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116. **Kikuo Igarashi** : Studies on the Steroidal Components of Domestic Plants. XXXV.[*1] Structure of Meteogenin. (1).

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Recently, a new steroidal sapogenin having an aromatic ring in the molecule, was isolated from *Metanarthecium luteo-viride* Maxim. and named "Luvigenin." Its structure was shown to be 4-methyl-19-nor-25D-spirosta-1,3,5(10)-triene (I).[*1] This is the first example of the occurrence of a steroidal sapogenin having an aromatic ring in the molecule. This paper deals with the structural investigation of another new steroidal sapogenin, named "Meteogenin" having a hydroxyl group and an aromatic ring from the rhizome and the epigeous part of the same plant.

Meteogenin (IIa), $C_{27}H_{38}O_3$, m.p. 157~158°, $[\alpha]_D^{21}$ $-174.2°$, is a 25D-sapogenin and was obtained by repeated recrystallization from the mixture of 25D- and 25L-isomers, which were obtained in a 0.045% yield by repeated chromatography of the aglycone from the rhizome extract. The infrared spectrum of this sapogenin exhibits no carbonyl band but the absorption bands corresponding to a hydroxyl and an aromatic ring. Comparisons[1] of the intensities of the characteristic absorption bands at 920 and 895 cm^{-1} showed the latter band to be stronger than the former. The out-of-plane vibrations of the benzenoid function in the infrared spectrum show bands at 773 and 748 cm^{-1}, and the ultraviolet spectrum exhibits absorption maxima at 263 mμ (log ε 2.42) and 270 mμ (log ε 2.32). These findings suggest that meteogenin is a 25D-sapogenin having one hydroxyl group and a 1,2-di- or 1,2,3-trisubstituted benzenoid group[2] and that the A ring of meteogenin is aromatic.

Meteogenone (III), m.p. 177~178°, $[\alpha]_D^{23}$ $+180.5°$, was obtained from (IIa) by chromium trioxide-pyridine oxidation in a good yield. (III) showed an isolated ketone band in the infrared and ultraviolet spectra. Thus the hydroxyl group of (IIa) is secondary and not located in the carbon atom adjacent to the benzene ring.

On the other hand, a substance, $C_{27}H_{38}O_3$, m.p. 177~178°, $[\alpha]_D^{23}$ $-176.8°$, was isolated from the mother liquor of (IIa) by repeated recrystallization from ether. This compound has properties similar to those of (IIa) except that when the intensities of the characteristic absorption bands at 919 and 893 cm^{-1} are compared, the former band is stronger than the latter. Thus this compound is a 25L-isomer of (IIa), and has been named "Neometeogenin" (IV). Neometeogenin was readily converted to the ketone (V), m.p. 194~195°, $[\alpha]_D^{19}$ $+162.2°$, by chromium trioxide-pyridine oxidation.

Meteogenin (IIa) was refluxed in 60% nitric acid for 20 hours and the product was esterified with diazomethane and purified, but attempts to isolate a crystalline product failed. When the oily product was saponified with sodium carbonate, a substance, m.p. 151~152°, was obtained. The infrared spectrum of this compound showed carboxylic acid, ester and nitro groups. This substance formed a methyl ester, m.p. 75~76°. The analytical values of these two substances correspond to structures of $C_{10}H_9O_6N$ (VI) and $C_{11}H_{11}O_6N$ (VII) respectively. These results suggested that meteogenin (IIa) was aromatized in ring A and that the C_{10}-methyl group of the steroid was rearranged in ring A. Furthermore the position of the methyl group of (IIa) might be assumed to be C_1 or C_4 because

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[*1] Part XXXIV. K. Takeda, T. Okanishi, K. Igarashi, A. Shimaoka : Tetrahedron, in contribution.

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1) M.E. Wall, C.R. Eddy, M.L. McClennen, M.E. Klumpp : Analyt. Chem., **24**, 1337 (1952); R.N. Jones, E. Katzenellenbogen, K. Dobriner : J. Am. Chem. Soc., **75**, 158 (1953).

2) L.J. Bellamy : "The Infra-red Spectra of Complex Molecule," 2nd Ed., 1958. D.M.S. Spectro-Cards.

