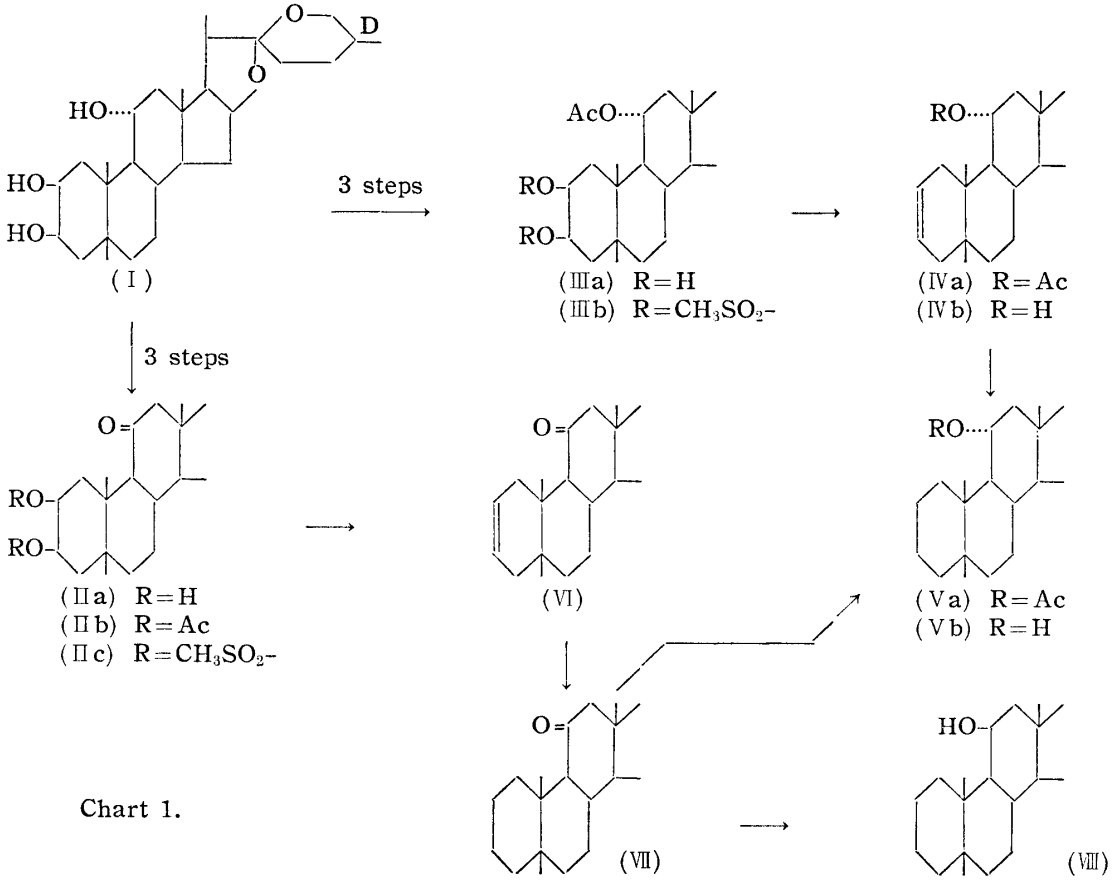

Chart 1.

Next, 5β,25D-spirostan-11α-ol (Vb) or its acetate (Va) was synthesized from 11α-hydroxytigogenin[9] (X) through 11α-acetoxytigogenone[10] (XIb). Introduction of the double bond at C-4 was carried out by the method reported by Romo,[10] but the bromine atom at C-23 was eliminated after saturation of the double bond, since 11α-acetoxy-23-bromo-25D-spirost-4-en-3-one (XIIa) (its free alcohol (XIIb), m.p. 197°(decomp.)) was rather resistant to debromination with zinc and alcohol, and yield of the debromination product (XIII) was very low. The Δ^4-compound (XIIa) was hydrogenated catalytically to give a saturated 23-bromo compound[11] (XIVa) (its free alcohol (XIVb), m.p. 200°(decomp.)), which should have a

9) (*a*) J. H. Chapman, J. Elks, G. H. Phillipps, L. J. Wyman : J. Chem. Soc., **1956**, 4344; (*b*) C. Djerassi, E. Batres, M. Velasco, G. Rosenkranz : J. Am. Chem. Soc., **74**, 1712 (1952); (*c*) F. Sondheimer, O. Mancera, G. Rosenkranz, C. Djerassi : *Ibid.*, **75**, 1282 (1953).

