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STRUCTURE OF YONONIN

A NOVEL TYPE OF SPIROSTANOL GLYCOSIDE

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Abstract—Two isomeric monomethyl ethers of yonogenin (25D,5β-spirostane-2β,3α-diol) have been synthesized and the 3-methyl ether identified as the aglycone of permethyl yononin. Thus, yononin, an α-L-arabinoside of yonogenin from the rhizome of *Dioscorea Tokoro* Makino, is shown to be a novel type of spirostanol glycoside in which the sugar moiety is attached to the hydroxyl group at C-2, and not at C-3, of the aglycone.

YONONIN, one of the spirostanol glycosides in the rhizome of *Dioscorea Tokoro* Makino, is an α-L-arabinoside[1] of yonogenin which was first isolated from the epigeous part of the same plant in a free state and assigned the structure, 25D,5β-spirostane-2β,3α-diol, by Okanishi *et al.* and Takeda *et al.*[2]

Usually natural spirostanol has a 3β-hydroxyl group and occurs in the plant mainly as its glycoside (steroid saponin)[3] and the site of sugar linkage has been regarded as the hydroxyl group at C-3 of the aglycone.[4] However, in the glycoside of a spirostanol with more than two hydroxyl groups, no definite evidence to support this presumption has been presented. In the previous paper[5] we proved the conjugation of lycotetraose with 3β-hydroxyl group of gitogenin (25D,5α-spirostane-2α,3β-diol) to form F-gitonin, and the present paper deals with the determination of the yononin structure, the point of attachment of arabinose to this unusual[3] spirostanol, yonogenin.

Yononin permethylate prepared by the Kuhn method[6] provides, on hydrolysis, an aglycone (I), m.p. 184 ~ 186°, $[\alpha]_D$ −58°, R_f 0·34 (yonogenin R_f 0·06). The aglycone (I) must be a yonogenin monomethyl ether and the synthesis of the 2- and 3-methyl ethers and the direct comparison with I were undertaken.

The synthetic route of yonogenin 2-methyl ether (II) starting from diosgenin, 25D-spirost-5-en-3β-ol, is shown in Scheme 1.

2α-Methoxy-4-en-3-one (IV) is prepared by methylation with methyl iodide and

[1] T. Kawasaki and T. Yamauchi, *Yakugaku Zasshi* **83**, 757 (1963).

[2] T. Okanishi and A. Shimaoka, *Ann. Repts. Shionogi Research Lab.* **6**, 78 (1956); K. Takeda, T. Okanishi and A. Shimaoka, *Yakugaku Zasshi* **77**, 822 (1957); *Chem. Pharm. Bull., Tokyo* **6**, 532 (1958).

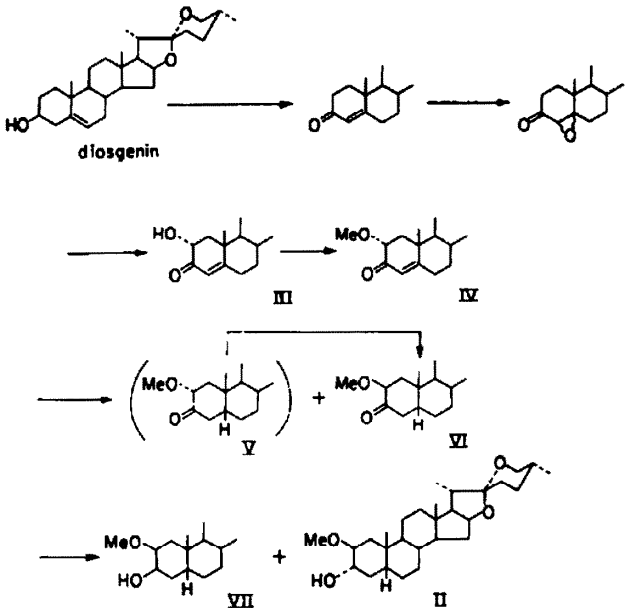
[3] Yonogenin and the related tri- and tetraols, tokorogenin (K. Morita, *Pharm. Bull., Tokyo* **5**, 494 (1957); *Bull. Chem. Soc. Japan* **32**, 791 (1959)) and kogagenin (T. Kubota, *Tetrahedron* **7**, 62 (1959); *Chem. Pharm. Bull., Tokyo* **7**, 898 (1959)), are the only three spirostanols shown to have an unusual 3α-hydroxyl group. These are mainly present in a free state in the epigeous part of *Dioscorea Tokoro* Makino in contrast to diosgenin which has the 3β-hydroxyl group and is contained as its glycosides in the rhizome of the same plant (A. Akahori, *Ann. Repts. Shionogi Research Lab.* **11**, 93 (1961); **10**, 1411 (1960)).