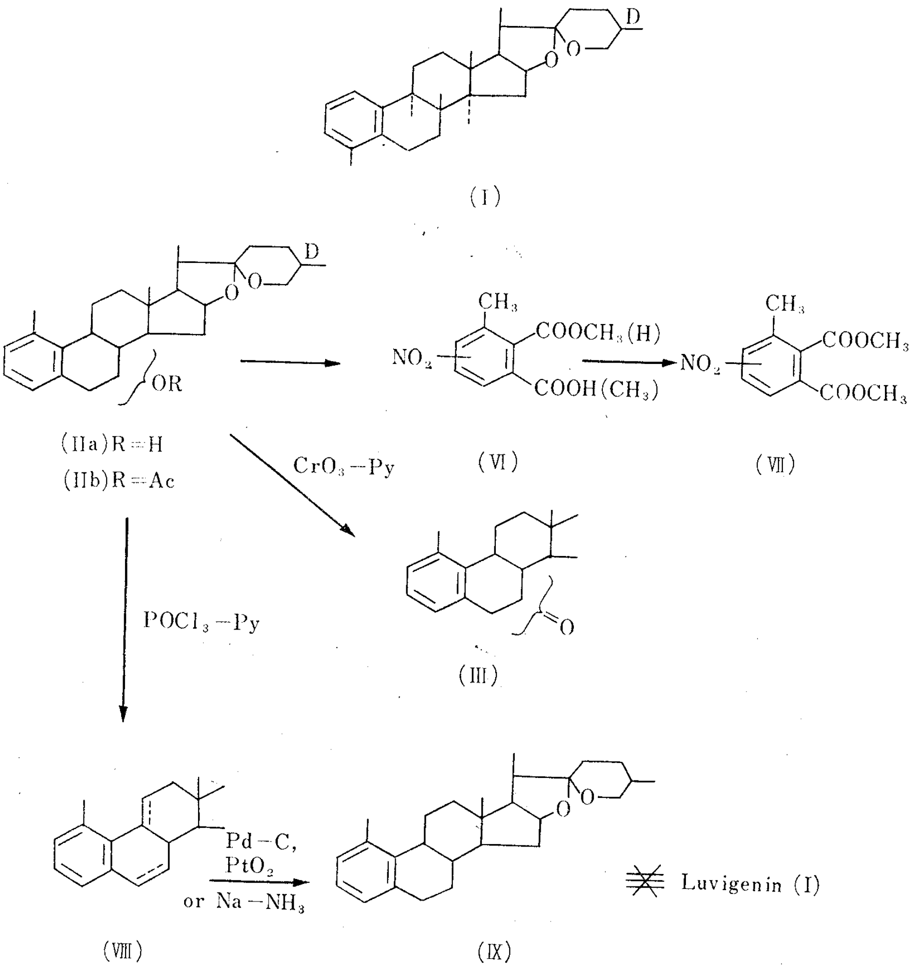

Chart 1.

the infrared spectrum of (IIa) suggested a presence of a 1,2-di- or 1,2,3-trisubstituted benzene ring.

Meteogenin (IIa) afforded an acetate (IIb), m.p. 162~163°, with acetic anhydride-pyridine at room temperature but another acetate, m.p. 147~148°, was isolated when the acetylation was conducted at 100°. These two acetates were dimorphous because meteogenin was obtained from both of them by saponification, and the infrared spectra of both acetates in carbon disulfide solution were identical. (IIa) was easily dehydrated to an oily anhydrometeogenin (VIII) with phosphoryl chloride and pyridine. The ultraviolet spectrum of (VIII) exhibited an absorption maximum at 245 mμ (log ε 4.02), which indicated that the introduced double bond of (VIII) was conjugated to the benzene ring. When (VIII) was hydrogenated catalytically with palladized charcoal or platinum oxide, or reduced with metallic sodium in liquid ammonia, only the same product, deoxymeteogenin (IX), m.p. 188.5~190°, $[\alpha]_D^{23}$ +53.6°, was obtained in 70% and 50% yields respectively. (IX) gave a depression with luvigenin (I) in mixed melting point determination, and the infrared spectrum of (IX) differed markedly from that of luvigenin. From these results it seemed that the double bond of (VIII) was not migrated during hydrogenation and located at C_6 or $C_{9(11)}$ and not at $C_{8(9)}$, and that (X) possessed a thermodynamically stable conformation and was an isomer of luvigenin due to the difference of the position of the methyl group.

On the other hand, from the standpoint of biogenesis of meteogenin as well as luvigenin, it seems probable that the true saponins of the plant do not contain as aglycones meteogenin and luvigenin themselves, but exist as the saponins (X) containing proto-type sapogenins, which undergo a rearrangement, perhaps the dienol-benzene rearrangement, to meteogenin and luvigenin during the acid hydrolysis of the saponins. Further experiments to study this mechanism are being continued. In the dienone-phenol rearrangement of steroid by acid, it is well known that 1-hydroxy-4-methyl derivative (XII) (*para*-type) was obtained from 1,4-dien-3-one (XI)[3] and that 1-methyl-3-hydroxy derivatives (XV) or (XVI) (*meta*-type) was obtained from 1,4,6-trien-3-one (XIII)[4] or 1,4-diene-3,11-dione (XIV).[5] In the case of the dienol-benzene rearrangement, however, only the 4-methyl derivative (XVIII) is known to form from 1,4-dien-3-ol (XVII).[6] As shown in the previous paper,[*1] we succeeded in the partial synthesis of luvigenin (I) from diosgenin (XIX) by this rearrangement. Also in the dienol-benzene rearrangement it may be assumed that the 1-methyl derivative is formed from 1,4,6-trien-3-ol or 3-hydroxy-1,4-dien-11-one. Furthermore, if