10) J. Romo : Bol. inst. quim. U. N. A. M., **7**, 53 (1955) (C. A., **50**, 12088 (1956)).

11) 23-Bromine was not eliminated by hydrogenation; cf. M. E. Wall, H. W. Jones : J. Am. Chem. Soc., **79**, 3222 (1957).

5β-configuration by the effect of 11α-hydroxyl group.[12] The bromine atom at C-23 in the saturated product (XIVa) was eliminated naturally with zinc and acetic acid, affording 11-acetoxyspirostanone (XVa), m.p. 205~207°, and its free alcohol (XVb), m.p. 243~244°. The latter was oxidized with chromium trioxide in pyridine to give the known 3,11-diketone[13] (XVI), m.p. 206~207°. The Huang-Minlon reduction of the acetoxy-ketone*3 (XVa) proceeded in the usual manner and the reduction product, 5β,25D-spirostan-11α-ol (Vb), m.p. 187~188°, and its acetate (Va), m.p. 181~182°, were identical in all respects with the corresponding degradation product of metagenin. Thus the structure of metagenin, which had been assumed to be 5β,25D-spirostane-2β,3β,11α-triol from chemical evidence, was confirmed finally by the present synthetic method from 11α-hydroxytigogenin.

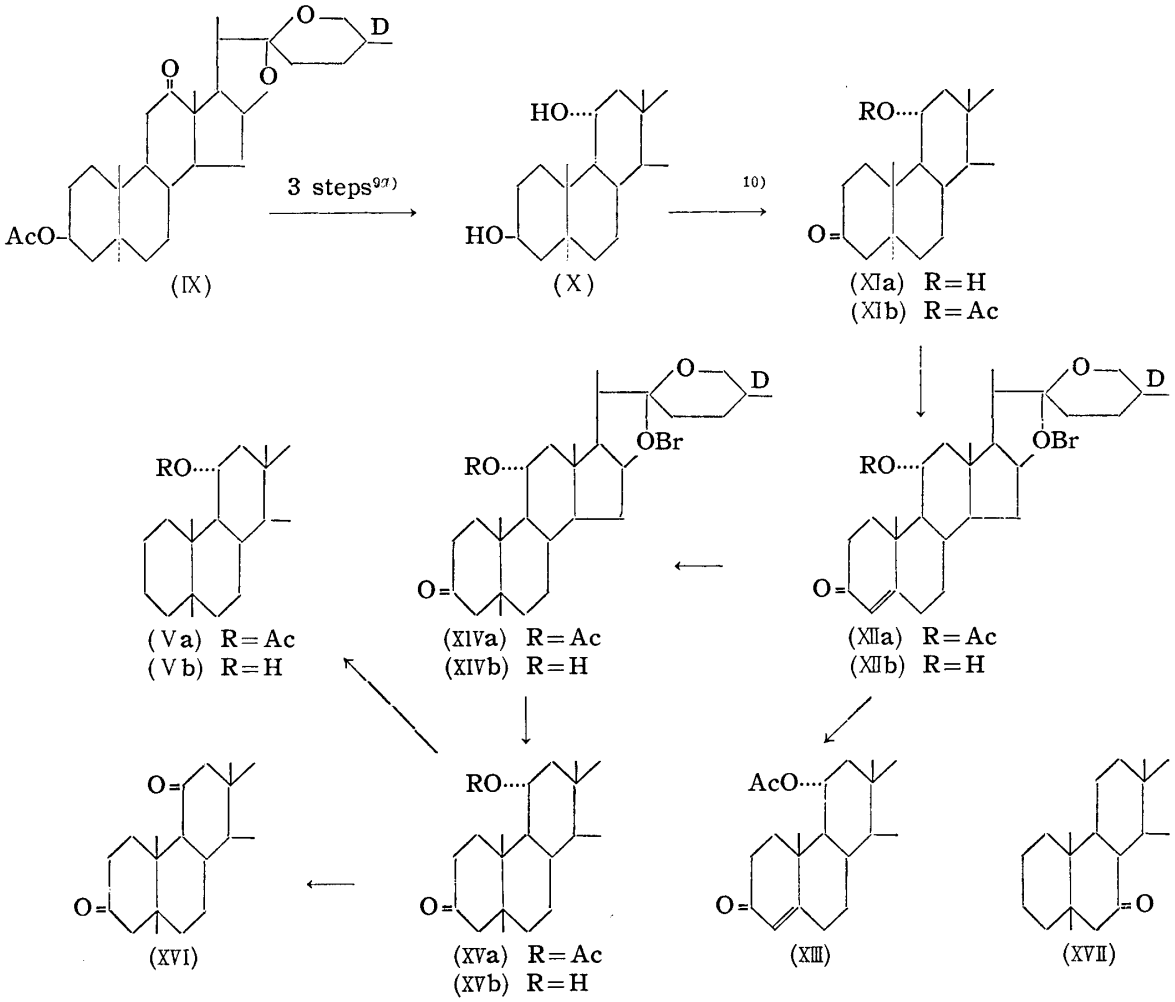

Chart 2.

The rotatory dispersion curves*2 of metagenone (IIa), 5β,25D-spirostan-11-one (VII), and -7-one (XVII)*4 are shown in Fig. 1, in comparison with those of 11-oxo- and 7-oxo-cholanic acid derivatives. It is instructive to note that there is a parallel correlation in