[4] R. Tschesche and G. Wulff, *Planta Medica* **12**, 272 (1964).

[5] T. Kawasaki, I. Nishioka, T. Komori, T. Yamauchi and K. Miyahara, *Tetrahedron* **21**, 299 (1965).

[6] R. Kuhn, I. Löw and H. Trischmann, *Chem. Ber.* **88**, 1492, 1690 (1955).

Scheme 1



silver oxide of the corresponding 2α-hydroxy compound (III) which is synthesized from 4,5-epoxy-25D-spirostan-3-one by the method of Camerino *et al.*[7] The structures III and IV are confirmed by the UV, IR and ORD (Fig. 1) spectra in comparison with those of the analogous compounds.[7,8] When IV is hydrogenated in ethanol over Pd two saturated compounds are provided of which the main product (R_f 0·62) is converted to the minor one (R_f 0·45), partly, on passing through an alumina column or boiling in methanol and, completely, on treatment with potassium hydroxide in methanol. It suggests that the less polar product (main) is 2α(axial)-methoxy-5β-spirostan-3-one (V) and the polar one the 2β(equatorial)-epimer (VI). The desired VI is obtained in a pure form by chromatography of the mixture on alumina or by treatment with alkali followed by recrystallization, and its β-configuration at C-5 and C-2 is supported by a negative Cotton curve[9,10] of the ORD spectrum (Fig. 2)

[7] B. Camerino, B. Patelli and A. Vercellone, *J. Amer. Chem. Soc.* **78**, 3540 (1956).

[8a] A. Meyer, *J. Org. Chem.* **20**, 1240 (1955); [b] P. Narasimha Rao and L. R. Axelrod, *J. Amer. Chem. Soc.* **82**, 2830 (1960); P. Narasimha Rao, H. R. Gollberg and L. R. Axelrod, *J. Org. Chem.* **28**, 270 (1963); S. Burstein and H. L. Kimball, *Steroids* **2**, 1 (1963); S. L. Patashnik, H. L. Kimball and S. Burstein, *Ibid.* **2**, 19 (1963); K. Kuriyama, E. Kondo and K. Tori, *Tetrahedron Letters* 1485 (1963).

[9] Cf. 5β-Spirostan-2- and 3-ones [K. Takeda and H. Minato, *Steroids* **1**, 345 (1963)]. An hydroxyl or acetoxyl group adjacent to a carbonyl group does not affect the sign of the Cotton effect of the parent steroid ketone [C. Djerassi, *Optical Rotatory Dispersion*, p. 112, 113. McGraw-Hill, New York, N.Y. (1960)]. The ORD curves of the methylethers of 2α-ol-3-one and 3β-ol-2-one in 5α-cholestane[11] and 5α-spirostane[6] series are similar to those of the corresponding acetates.

[10] According to the unpublished data kindly informed of (Oct. 14, 1964) by Dr. K. Takeda, ORD (in MeOH) and IR (in CCl_4) spectra of 5β-spirostan-2- and 3-ones are as follows: 2-one, trough $[\alpha]_{309}$ −615°, peak $[\alpha]_{278}$ +131°, $\nu_{C=O}$ 1719 cm^{-1}; 3-one, trough $[\alpha]_{306}$ −394°, peak $[\alpha]_{271}$ 0°, $\nu_{C=O}$ 1718 cm^{-1}.