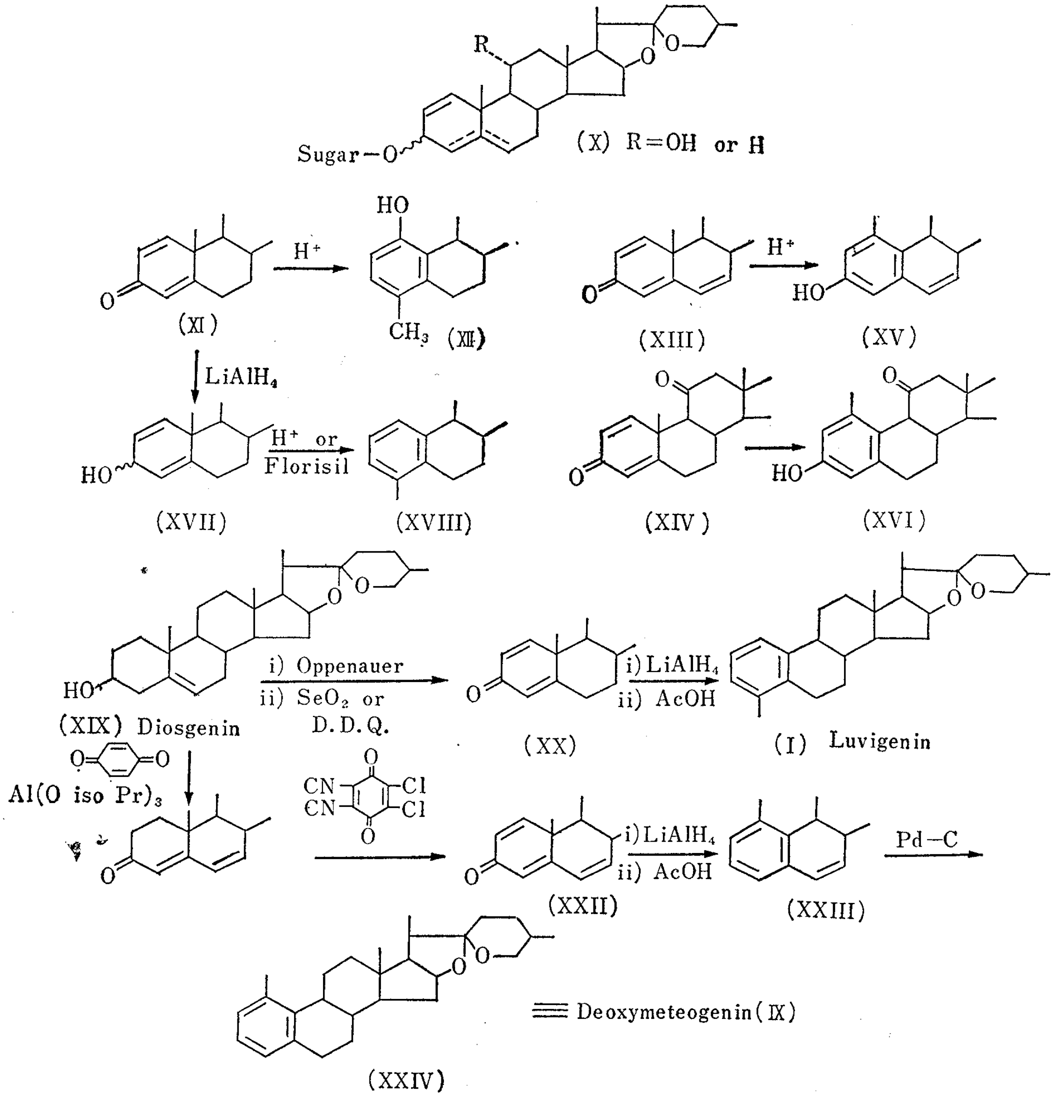

Chart 2.

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3) R.B. Woodward, T. Singh: J. Am. Chem. Soc., **72**, 494 (1950).

4) C. Djerassi, G. Rosenkranz, J. Romo, J. Pataki, St. Kaufmann: J. Am. Chem. Soc., **72**, 4540 (1950); J. Romo, C. Djerassi, G. Rosenkranz: J. Org. Chem., **15**, 896, 1289 (1950).

5) J. Elks, J.F. Oughton, L. Stephenson: Proc. Chem. Soc., **1959**, 6.

6) M.J. Gentles, J.B. Moss, H.L. Herzog, E.B. Hershberg: J. Am. Chem. Soc., **80**, 3702 (1958); H. Dannenberg, Ch. H. Doering: Z. physiol. Chem., **311**, 84 (1958); H. Dannenberg, Ch. H. Doering, D. Dannenberg-von Dresler: Z. physiol. Chem., **317**, 174 (1959).

the C_{11}-hydroxyl group is considered to have the same effect as the C_{11}-ketone, the relationship between luvigenin and meteogenin may well be interpreted from the above-mentioned rearrangement since meteogenin is assumed to possess $C_{11\alpha}$-ol from its biogenesis. Thus meteogenin was proposed to be formulated as 1-methyl-19-nor-25D-spirosta-1,3,5(10)-trien-11α-ol. From this point of view the partial synthesis of deoxymeteogenin (IX) was first attempted.

