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Soil Bacterial Hydrolysis leading to Genuine Aglycone. X.[1] On the Structure of a Genuine Sapogenol of Meteogenin, an A-Ring Aromatized Spirostanol from *Metanarthecium luteo-viride* Maxim.

Isao Kitagawa, Tsutomu Nakanishi,[2] Yoshinobu Morii,[2a] and Itiro Yosioka[2b]

Faculty of Pharmaceutical Sciences, Osaka University[2]

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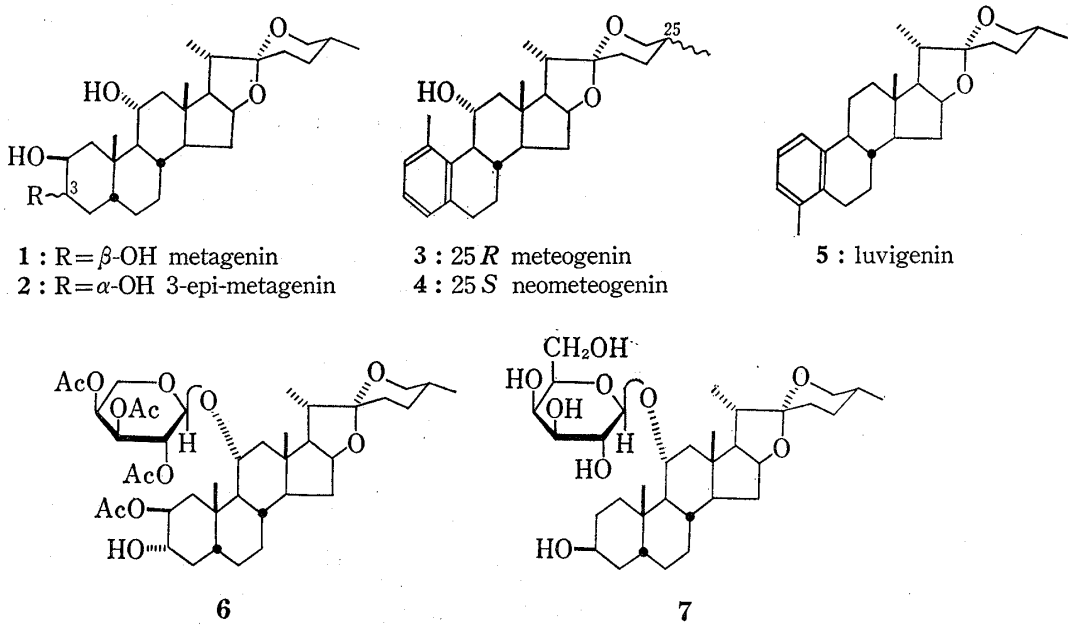
By using the soil bacterial hydrolysis method for a glycoside mixture isolated from the subterranean part of *Metanarthecium luteo-viride* Maxim. (Liliaceae), a mixture of prosapogenols has been isolated. Purification of the mixture by repeated chromatography and acetylation, a prosapogenol has been isolated as its peracetate. On the basis of chemical and physicochemical evidence, the structure of the peracetate has been established as a pentaacetate of 11-α-L-arabinopyranosyloxy-2β,3β-dihydroxy-25R-spirost-4-ene (=11-O-α-L-arabinopyranosyl-protometeogenin) (**8a**) and it has been shown that protometeogenin is a genuine sapogenol of meteogenin (3) which is one of nine spirostane-type sapogenols hitherto isolated from the titled plant and is characterized by having an A-ring aromatized spirostanol skeleton.

Keywords——*Metanarthecium luteo-viride* Maxim.; soil bacterial hydrolysis; genuine sapogenol; meteogenin; protometeogenin; 11-O-α-L-arabinopyranosyl-protometeogenin; CD spectra; mass spectra

Both epigeous and subterranean parts of *Metanarthecium luteo-viride* Maxim. (nogiran in Japanese, Liliaceae) have hitherto been elucidated to contain rich amount of the glycosidic component which, on acid hydrolysis, give nine spirostanol-type sapogenols: metagenin (**1**) (major), 3-epi-metagenin (**2**) (second major), nogiragenin, neonogiragenin, narthogenin, isonarthogenin, meteogenin (**3**), neometeogenin (**4**), and luvigenin (**5**).[1,3] Among these spirostanols, three minor sapogenols: meteogenin (**3**), neometeogenin (**4**), and luvigenin (**5**) have been characterized by having an aromatized A-ring and have been considered to be the artifacts which were secondarily formed from their respective genuine sapogenols during the acid hydrolysis.[3d,e]

By using the soil bacterial hydrolysis method,[4] we have initially attempted to clarify the structure of genuine sapogenols of **3**, **4**, and **5**, and during the course of studies, we have isolated two prosapogenols and have elucidated their structures to be 2-O-acetyl-11-O-(tri-O-acetyl-α-L-arabinopyranosyl)-3-epi-metagenin (**6**)[1] and 11-O-galactopyranosyl-nogiragenin (**7**).[5] Since these prosapogenols possess an O-glycoside linkage at C-11 of their steroidal aglycones, it has been presumed that the plant may be rich in saponins having an 11-O-glycosyl residue in their aglycones.