*3 It is doubtful that the Huang-Minlon reduction product of 23-bromo derivative (XIVa), which was mentioned in a communication (Tetrahedron Letters, **3**, 1 (1960)), is the same as (Vb), because of the feature of the spiroketal side-chain in its infrared spectrum, in spite of no depression of a mixed melting point.

*4 This compound, m.p. 155~156°, $[\alpha]_D$ −126.9°, was synthesized in this laboratory and will be reported in the near future.

12) O. Mancera, H.J. Ringold, C. Djerassi, G. Rosenkranz, F. Sondheimer : *Ibid.*, **75**, 1286 (1953).

13) A. J. Lemin, C. Djerassi : *Ibid.*, **76**, 5672 (1954).

the peaks of dispersion curves of these compounds 11-ketone > 7-ketone and oxocholanic acids > 5β,25D-spirostanone, and the differences of the peaks show very similar values in all cases (cf. Table I).

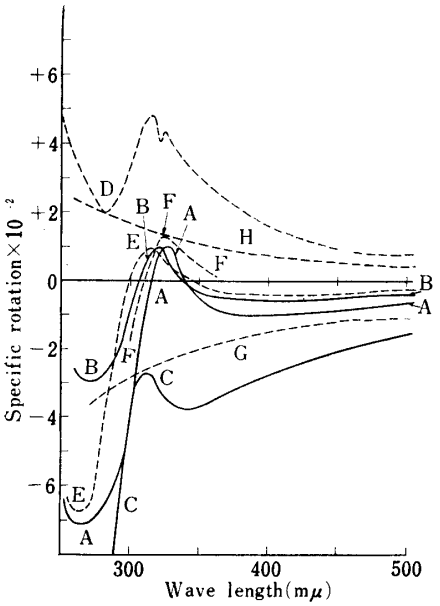

Fig. 1. Rotatary Dispersion Curves

(A) metagenone (IIa)
(B) 5β,25D-spirostan-11-one (VII)
(C) 5β,25D-spirostan-7-one (XVII)
(D) in comparison with those of methyl 3α-acetoxy-11-oxocholanate[5]
(E) 3α-hydroxy-7-oxocholanic acid[5]
(F) 11-oxotigogenone[6]
(G) smilagenin[6]
(H) methyl cholanate[5]