[11] S. S. Stradling and D. S. Tarbell, *J. Org. Chem.* **29**, 1170 (1964).

and by a carbonyl absorption[12,13] shift from 1718 cm^{-1} [10] of the parent ketone to 1732 cm^{-1}. The reduction of VI with sodium borohydride in methanol or with lithium borohydride in pyridine[14] gives a mixture of epimeric 2β-methoxy-3-ols (VIII and II). They are separated by chromatography on silica gel or alumina and, taking into account the R_f-conformation relationship in steroid,[15] the more readily eluted isomer, m.p. 205 ~ 208°, $[\alpha]_D$ −49°, R_f 0·43, is regarded as 3β(axial)-ol (VII) and the less

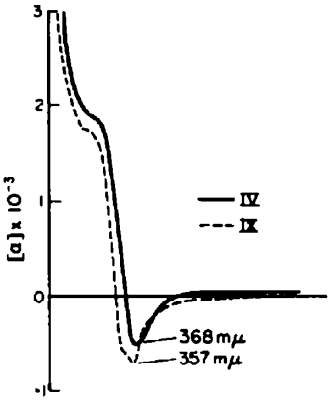


FIG. 1.

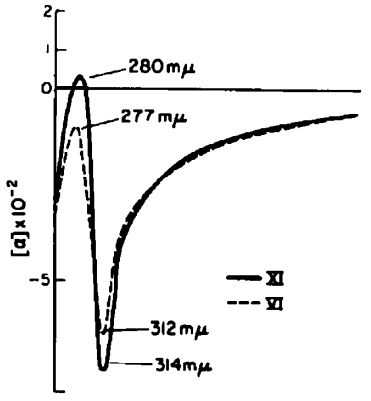


FIG. 2.

readily eluted one, m.p. 265 ~ 266°, $[\alpha]_D$ −67°, R_f 0·30, as 3α(equatorial)-ol, that is, yonogenin 2-methyl ether (II).

Yonogenin 3-methyl ether (VIII) is synthesized as shown in Scheme 2.

2α-Acetoxy-4-en-3-one (IX) is prepared by acetylation of III with acetic anhydride and pyridine and the structure is confirmed as in the case of the corresponding methoxy derivative (IV). Compound IX is hydrogenated in ethyl acetate over Pd and the product is further reduced with sodium borohydride in methanol. The resultant saturated diol monoacetates are methylated and subsequently hydrolysed with alkali to afford a mixture of four isomeric 3-methoxy-25D-spirostan-2-ols (Xa, b and c).[16] Chromatography of the mixture on alumina gives a pure compound (X'), m.p. 161 ~ 162°, $[\alpha]_D$ −31°, R_f 0·61, as the major component and this is assumed to be 3-methoxy-5β-spirostan-2α-ol[16] (Xa or Xb). The diol monomethyl ether is oxidized with chromium trioxide to provide a methoxy ketone, m.p. 198°, IR 1733 cm^{-1}, ORD (Fig. 2), which is assigned the structure, 3α(equatorial)-methoxy-

[12] It is reported[11] that the equatorial methoxyl group adjacent to the carbonyl group in 5α-cholestan-2- and 3-ones raises the carbonyl absorption frequency, whereas the axial one does not have a significant effect. It is also the case in 5α-spirostane series.[8]

[13] According to the unpublished data kindly informed of (Sept. 15, 1964) by Dr. K. Takeda, 3α-(equatorial)-acetoxy-5β-spirostan-2-one and its isomer, 2β(equatorial)-acetoxy-3-one, show their carbonyl absorptions (in CS_2) both at 1735 cm^{-1} which is shifted from those of the respective parent ketones,[10] and the former has a larger ORD amplitude than that of the latter.

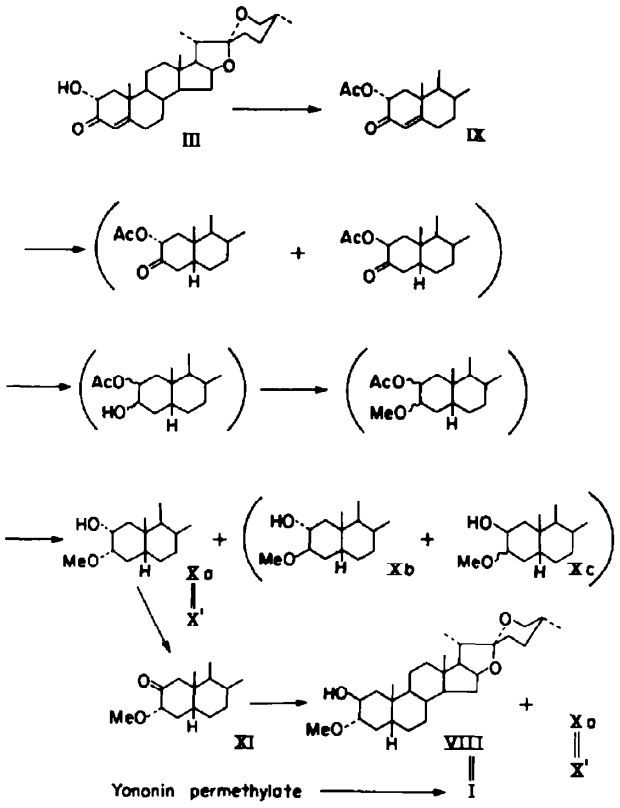
[14] C. D. Ritchie, *Tetrahedron Letters* 2145 (1963).