Diosgenin (XIX) was converted by Wettstein Oppenauer oxidation to 25D-spirosta-4,6-dien-3-one (XXI)[7] from which 25D-spirosta-1,4,6-trien-3-one (XXII), m.p. 202.5~204°, $[\alpha]_D^{21}$ $-116.5°$, was obtained by oxidation with dichlorodicyanobenzoquinone[8] (D.D.Q.) in a good yield. (XXII) was reduced with lithium aluminium hydride, then refluxed in 80% acetic acid and the product was chromatographed on alumina. A substance, $C_{27}H_{36}O_2$, m.p. 104~106°, $[\alpha]_D^{26}$ $-172.9°$, was obtained in 10% yield from the first eluted fraction. This possessed a benzene ring in the infrared spectrum and its ultraviolet spectrum showed an absorption maximum at 265 mμ (log ε 3.94). Thus this compound was formulated as 1-methyl-19-nor-25D-spirosta-1,3,5(10),6-tetraene (XXIII). From the next eluted fraction 25D-spirosta-4,6-dien-3-one (XXI) was isolated in 50% yield. (XXI) was also obtained by reduction of (XXII) with lithium aluminium hydride without treatment with acid. It was an interesting fact that only one double bond at C_1 of (XXII) was reduced with lithium aluminium hydride. When (XXIII) was hydrogenated catalytically with palladized charcoal, hydrogen was rapidly absorbed and (XXIV) was obtained. This substance was shown to be identical with deoxymeteogenin (IX) by mixed melting point determination and by direct comparison of their infrared spectra. As mentioned above, (IX) was assumed to be a 1-methyl isomer of luvigenin, which was obtained from 25D-spirosta-1,4-dien-3-one (XX) prepared from diosgenin by similar rearrangement. These facts indicate that the methyl group of deoxymeteogenin (IX) and also of meteogenin (IIa) should be at C_1-position, and that the double bond of anhydrometeogenin (VIII) should be located at $C_{9(11)}$ because (XXIII) is different from (VIII). The direction of the dienol-benzene rearrangement as well as that of the dienone-phenol rearrangement may vary according to the presence of a double bond at C_6.

It seemed likely that the hydroxyl group of meteogenin should be at $C_{11\alpha}$ not only from its biogenesis but also from the fact that the double bond of anhydrometeogenin (VIII) was proved to be located at $C_{9(11)}$. On the basis of this assumption the partial synthesis of meteogenin was then undertaken.

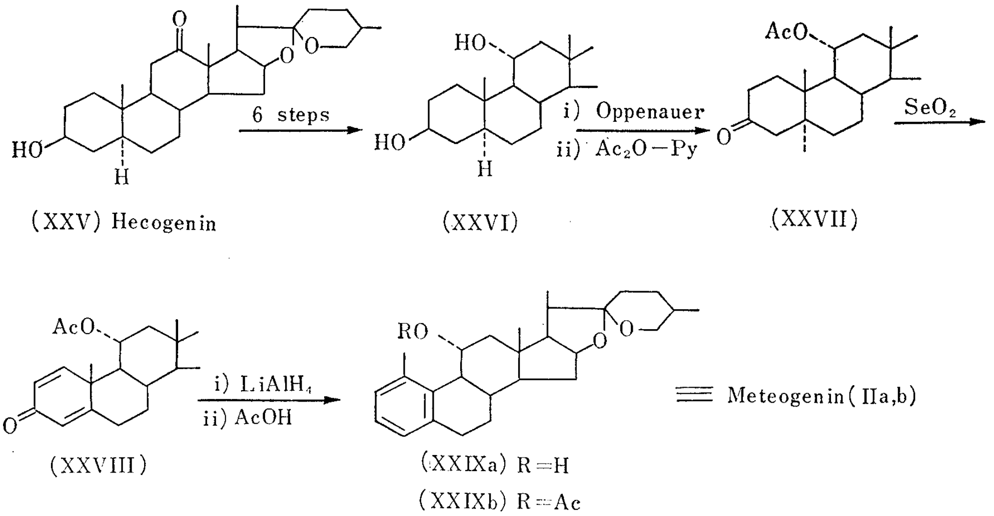

Chart 3.

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[7] L. Mandell: J. Am. Chem. Soc., **78**, 3199 (1956).

[8] D. Burn, D.N. Kirk, V. Petrow: Proc. Chem. Soc., **1960**, 14.

Hecogenin (XXV) was converted to 25D,5α-spirostane-3β,11α-diol (XXVI),[9] which led to 11α-hydroxy-25D,5α-spirostan-3-one acetate (XXVII)[10] by the method described in the literature. (XXVII), on dehydrogenation with selenium dioxide, gave 11α-hydroxy-25D-spirosta-1,4-dien-3-one acetate (XXVIII), m.p. 244~245°, $[\alpha]_D^{21}$ $-32.8°$. (XXVIII) was reduced with lithium aluminium hydride, then refluxed in 80% acetic acid and the product was chromatographed on alumina. A crystalline compound, m.p. 157~158°, $[\alpha]_D^{39}$ $-169.1°$, was obtained in 20% yield. This substance was shown to be identical with meteogenin (IIa) by mixed melting point determination and by direct comparison of their infrared spectra. The acetate was also identical with meteogenin acetate (IIb). From this result it was confirmed that meteogenin should be formulated as 1-methyl-19-nor-25D-spirosta-1,3,5(10)-trien-11α-ol. It is also deduced that the presence of the hydroxyl group at C-11 affects the direction of the rearrangement as in the case of the C-11 oxo derivative, thus giving C-1 methyl benzenoid derivative.

Experimental[*3]

Isolations and Purifications of Meteogenin (IIa) and Neometeogenin (IV)——In October 1959, the rhizome of *Metanarthecium luteoviride* Maxim. was collected in fields and hills near Shiga Prefecture. To 30 kg. of the rhizome 50 L. of 90% MeOH was added, the mixture was refluxed for 8 hr., filtered after cooling, and the filtrate concentrated to ca. 20 L. The MeOH-insoluble material was reextracted with MeOH and treated as above.