TABLE I. The Peaks of Rotatory Dispersion Curves of 11- and 7-Ketones in Cholic Acids and 5β,25D-Spirostanes

Steroids / Ketone	Cholic Acids ⓐ	5β,25D-Spirostanes ⓑ	ⓐ − ⓑ
11-Ketone ⓒ	(D) $[\alpha]_{317}+499°$[5]	(A) $[\alpha]_{330}+110°$	+389°
		(B) $[\alpha]_{317}+110°$	
7-Ketone ⓓ	(E) $[\alpha]_{312}+95°$[5]	(C) $[\alpha]_{312}-260°$	+345°
ⓒ − ⓓ	+404°	+370°	

(A)~(E) refer to the same symbols in Fig. 1.

Although naturally occurring sarmentogenin and many other 11-oxygenated cardenolide aglycones, and a toad bufadienolide, gamabufotalin, are known in the literature,[14] this is the first example of an 11-oxygenated steroidal sapogenin isolated from a plant source. The steroidal sapogenin is a very important source for steroidal hormone synthesis because its spiroketal side chain is converted easily into the corticoid side chain. Thus, it is very interesting that such a 2, 3, and 11-hydroxylated steroidal sapogenins have been found.

The reason why metagenone underwent the Huang-Minlon reduction is not clear at this stage, but studies on this problem are being continued in this laboratory.

Experimental*5

2β,3β-Bis(methanesulfonyloxy)-11α-acetoxy-5β,25D-spirostane (IIIb)—To a solution of 2.2 g. of metagenin 11-monoacetate (IIIa) in 17 cc. of pyridine 11 cc. of $MeSO_2Cl$ was added and the mixture was left for 42 hr. at room temperature (20°). The dark-brown mixture was poured into mixture of $CHCl_3$ and 10% HCl, extracted with $CHCl_3$, and the $CHCl_3$ layer was washed with water, dried, and evaporated. The crude product (2.5 g.) was chromatographed on alumina and the eluate with benzene

*5 All m.p.s are uncorrected. Rotations were measured in $CHCl_3$ solution.
14) L. F. Fieser, M. Fieser : "Steroids," 727 (1959). Reinhold Publ. Corp., New York.

furnished 2.2 g. of needles, m.p. 225° (decomp.); $[\alpha]_D^{25}$ −84.8° *Anal.* Calcd. for $C_{31}H_{50}O_{10}S_2$: C, 57.56; H, 7.79. Found : C, 57.59; H, 7.85.

11α-Acetoxy-5β,25D-spirost-2-ene (IVa)—Dimethanesulfonate (IIIb) (2.1 g.) was heated with 67 cc. of Me_2CO and 5.7 g. of NaI in a glass-tube in an autoclave at 115~120° for 24 hr. The red-brown mixture was evaporated, diluted with $CHCl_3$, washed with $Na_2S_2O_3$ solution and water, dried, and evaporated. The oily residue (1.9 g.) was chromatographed on alumina and the eluate with benzene-petr. ether (1:1) yielded 1.2 g. of (IVa), m.p. 165.5~166° (from MeOH). $[\alpha]_D^{25}$ −84.6°. *Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.27; H, 9.71. Found : C, 76.17; H, 9.79. IR λ_{max}^{Nujol} μ : 8.06; 5.64 (AcO); 5.99 (double bond at C-2).

5β,25D-Spirost-2-en-11α-ol (IVb)—A solution of 100 mg. of acetoxyspirostene (IVa) in 20 cc. of 5% KOH-MeOH was refluxed for 1 hr. and was processed in the usual manner. The crude product was recrystallized from $CHCl_3$-MeOH to give crystals of (IVb), m.p. 170~172°. $[\alpha]_D^{15}$ −98.7°. *Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found : C, 78.11; H, 10.19. IR λ_{max}^{Nujol} μ : 6.03 (double bond at C-2); 2.83 (OH).