[15] K. Savard, *J. Biol. Chem.* **202**, 457 (1953); S. Hara and M. Takeuchi, *J. Chromatog.* **11**, 565 (1963); M. Takeuchi, *Chem. Pharm. Bull., Tokyo* **11**, 1183 (1963).

[16] By analogy with the hydrogenation of IV, IX is thought to be reduced to give mainly 2α-acetoxy-5β-spirostan-3-one together with a minor amount of its 2β-epimer. Therefore X is assumed to be a mixture of four isomeric 5β-derivatives in which Xa or Xb is predominant.

5β-2-one (XI), on the basis of its negative Cotton curve[9,10] with larger[17] amplitude than that of the curve of II and a hypsochromic shift of the carbonyl absorption from 1719 cm^{-1} [10] of the parent ketone. The equatorial orientation of the methoxyl group is supported also by the fact that the methoxy ketone is not epimerized with alkali. When XI is treated with sodium borohydride in methanol the carbonyl group at C-2 is reduced only to regenerate the original diol monomethyl ether (X′) indicating the α- and β-configurations, respectively at C-3 and C-5 in X′, while the reduction with lithium borohydride in pyridine[14] yields a mixture of X′ (R_f 0·61) and

Scheme 2



its 2-epimer (R_f 0·34). They are cleanly separated on alumina to give the former from the first fraction and the latter, m.p. 185 ~ 188°, $[\alpha]_D$ −53°, from the second. Since 3α-methoxy-5β-spirostan-2α(axial)-ol (Xa) is considered[15] to move faster on alumina and on silica gel than its 2β(equatorial)-epimer (VIII), X′ is assigned the structure Xa and the less mobile product is regarded as 3α-methoxy-25D,5β-spirostan-2β-ol (VIII), that is, yonogenin 3-methyl ether.

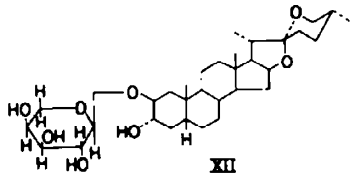
The aglycone (I) of permethyl yononin is compared with VIII and II, and identified

[17] The amplitude of the dispersion curve of 5β-spirostan-2-one is much larger than that of 3-one.[9,10] In 5α-cholestane[11] and 5α-spirostane[5] series the ORD curves of 3β-methoxy(acetoxy)-2-ones show larger amplitude than those of the corresponding 2α-methoxy(acetoxy)-3-ones. Cf. also footnote 13.

with VIII by undepressed mixed m.p., superimposable IR spectra and single spot on a co-chromatogram.

Consequently yononin is defined as 0-α-L-arabinosyl(1-2)-25D,5β-spirostane-2β,3α-diol (yonogenin 2-α-L-arabinoside) (XII).

This is the first[4] spirostanol glycoside shown to have the sugar moiety combined with a hydroxyl group other than that at C-3 of the aglycone.



XII

EXPERIMENTAL

All m.ps were taken on a Kofler block and are uncorrected; rotations were determined in $CHCl_3$; IR spectra were obtained with a Koken IR Recording Spectrophotometer; UV spectra were run in EtOH on a Shimadzu Automatic Recording Spectrophotometer; ORD curves were measured using a Rudolph Recording Spectropolarimeter. R_f values were determined by TLC on silica gel G (Merck) using cyclohexane–ethyl acetate (3:1) mixture as a solvent and 10% H_2SO_4 (spraying followed by heating) as a visualizing agent.