To the combined MeOH extracts 60 L. of MeOH and 13 L. of conc. HCl were added and the mixture was refluxed for 7 hr. To the solution 20 L. of H_2O was added and the MeOH was evaporated *in vacuo*. After cooling the deposited precipitate (5 kg.) was collected, washed well with H_2O and saponified by refluxing with a solution prepared from 50 L. of MeOH, 10 L. of H_2O and 1.5 kg. of KOH for 2 hr. To the solution 20 L. of H_2O was added and the MeOH was evaporated *in vacuo*. The solution which remained was extracted with $CHCl_3$ and the $CHCl_3$ solution washed with H_2O, dried, and evaporated. The residue (680 g.) was extracted with benzene, the benzene-insoluble material (abundant in metagenin) was removed by filtration and the filtrate was chromatographed on 10 kg. of Al_2O_3. Each eluate was examined by paper chromatography.[11] The eluates with benzene and benzene-$CHCl_3$, which were abundant in meteogenin (Rf. 0.78), were collected and treated with MeOH. The MeOH-insoluble material was removed, the filtrate was evaporated *in vacuo* to dryness, leaving an oily product (142 g.). This oil was rechromatographed on 1.5 kg. of Al_2O_3. An oily product and a sterol eluted with petr. ether and petr. ether-benzene (9:1) were removed and the crystalline products (48.8 g.) eluted with petr. ether-benzene (8:2~1:9), benzene and benzene-ether (9:1) were collected. They were rechromatographed on 600 g. of Al_2O_3 and the products eluted with petr. ether-benzene, benzene and benzene-$CHCl_3$ (9:1) were collected and crystallized from MeOH whereupon 13.5 g. (0.0045% yield) of crystals, m.p. 130~146°, were obtained. They were dissolved in hot MeOH and the solution was treated several times with charcoal to remove an amorphous material. The filtrate was concentrated and cooled in an ice-box and the precipitated crude meteogenin was collected and repeatedly recrystallized from MeOH to give 6.345 g. of prisms, m.p. 154~156°. Further recrystallization from MeOH gave the pure meteogenin (IIa), m.p. 157~158°, $[\alpha]_D^{21}$ $-174.2° \pm 2°$ (c=1.024). *Anal.* Calcd. for $C_{27}H_{38}O_3$: C, 78.93; H, 9.33. Found: C, 78.73; H, 9.29. IR $\lambda_{max}^{CS_2}$ cm^{-1}: 3613, 3540~3300 (OH), 3060 (╒), 980, 920, 895, 860 (F-ring: 895>920), 773, 748 (benzene). UV λ_{max} mμ (log ε): 204 (4.24), 217 (shoulder), 263 (2.42), 270 (2.38).

The mother liquor was crystallized and after repeated recrystallization from Et_2O, 350 mg. of neometeogenin (IV) as needles, m.p. 177~178°, $[\alpha]_D^{23}$ $-176.8° \pm 5°$ (c=0.422), was obtained. *Anal.* Calcd. for $C_{27}H_{38}O_3$: C, 78.93; H, 9.33. Found: C, 79.10; H, 9.39. IR $\lambda_{max}^{CS_2}$ cm^{-1}: 3620, 3500~3300 (OH), 3075 (╒), 985, 919, 893, 847 (F-ring: 919>893), 774, 749 (benzene). UV λ_{max} mμ (log ε): 204 (4.24), 217 (shoulder), 263 (2.42), 269.5 (2.30).

[*3] All melting points were determined with H. Bock, Monoscop IV (Frankfurt/M) and uncorrected. Infrared spectra were measured with the Nihon Bunko Infrared Spectrophotometer, Model DS-301. Ultraviolet spectra were measured in 95% EtOH with the Hitachi Recording Ultraviolet Spectrophotometer, EPS-2. Rotations were measured in $CHCl_3$ with the Rudolf Photoelectric Polarimeter, Model 200.

9) C. Djerassi, H. Martinez, G. Rosenkranz: J. Org. Chem., **16**, 303 (1951); J.H. Chapman, J. Elks, G.H. Phillips, L.J. Wyman: J. Chem. Soc., **1956**, 4344.

10) J. Romo: Bol. inst. quim. univ. nal. auton. Mé., **7**, 53 (1955) (C.A., **50**, 12088 (1956)).

11) The chromatography was carried out using heptane-$CHCl_3$-AcOH (50:10:3) and colored with $SbCl_3$

Meteogenone (III) and Neometeogenone (V)——To an ice-cold pyridine-CrO_3 complex prepared from 10 cc. of pyridine and 600 mg. of CrO_3 was added with stirring a solution of 610 mg. of meteogenin (IIa), m.p. 157~158° in 5 cc. of pyridine, the mixture was allowed to stand at room temperature overnight and poured into ice-water. The precipitate was collected, washed well with H_2O and extracted with hot AcOEt. The AcOEt solution was washed with H_2O, dried and evaporated. Recrystallization of the residue from MeOH yielded 490 mg. of meteogenone (III) as prisms, m.p. 177~178°, $[\alpha]_D^{23}$ +180.5°±2° (c=1.107). *Anal.* Calcd. for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88. Found : C, 79.45; H, 8.99. IR $\lambda_{max}^{CS_2}$ cm^{-1}: 3100 (╒), 1721 (ketone), 768 (benzene). UV λ_{max} mμ (log ε) : 265 (2.42), 271 (2.34), 291 (1.57).