11α-Acetoxy-5β,25D-spirostane (Va)—11α-Acetoxyspirostene (IVa) (1.1 g.) was dissolved in 40 cc. of EtOAc and hydrogenated catalytically over 100 mg. of PtO_2. The crude product, m.p. 186~188° (1.1 g.), was recrystallized from MeOH-$CHCl_3$ to (Va), needles of m.p. 187~188°. $[\alpha]_D^{25}$ −98.4°. *Anal.* Calcd. for $C_{29}H_{46}O_4$: C, 75.94; H, 10.11. Found : C, 75.77; H, 10.16. IR λ_{max}^{Nujol} μ : 8.07, 5.78 (AcO).

5β,25D-Spirostan-11α-ol (Va)—a) From 11-Acetate (Va) : 11-Acetate (Va) (1.0 g.) in 20 cc. of 10% KOH-EtOH was refluxed for 1 hr. and processed in the usual manner. The crude product (m.p. 175~177°) was recrystallized from MeOH-$CHCl_3$ to 0.9 g. of (Vb), m.p. 182.5~183°. $[\alpha]_D^{25}$ −77.1°. *Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.83; H, 10.65. Found : C, 77.81; H, 10.83. IR : λ_{max}^{Nujol} 2.81 μ (OH).

b) From 11-Ketone (VII) : To a solution of 100 mg. of 11-ketone (VII) in 4 cc. of iso-PrOH 200 mg. of Na was added under reflux, which was continued until complete dissolution of Na (35 min.). The solidified reaction mixture was diluted with water and extracted with Et_2O, which was washed with water, dried, and evaporated. The crude product (m.p. 162~167°) was recrystallized from MeOH-$CHCl_3$ to crystals of (VII), m.p. 181~182°, which proved to be identical with the sample obtained by method (a) by admixture.

c) From 11α-Acetoxy-5β,25D-spirostan-3-one (XVa) by Huang-Minlon reduction : 11-Acetoxyspirostan-3-one (XVa) (160 mg.) was refluxed with 5 cc. of triethylene glycol, 0.5 cc. of 80% $NH_2NH_2 \cdot H_2O$ and 0.5 g. of KOH at 120~130° for 1 hr. and heated at 190~200° for 4 hr. The reduction product was processed in the usual manner and yielded 120 mg. of pale-brown syrup, which was chromatographed on alumina. The eluate with petr. ether-benzene (4:1) yielded 80 mg. of crystals of m.p. 176~182°, which was raised on further recrystallization from MeOH to m.p. 181~182°. Identity with the sample from (a) was established by comparison of IR spectrum and admixture.

The above crystals of m.p. 181~182° (40 mg.) was acetylated with 2 cc. of Ac_2O by refluxing for 1 hr., yielding 30 mg. of acetate (Va), m.p. 187~187.5°, which proved to be identical with the sample mentioned above by a mixed m.p. and IR comparison.

2β,3β-Bis(methanesulfonyloxy)-5β,25D-spirostan-11-one (IIc)—A mixture of 1.0 g. of metagenone (IIa) with 7.5 cc. of pyridine and 5 cc. of $MeSO_2Cl$ was left for 40 hr. at room temperature (20°) and processed as described for (IIIb). The crude product was purified on alumina, yielding from the eluate with Et_2O-$CHCl_3$ (1:1) 1.1 g. of (IIc), m.p. 208° (decomp.) (from $CHCl_3$-MeOH). $[\alpha]_D^{25}$ −78.9°. *Anal.* Calcd. for $C_{29}H_{46}O_9S_2$: C, 57.78; H, 7.69. Found : C, 57.72; H, 7.82.