Aglycone (I) *of yononin permethylate*

Yononin[1] (200 mg) was methylated in dimethylformamide (5 ml) with MeI (2·3 g) and Ag_2O (1 g) according to the Kuhn method[6] and the procedure was repeated twice. A syrup thus obtained, showing no hydroxyl absorptions in the IR spectrum, was refluxed with 2N HCl in 50% EtOH (4 ml) for 2 hr and the mixture diluted with water. The precipitates (90 mg) were collected by filtration and chromatographed on alumina followed by recrystallization from MeOH to provide pure I (24 mg), needles, m.p. 184 ~ 186°, $[\alpha]_D$ −58° (*c*, 0·55), R_f 0·34 (yonogenin, R_f 0·06); ν_{max}^{KBr} 3658, 3585, 981, 917 < 897, and 863 cm^{-1}.

4,5-*Epoxy*-25D-*spirostan*-3-*one*

25D-spirost-4-en-3-one (5 g; m.p. 185 ~ 186°, $[\alpha]_D$ +4° (*c*, 0·52), λ_{max} 242 mμ (ε, 13,100), ν_{max}^{Nujol} 1683 and 1622 cm^{-1}) prepared from diosgenin was dissolved in MeOH (350 ml) and a cold mixture of 30% H_2O_2 (20 ml) and 4N NaOH (20 ml) was added in 10 min. The reaction mixture was stirred at 2° for 7 hr, left stand in a refrigerator overnight and diluted with water (400 ml). The precipitates were collected by filtration, dried and recrystallized from EtOH to give the 4,5-oxide (3·91 g), plates, m.p. 200°. Further recrystallization from MeOH gave a pure sample, needles, m.p. 205 ~ 207°, $[\alpha]_D$ + 23° (*c*, 0·53). (Found: C, 75·55; H, 9·45. Calc. for $C_{27}H_{40}O_4$: C, 75·66; H, 9·41%.)

2α-*Hydroxy*-4-*en*-3-*one* (III)

To a solution of the above oxide (2·98 g) in acetone (100 ml) was added 25% H_2SO_4 (6 ml) in dropwise and the mixture was left stand at 20° for 4 days. Crystals separated out were filtered off (1·175 g) and the filtrate diluted with water (300 ml) to yield precipitates (1·73 g). Both crops were combined and recrystallized from acetone to provide III, plates, m.p. 213·5 ~ 215·5°, $[\alpha]_D$ +21° (*c*, 0·65); λ_{max} 242·5 mμ (ε, 13,700); $\lambda_{max}^{0.005N\ KOH-MeOH}$ 238 (3 min), 234 (2 hr), 233 mμ (46 hr);[8c] ν_{max}^{KBr} 3528, 3432, 1672 and 1619 cm^{-1}. (Found: C, 75·63; H, 9·43. $C_{27}H_{40}O_4$ requires: C, 75·66; H, 9·41%.)

2α-*Methoxy*-4-*en*-3-*one* (IV)

Compound III (1 g) in dry benzene (25 ml) was stirred with MeI (3 g) and Ag_2O (3 g) for 20 hr. The precipitates were removed by filtration, the filtrate was evaporated *in vacuo* to dryness and the residue (1 g) was crystallized from MeOH to give IV (820 mg). Pure sample was obtained by recrystallization from hexane, needles, m.p. 198 ~ 201°, $[\alpha]_D$ +29° (*c*, 0·44); λ_{max} 241·6 mμ (ε, 14,600); ν_{max}^{KBr}

1677 and 1629 cm^{-1} (no hydroxyl absorptions); ORD (Fig. 1), trough $[\alpha]_{366}$ −498° (*c*, 0·061, dioxan). (Found: C, 76·10; H, 9·45. $C_{28}H_{42}O_4$ requires: C, 75·97; H, 9·65%.)

Catalytic hydrogenation of IV

Compound IV (200 mg) in EtOH (40 ml) was hydrogenated over 10% Pd–C (50 mg). After absorption of 1 mole H_2 catalysts were removed and EtOH was evaporated to give a crystalline solid (205 mg). The product revealed on TLC one distinct spot (R_f 0·62) accompanied by two faint ones (R_f 0·45, 0·27), but when chromatographed on alumina (neutral, 4 g) the compound of R_f 0·45 was mainly obtained: Fr 1 (benzene–hexane (3:2) mixture), 23 mg, R_f 0·62; Fr 2 (benzene), 155 mg, R_f 0·45; Fr 3 (benzene–$CHCl_3$ (1:1) mixture), 19 mg, (R_f 0·27[18]). Crystallization of Fr 1 from MeOH gave a mixture of two compounds, R_f 0·62, 0·45.