In a similar manner neometeogenin (IV) gave neometeogenone (V), m.p. 194~195°, $[\alpha]_D^{19}$ +162.2°±2° (c=0.928). *Anal.* Calcd. for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88. Found : C, 79.40; H, 8.86. IR $\lambda_{max}^{CS_2}$ cm^{-1}: 3080 (╒), 1719 (ketone), 768 (benzene). UV λ_{max} mμ (log ε) : 265 (2.43), 271 (2.32), 291 (1.60).

Nitric Acid Oxidation of Meteogenin——A solution of 1.0 g. of meteogenin in 35 cc. of 60% HNO_3 was refluxed for 20 hr. and evaporated *in vacuo* to dryness. To the residue, a solution of CH_2N_2 in Et_2O was added, the Et_2O-insoluble material was removed and the filtrate was evaporated. The residue was dissolved in benzene and the benzene solution filtered through 6 g. of Al_2O_3 but no crystalline product was isolated after evaporation of the solvent. The residue was saponified by refluxing with 500 mg. of K_2CO_3 in MeOH-H_2O for 1 hr., and the solution was poured into H_2O and acidified with dil. HCl. The product was extracted with $CHCl_3$ and the $CHCl_3$ solution was washed with H_2O, dried and evaporated. The residue was dissolved in boiling Et_2O, the Et_2O-insoluble material was removed, and the filtrate was treated with Norit and then evaporated. Recrystallization of the residue from Et_2O-petr. ether yielded 80 mg. of plates (VI), m.p. 151~152°. *Anal.* Calcd. for $C_{10}H_9O_6N$: C, 50.21; H, 3.79; N, 5.86. Found : C, 50.37; H, 3.92; N, 5.76. IR λ_{max}^{Nujol} cm^{-1} : 2700~2600 (COOH), 1737 (ester), 1705 (COOH), 1600, 1585 (benzene), 1545, 1369 (NO_2).

(VI) was esterified with CH_2N_2 and the product was recrystallized from Et_2O-petr. ether to give plates (VII), m.p. 75~76°. *Anal.* Calcd. for $C_{11}H_{11}O_6N$: C, 52.17; H, 4.38; N, 5,53. Found : C, 52.39; H, 4.45; N, 5.44. IR λ_{max}^{Nujol} cm^{-1} : 3160, 3020 (╒), 1736 (ester), 1606, 1591 (benzene), 1535, 1359 (NO_2).

Meteogenin Acetate (IIb)——A solution of 50 mg. of meteogenin in 1 cc. of pyridine and 0.2 cc. of Ac_2O was allowed to stand overnight at room temperature and poured into H_2O. The crystalline product was collected, dried and recrystallized from MeOH to give the acetate, m.p. 162~163°, $[\alpha]_D^{17}$ −162.8°±2° (c=1.077). *Anal.* Calcd. for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91. Found : C, 76.95; H, 9.11. IR $\lambda_{max}^{CS_2}$ cm^{-1} : 1737 (acetate).

When the acetylation was conducted at 100° for 3 hr. and the product was recrystallized from MeOH, another acetate, m.p. 147~148°, $[\alpha]_D^{18}$ −165.2°±2° (c=1.024), was obtained. *Anal.* Calcd. for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91. Found : C, 76.99; H, 8.95.

The infrared spectrum in nujol mull of the former was different from that of the latter but was identical in CS_2 solution. Meteogenin was obtained from both of the above acetates by saponification.

Anhydrometeogenin (VIII)——To an ice-cold solution of 50 mg. of meteogenin (IIa), m.p. 157~158° in 2 cc. of pyridine was added dropwise 0.2 cc. of $POCl_3$ and the solution was allowed to stand at room temperature overnight, poured into ice-water and extracted with $CHCl_3$. The $CHCl_3$ solution was washed with H_2O, dil. HCl, H_2O, dil. Na_2CO_3 and H_2O, dried and evaporated, giving 35 mg. of an oily product. UV λ_{max} 245 mμ (log ε 4.02).

Conversion of Anhydrometeogenin (VIII) to Deoxymeteogenin (IX)

a) Catalytic Hydrogenation with Pd-C——A solution of 30 mg. of anhydrometeogenin (VIII) in 5 cc. of AcOEt was shaken with 30 mg. of 10% Pd-C in H_2 for 1 hr. After removal of the catalyst, the filtrate was evaporated and recrystallization of the residue from Me_2CO gave 21 mg. of prisms, m.p. 181~184°. Further recrystallization from Me_2CO furnished the pure sample, m.p. 188.5~190°, $[\alpha]_D^{33}$ +53.6°±2° (c=1.069). *Anal.* Calcd. for $C_{27}H_{38}O_2$: C, 82.18; H, 9.71. Found : C, 81.98; H, 9.74. IR $\lambda_{max}^{CS_2}$ cm^{-1} : 3030 (╒), 770, 746 (benzene).