5β,25D-Spirost-2-en-11-one (VI)—Dimethanesulfonate (IIc) (1.1 g.) was heated with 35 cc. of Me_2CO and 3.0 g. of NaI in a glass-tube in an autoclave at 116~120° for 24 hr. and the red-brown reaction mixture was processed as described for (IVa). The crude product was purified on alumina and the eluates with petr. ether was recrystallized from $CHCl_3$-MeOH to 0.5 g. of (VI), m.p. 177~178°. $[\alpha]_D^{25}$ −30.3°. *Anal.* Calcd. for $C_{27}H_{40}O_3$: C, 78.59; H, 9.77. Found : C, 78.61; H, 9.94. IR λ_{max}^{Nujol} μ : 5.88 (C=O); 3.31 (double bond at C-2).

5β,25D-Spirostan-11-one (VII)—Spirostenone (VI) (500 mg.) in 30 cc. of EtOAc was hydrogenated catalytically over Pd-C and processed in the usual manner. The crude product (m.p. 168~169°) was recrystallized from $CHCl_3$-MeOH to 300 mg. of saturated ketone (VII), m.p. 172~173°. $[\alpha]_D^{25}$ −40.1°. *Anal.* Calcd. for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found : C, 78.35; H, 10.16. IR : λ_{max}^{Nujol} 5.88 μ (C=O).

5β,25D-Spirostan-11β-ol (VIII)—To a solution of 100 mg. of 11-ketone (VII) in 10 cc. of tetrahydrofuran, 100 mg. of $LiAlH_4$ was added and the mixture was refluxed for 2 hr. The crude product, obtained by the usual manner, was chromatographed on alumina affording from the eluate with benzene 80 mg. of (VIII), m.p. 174~176°, raised on further recrystallization from $CHCl_3$-MeOH to m.p. 176~177°. $[\alpha]_D^{25}$ −52.0°. *Anal.* Calcd. for $C_{27}H_{44}O_3$: C, 77.83; H, 10.65. Found : C, 77.73; H, 10.63. IR: λ_{max}^{Nujol} 2.83 μ (OH).

A mixed m.p. with the starting material (VII), m.p. 172~173°, or 11α-alcohol (IVb), m.p. 182.5~183°, was depressed to 163~169° or to 158~173°, respectively.

11α-Hydroxy-23-bromo-25D-spirost-4-en-3-one (XIIb)—Bromination and Δ^4-formation of 11α-

acetoxy-5α,25D-spirostan-3-one (XIb) were carried out exactly according to the procedure of Romo.[10] A solution of 4 g. of (XIb), m.p. 194~196°, synthesized from hecogenin acetate[9a] (IX) via 11α-hydroxytigogenin,[10] in 70 cc. of AcOH containing 5 drops of 4*N* HBr-AcOH was brominated with a solution of 4 g. of Br_2 in 45 cc. of AcOH and yielded 5.2 g. of crude 2,4,23-tribromo derivative. The tribromo compound (5.2 g.) in 350 cc. of Me_2CO was treated with 15 g. of NaI for 20 hr. under refluxing and processed as described in the literature,[10] affording 4.4 g. of syrupy residue (2-iodo-11α-acetoxy-23-bromo-25D-spirost-4-en-3-one; λ_{max}^{EtOH} 241 mμ (ε 10600)). This was dissolved in a mixture of 190 cc. of Me_2CO and 25 cc. of dioxane, and deiodized with $CrCl_2$ solution. The oily residue, obtained by the usual manner, was chromatographed on alumina and gave from the eluates with petr. ether-benzene(1:1) and benzene, 1.8 g. of an oily product (11α-acetoxy-23-bromo-25D-spirost-4-en-3-one (XIIa), λ_{max}^{EtOH} 241 mμ (ε 16100)). As the acetate (XIIa) did not crystallize by recrystallization or chromatography on alumina, it was saponified with 10% KOH-MeOH under reflux, followed by purification on alumina to give from the benzene-Et_2O (4:1) eluate 1.3 g. of (XIIb), m.p. 197° (decomp.). $[\alpha]_D^{16}$ −16.1°. Beilstein's test for halogen was positive. *Anal.* Calcd. for $C_{27}H_{39}O_4Br$: C, 63.90; H, 7.75; Br, 15.75. Found: C, 64.18; H, 7.75; Br, 15.45. IR λ_{max}^{Nujol} μ: 6.24 (C=C), 6.03 (conjugated C=O), 2.85 (OH).