2β-Methoxy-25D,5β-spirostan-3-one (VI)

Fr 2 in the above chromatography was recrystallized from hexane and MeOH to give VI, needles, m.p. 212°; $\nu_{max}^{CCl_4}$ 1732 cm^{-1} (25D,5β-spirostan-3-one, $\nu_{max}^{CCl_4}$ 1718 cm^{-1} [10]); ORD (Fig. 2), trough $[\alpha]_{313}$ −640°, peak $[\alpha]_{277}$ −101° (*c*, 0·308, MeOH). (Found: C, 75·52; H, 10·06. $C_{28}H_{44}O_4$ requires: C, 75·63; H, 9·97%.) In another experiment the hydrogenation product of IV (90 mg) was boiled with 5% KOH in MeOH (30 ml) for 30 min, the reaction mixture was diluted with water (150 ml) and the precipitates (R_f 0·45, 0·27 (trace)) were recrystallized from MeOH to give VI.

Reduction of VI

(a) Compound VI (80 mg) in MeOH (20 ml) was reduced with $NaBH_4$ (18 mg) to give a crystalline mass (81 mg), R_f 0·43, 0·30. The product was placed on a silica gel (16 g) column and eluted with hexane–ethyl acetate (3:1) mixture: Fr 1, 52 mg, R_f 0·43; Fr 2, 4 mg, R_f 0·43, 0·30; Fr 3, 21 mg, R_f 0·30.

(b) Compound VI (20 mg) was added to a solution of $LiBH_4$ (5 mg) in anhydrous pyridine (2 ml). The reaction mixture was stirred for 4 hr, diluted with water (100 ml), extracted with ether (20 ml × 3) and the ether layer was washed, dried and evaporated. The residue, R_f 0·43, 0·30, was chromatographed on alumina (1 g) using benzene–$CHCl_3$ (95:5) mixture: Fr 1, 10 mg, R_f 0·43; Fr 2, 8 mg, R_f 0·30.

2β-Methoxy-25D,5β-spirostan-3β-ol (VII)

Fr 1 in the above experiments (a) and (b) was recrystallized from MeOH to give VII, plates, m.p. 205 ~ 208°, $[\alpha]_D$ −49° (*c*, 0·51). (Found: C, 75·33; H, 10·36. $C_{28}H_{46}O_4$ requires: C, 75·29; H, 10·38%.)

2β-Methoxy-25D,5β-spirostan-3α-ol = yonogenin 2-methyl ether (II)

Fr 3 in the experiment (a) or Fr 2 in (b) was recrystallized from acetone to give II, needles, m.p. 265 ~ 266°, $[\alpha]_D$ −119° (*c*, 0·37); ν_{max}^{KBr} 3529, 982, 917 < 903 and 863 cm^{-1}. (Found: C, 75·27; H, 10·37. $C_{28}H_{46}O_4$ requires: C, 75·29; H, 10·38%.)

2α-Acetoxy-4-en-3-one (IX)

Compound III (770 mg) was acetylated overnight at room temp with acetic anhydride (5 ml) and pyridine (15 ml). Pure IX (740 mg) was obtained by recrystallization from EtOH. Plates, m.p. 248 ~ 250·5°, $[\alpha]_D$ −15° (*c*, 0·66): λ_{max} 242·5 mμ (ε, 16,400); ν_{max}^{KBr} 1756, 1692, 1623, 1251 and 1222 cm^{-1}; ORD (Fig. 1), trough $[\alpha]_{337}$ −688° (*c*, 0·065, dioxan). (Found: C, 74·11; H, 9·01. $C_{29}H_{42}O_5$ requires: C, 74·01; H, 9·00%.)