The melting point was depressed to 153~177° on admixture with luvigenin, m.p. 183~184°. The infrared spectrum of deoxymeteogenin was also different from that of luvigenin.

b) Catalytic Hydrogenation with PtO_2——A solution of 35 mg. of anhydrometeogenin in 5 cc. of AcOEt was shaken with 17 mg. of Adams catalyst in H_2 for 2 hr. The product was crystallized from Me_2CO to form prisms (25 mg.), m.p. 173~183°. Further recrystallization from Me_2CO gave the pure sample, m.p. 188~190°, which was identical with the authentic sample of deoxymeteogenin by mixed melting point determination and by direct infrared spectra comparison.

c) Reduction with Metallic Na in Liquid NH_3——To a stirred solution of 30 mg. of metallic Na dissolved in ca. 50 cc. of liquid NH_3 was added dropwise a solution of 31 mg. of anhydrometeogenin in 5 cc. of dehyd. Et_2O under cooling with dry ice-Me_2CO at −70°. The blue color of Na disappeared and a small amount of Na was added until the blue color persisted. Stirring was continued for 20 min., the excess of Na was destroyed with NH_4Cl and the NH_3 was evaporated. To the residue H_2O was added, the product was extracted with Et_2O and the Et_2O solution was washed with H_2O, dried, and evaporated. The residue (30 mg.) dissolved in petr. ether was purified by filtration through 1 g. of Al_2O_3 and crystallized from MeOH to give 10 mg. of prisms, m.p. 188～190°, identical with the above deoxymeteogenin. The second crop (7 mg.), m.p. 185～189°, was also identical with deoxymeteogenin by comparison of each infrared spectrum.

25D-Spirosta-1,4,6-trien-3-one (XXII)——From a solution of 2.0 g. of 25D-spirosta-4,6-dien-3-one (XXI)[7] in 100 cc. of dry benzene ca. 20 cc. of benzene was distilled off in order to remove any trace of moisture present. Then, 1.440 g. of 2,3-dichloro-5,6-dicyanobenzoquinone[8] was added and the solution was refluxed for 10 hr. The precipitated hydroquinone was removed and the filtrate was washed well with 3% KOH solution and H_2O, dried, purified by filtration through 10 g. of Al_2O_3 and evaporated. The residue was crystallized from MeOH to give 1.55 g. of plates (XXII), m.p. 201～203°. Further recrystallization furnished the pure sample, m.p. 202.5～204°, $[\alpha]_D^{30}$ $-116.5°\pm2°$ (c=1.080). *Anal.* Calcd. for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88. Found : C, 79.29; H, 9.00. IR λ_{max}^{Nujol} cm^{-1} : 3030 (╒), 1660, 1608, 1585 (1,4,6-trien-3-one). UV : λ_{max} mμ (log ε) : 223 (4.06), 257 (3.99), 301 (4.11).

1-Methyl-25D-19-nor-25D-spirosta-1,3,5(10),6-tetraene (XXIII)——To a suspension of 500 mg. of $LiAlH_4$ in 30 cc. of dehyd. Et_2O was added dropwise with stirring a solution of 1.000 g. of (XXII), m.p. 202.5～204°, dissolved in 10 cc. of dehyd. tetrahydrofuran and 10 cc. of dehyd. Et_2O under ice-cooling. The solution was refluxed gently for 1 hr. and cooled with ice. The excess of $LiAlH_4$ was decomposed by dropwise addition of 3 cc. of AcOEt, then 3 cc. of H_2O was added and the precipitate was removed by filtration. To the filtrate Et_2O was added and the solution was washed with H_2O, dried and evaporated. The residue was dissolved in 60 cc. of 80% AcOH and the solution was refluxed for 10 min., poured into H_2O and the product was extracted with $CHCl_3$. The $CHCl_3$ solution was washed with dil. Na_2CO_3 and H_2O, dried and evaporated. The residue was chromatographed on 30 g. of Al_2O_3. The product (171 mg.) eluted with petr. ether-benzene (8:2) was crystallized from MeOH-Et_2O to give 97 mg. of leaflets (XXIII), m.p. 88～100°. Further recrystallization gave the pure sample, m.p. 104～106°, $[\alpha]_D^{26}$ $-172.9°\pm2°$ (c=0.936). *Anal.* Calcd. for $C_{27}H_{36}O_2$: C, 82.60; H, 9.24. Found: C, 82.65; H, 9.38. IR λ_{max}^{Nujol} cm^{-1} : 3070, 3030 (╒), 1589, 1570 (weak), 799, 785, 752, 722 (benzene). UV λ_{max} 265 mμ (log ε 3.94).

The product eluted with benzene and benzene-Et_2O (9:1) was crystallized from MeOH to give 549 mg. of rods, m.p. 208～210°, identical with the authentic sample of 25D-spirosta-4,6-dien-3-one by mixed melting point determination and by comparison of each infrared spectrum.

Catalytic Hydrogenation of (XXIII)——A solution of 53 mg. of (XXIII), m.p. 102～105° in 5 cc. of AcOEt was shaken with 30 mg. of 10% Pd-C in H_2. The uptake of H_2 ceased after 2～3 min. After removal of the catalyst, the product was crystallized from Me_2CO to give 30 mg. of prisms, m.p. 189～190.5°, identical with the authentic sample of deoxymeteogenin by mixed melting point determination and by direct infrared spectra comparison.