11α-Hydroxy-23-bromo-5β,25D-spirostan-3-one (XIVb)—Above-mentioned 23-bromo compound (XIIb) (1.2 g.) was acetylated with Ac_2O and pyridine, and the oily acetate (XIIa) (1.1 g.) was hydrogenated with 0.6 g. of 30% Pd-C in 50 cc. of EtOAc to give 1.0 g. of saturated 23-bromo derivative (XIVa). The acetate (XIVa) (0.5 g.), which did not crystallize by the usual treatment, was saponified with 30 cc. of 10% KOH-MeOH under reflux for 1 hr. The oily residue (0.5 g.) was purified on alumina and yielded from the benzene-Et_2O (1:1) eluate 400 mg. of (XIVb), m.p. 200° (decomp.). $[\alpha]_D^{20}$ −56.5°. *Anal.* Calcd. for $C_{27}H_{41}O_4Br$: C, 63.64; H, 8.11. Found: C, 63.81; H, 8.15. UV: no absorption maxima of Δ^4-3-one. IR λ_{max}^{Nujol} μ: 5.87 (C=O), 2.80 (OH).

11α-Acetoxy-5β,25D-spirostan-3-one (XVa)—A solution of 400 mg. of 11α-acetoxy-23-bromo compound (XIVa) (oil) in 25 cc. of AcOH was heated with 5 g. of Zn powder for 6 hr. on a water bath. Filtration, dilution with water, extraction with Et_2O, and evaporation of the solvent furnished 350 mg. of oily residue. Chromatography on alumina yielded from the petr. ether-benzene (1:1) and benzene eluates, 230 mg. of crystals, m.p. 188~194°, raised on further recrystallization from MeOH to m.p. 205~207°. $[\alpha]_D^{18}$ −80.0°. *Anal.* Calcd. for $C_{29}H_{44}O_5$: C, 73.69; H, 9.38. Found: C, 73.32; H, 9.28. IR λ_{max}^{Nujol} μ: 5.89, 8.06 (C=O and AcO).

11α-Hydroxy-5β,25D-spirostan-3-one (XVb)—The acetate (XVa) (230 mg.) was sponified with 5% KOH-MeOH yielding 180 mg. of a free alcohol (XVb), m.p. 243~244° (after recrystallization from MeOH-$CHCl_3$). $[\alpha]_D^{21}$ −76.3° *Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.31; H, 9.83. Found: C, 74.95; H, 9.80. IR λ_{max}^{Nujol} μ: 5.90 (C=O), 2.82 (OH).

5β,25D-Spirostane-3,11-dione (XVI)—11α-Hydroxyspirostan-3-one (XVb) (80 mg.) in 4 cc. of pyridine was oxidized with 80 mg. of CrO_3 in 2 cc. of pyridine for 48 hr. at room temperature. The crude product was recrystallized from $CHCl_3$-petr. ether to 30 mg. of (XVI), m.p. 206~207° (reported[13] m.p. 204~206°). $[\alpha]_D^{20}$ −25.9°. *Anal.* Calcd. for $C_{27}H_{40}O_4$: C, 75.69; H, 9.40. Found: C, 75.76; H, 9.49. IR: λ_{max}^{Nujol} 5.85 μ (C=O).

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Summary

Metagenin (I) and metagenone (IIa) were respectively converted to 5β,25D-spirostan-11α-ol (Vb) and -11-one (VII) by the elimination of the 2,3-dihydroxyl groups. Spirostan-11α-ol (Vb) was confirmed by comparison with the product synthesized from 11α-acetoxytigogenone (XIa) and thus the structure of metagenin was finally established as 5β,25D-spirostane-2β,3β,11α-triol. The rotatory dispersion curves of metagenone (IIa), 5β,25D-spirostan-11-one (VII), and -7-one (XVII) were measured and discussed.

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