3-Methoxy-25D-spirostan-2-ols (Xa, b *and* c)

Compound IX (400 mg) in ethyl acetate (30 ml) was hydrogenated over 10% Pd–C (50 mg). One mole H_2 was absorbed in 10 min to give a crystalline mass (395 mg), which was subjected to the subsequent reduction with $NaBH_4$ (100 mg) in MeOH (50 ml). The product (374 mg) was methylated

[18] This compound was identified with 2α-methoxy-25D-spirost-4-en-3-ol (needles, m.p. 201 ~ 202°, $[\alpha]_D$ +11° (*c*, 0·44). (Found: C, 75·49; H, 9·99. $C_{28}H_{44}O_4$ requires: C, 75·63; H, 9·97%)) prepared from IV by the $NaBH_4$ reduction in MeOH.

in dry benzene (15 ml) with MeI (300 mg) and Ag_2O (500 mg) for 40 hr and the resultant methyl ether acetate was hydrolysed on refluxing with 5% KOH in MeOH (30 ml) for 40 min to give a mixture of saturated 3-methoxy-2-ols (342 mg), R_f 0·61 (main), 0·34, 0·30, 0·26.

3α-Methoxy-25D,5β-spirostan-2α-ol (X′ = Xa)

The mixture of Xa, b and c (340 mg) was chromatographed on alumina (10 g) using benzene and the main component (X′; 248 mg), R_f 0·61, was obtained as the first eluate. Recrystallization from MeOH provided a pure sample, needles, m.p. 162 ~ 163°, $[\alpha]_D$ −31° (*c*, 0·70); ν_{max}^{KBr} 3492 cm^{-1}; (Found: C, 75·29; H, 10·20. $C_{28}H_{46}O_4$ requires: C, 75·29; H, 10·38%). This was identified with Xa described below by direct comparisons.

3α-Methoxy-25D,5β-spirostan-2-one (XI)

Compound X′ (16 mg) in 90% acetic acid (1 ml) was oxidized with the solution (0·1 ml) of CrO_3 (200 mg) in 90% acetic acid (1 ml) under stirring for 4·5 hr. Excess CrO_3 was decomposed with $NaHSO_3$aq, the reaction mixture was diluted with water (20 ml), extracted with ether and the ether layer was worked up as usual. The product was recrystallized from MeOH to give XI (10 mg), prisms, m.p. 198°, R_f 0·48; $\nu_{max}^{CCl_4}$ 1733 cm^{-1} (25D,5β-spirostan-2-one, $\nu_{max}^{CCl_4}$ 1719 cm^{-1} [10]); ORD (Fig. 2), trough $[\alpha]_{314}$ −741°, peak $[\alpha]_{280}$ +36° (*c*, 0·305, MeOH). (Found: C, 75·62; H, 9·95. $C_{28}H_{44}O_4$ requires: C, 75·63; H, 9·97%.) When XI is boiled with 5% KOH in MeOH for 30 min the product showed single spot of unchanged XI on a thin-layer.

Reduction of XI

(a) Compound XI (50 mg) in MeOH (5 ml) was treated with $NaBH_4$ (20 mg) to give a solid mass, which showed single spot, R_f 0·61, on thin-layer and crystallized from MeOH to give needles (42 mg), m.p. 161 ~ 162°.

(b) Compound XI (71 mg) was reduced with $LiBH_4$ (5 mg) in pyridine (1 ml) in the same way as for VI. The product consisted of two compounds, R_f 0·61, 0·34, and they were separated by chromatography on alumina (5 g): Fr 1 (benzene), 38 mg, R_f 0·61; Fr 2 (benzene–$CHCl_3$ (2:1) mixture) 28 mg, R_f 0·34. Fr 1 was recrystallized from MeOH to afford Xa, needles, m.p. 161 ~ 162°, which was identical with the product in experiment (a) and with X′ mentioned above.

3α-Methoxy-25D,5β-spirostan-2β-ol = yonogenin 3-methyl ether (VIII)

Fr 2 in the above experiment (b) was recrystallized from MeOH to give VIII, needles, m.p. 185 ~ 188°, $[\alpha]_D$ −58° (*c*, 0·63), R_f 0·34; ν_{max}^{KBr} 3658, 3585, 981, 918 < 897 and 864 cm^{-1}. (Found: C, 75·41; H, 10·44. $C_{28}H_{46}O_4$ requires: C, 75·29; H, 10·38%.) Mixed m.p. with the aglycone (I) of yononin permethylate showed no depression, co-chromatography revealed single spot and both IR spectra were superimposable.

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