11α-Hydroxy-25D-spirosta-1,4-dien-3-one Acetate (XXVIII)——To a solution of 960 mg. of 11α-Hydroxy-25D,5α-spirostan-3-one acetate (XXVII),[9,10] m.p. 188～190°, dissolved in 50 cc. of *tert.* BuOH and 0.5 cc. of glacial AcOH was added 300 mg. of SeO_2, and the mixture was refluxed for 20 hr. A further 300 mg. of SeO_2 was added and the mixture was refluxed for 30 hr. The precipitated Se was removed, the filtrate was evaporated to dryness and the residue was extracted with AcOEt. The AcOEt solution was washed with dil. $KHCO_3$, H_2O, freshly prepared ice-cold $(NH_4)HS$, ice-cold dil. NH_4OH, H_2O, dil. HCl and H_2O, dried and evaporated. The residue was chromatographed on 30 g. of Al_2O_3. The product eluted with benzene-Et_2O (8:2) was crystallized from MeOH to give 206 mg. of rods (XXVIII), m.p. 220～235°. Further recrystallization from MeOH gave the pure sample, m.p. 244～245°, $[\alpha]_D^{21}$ $-32.8°\pm2°$ (c=1.014). *Anal.* Calcd. for $C_{29}H_{40}O_5$: C, 74.32; H, 8.60. Found : C, 74.05; H, 8.70. IR λ_{max}^{Nujol} cm^{-1} : 3050 (╒), 1732 (acetate), 1668, 1630, 1606 (1,4-dien-3-one). UV λ_{max} 245 mμ (log ε 4.28).

Conversion of (XXVIII) to Meteogenin (IIa) and Its Acetate (IIb)——To a suspension of 60 mg. of $LiAlH_4$ in 20 cc. of dehyd. Et_2O was added with stirring a solution of 120 mg. of (XXVIII), m.p. 244～245°, dissolved in 2 cc. of dehyd. tetrahydrofuran and 5 cc. of dehyd. Et_2O under ice-cooling. The solution was refluxed gently for 1 hr. and treated as above. The product was refluxed in 80% AcOH for 10 min. and chromatographed on 4 g. of Al_2O_3. The eluates with petr. ether-benzene (4:6～1:9) and benzene were crystallized from MeOH to give 7 mg. of prisms, m.p. 157～158°, $[\alpha]_D^{30}$ $-169.1°\pm4°$ (c=0.635), identical with the authentic sample of meteogenin (IIa) by mixed melting point and infrared spectra determinations. The second crop (15 mg.), m.p. 152～156°, was also identical with meteogenin. The acetate, m.p. 162～163°, was also identical with the authentic sample of meteogenin acetate (IIb) by mixed melting point determination and by comparison of each infrared spectrum.

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Summary

The structure of meteogenin, isolated from the rhizome of *Metanarthecium luteoviride* Maxim., was shown to be 1-methyl-19-nor-25D-spirosta-1,3,5(10)-trien-11α-ol (IIa). The relationship between luvigenin (I) and meteogenin (IIa) was established, and at the same time it was proved that the direction of the dienol-benzene rearrangement varied according to the presence of the double bond at C_6 or of the C_{11}-ketone.

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117. **Kikuo Igarashi** : Studies on the Steroidal Components of Domestic Plants. XXXVI.[1] Structure of Meteogenin. (2). On Meteogenone.

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As described in the preceding paper,[1] the structure of meteogenin, isolated from the rhizome of *Metanarthecium luteoviride* Maxim., was established as 1-methyl-19-nor-25D-spirosta-1,3,5(10)-trien-11α-ol (I). The interesting properties of meteogenone (II) are the subject of the present paper.

When meteogenone (II), obtained from meteogenin (I) by oxidation with chromium trioxide and pyridine,[1] was reduced with lithium aluminium hydride, a new hydroxy compound (IIIa), m.p. 185~187°, $[\alpha]_D^{17}$ +67.1°, and meteogenin were obtained in the ratio of 3:1. (IIIa) gave the acetate (IIIb), m.p. 184~186°, $[\alpha]_D^{17}$ +42.2°, afforded meteogenone by the oxidation with chromium trioxide and pyridine. These facts indicate that meteogenone (II) possesses the same skeleton as meteogenin (I) and that the new hydroxy compound is the 11β-hydroxy epimer of meteogenin (I), named epimeteogenin (IIIa).

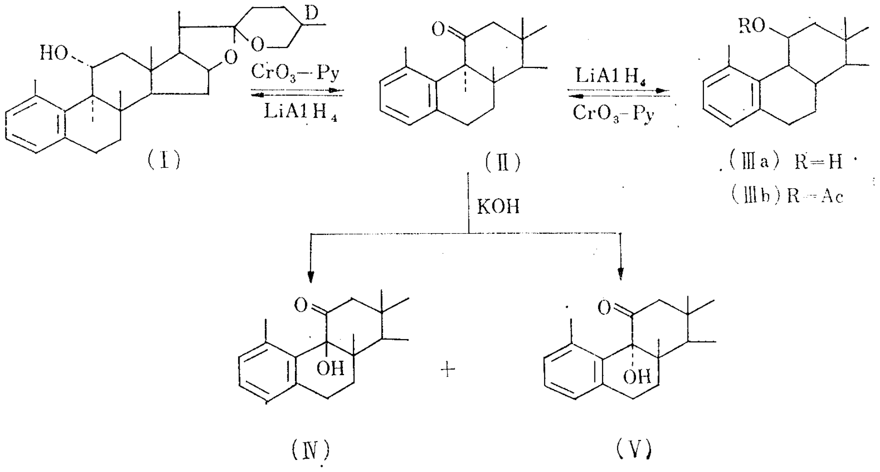

Chart 1.

[*1] Fukushima-ku, Osaka (五十嵐喜九男).

[1] Part XXXV. K. Igarashi : This Bulletin, 9, 722 (1961).