1) Part IX: I. Yosioka, K. Imai, Y. Morii, and I. Kitagawa, *Tetrahedron*, **30**, 2283 (1974).
2) Location: *133-1, Yamada-kami, Suita, Osaka 565, Japan*; *a*) Present address: *Fujisawa Pharm. Co., 1, Kashimacho, Higashiyodogawa-ku, Osaka 532, Japan*; *b*) Present address: *Tsumura Laboratory, 1421, Izumi, Komae, Tokyo 182, Japan*.
3) *a*) K. Hamamoto, *Chem. Pharm. Bull.* (Tokyo), **9**, 32 (1961); *b*) K. Takeda, T. Okanishi, H. Osaka, A. Shimaoka, and N. Maezono, *ibid.*, **9**, 388 (1961); *c*) H. Minato and A. Shimaoka, *ibid.*, **11**, 876 (1963); *d*) K. Igarashi, *ibid.*, **9**, 729 (1961); *e*) K. Takeda, T. Okanishi, K. Igarashi, and A. Shimaoka, *Tetrahedron*, **15**, 183 (1961).
4) I. Yosioka, M. Fujio, M. Osamura, and I. Kitagawa, *Tetrahedron Lett.*, **1966**, 6303.
5) I. Yosioka, Y. Morii, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), **21**, 2092 (1973).



1 : R=β-OH metagenin
2 : R=α-OH 3-epi-metagenin
3 : 25*R* meteogenin
4 : 25*S* neometeogenin
5 : luvigenin
6
7

Chart 1

In a continuing study, we have recently isolated a prosapogenol as its peracetate and have elucidated that the prosapogenol is an 11-O-arabinoside of a genuine sapogenol of meteogenin (**3**). The present paper provides the full account on the structure elucidation.[6]

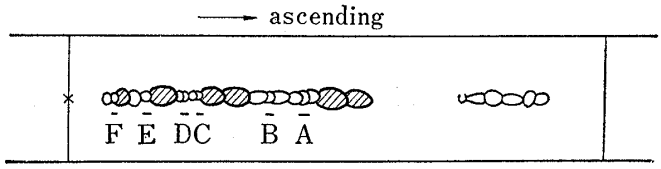


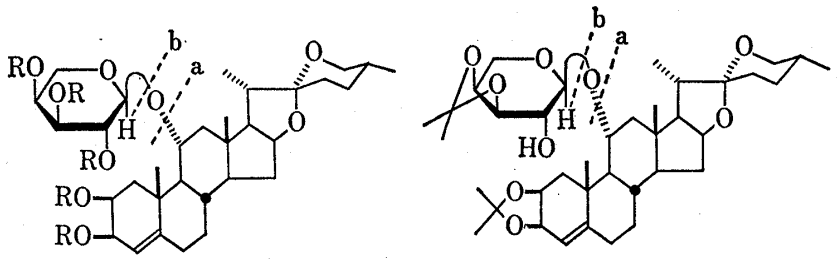
Fig. 1. TLC Diagram of the Soil Bacterial Hydrolysate of R-BEC

Solvent : benzene–ethanol (7 : 1) (developing twice).
Detection : 1% ceric sulfate in 10% sulfuric acid.
Adsorbent : silica gel (Camag D-5).

The soil bacterial hydrolysis[1,4] of the total glycoside mixture (designated as R–BEC), which was isolated from the subterranean part of the titled plant, afforded a complex mixture of the hydrolysates as shown on the thin–layer chromatogram (TLC) (Fig. 1). After several preliminary examinations, it has been found that a prosapogenol of **3**, **4**, or **5** is detected on TLC as a blue spot by spraying 1% ceric sulfate in 10% sulfuric acid with heating. Among several minor hydrolysates which were colored blue on TLC (spots A, B, C, D, E, and F, in Fig. 1), the isolation of a prosapogenol giving spot A has been effected as its peracetate (**8a**) by repeated chromatographic separation. After elucidation of the structures of **8a** and its desacetyl derivative **8**, whose aglycone is now named protometeogenin, it has been noticed by detailed TLC examinations that the prosapogenol giving spot A (Fig. 1) is equivalent to a partially acetylated derivative of **8**.

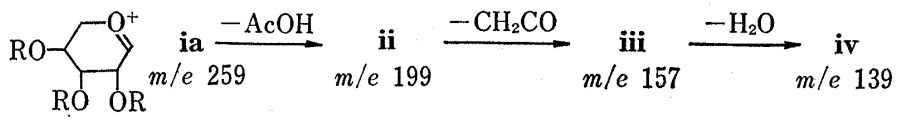
The peracetate (**8a**) possesses a molecular composition of $C_{42}H_{60}O_{14}$ as shown by high resolution mass spectrometry. The infrared (IR) spectrum of **8a** exhibits strong acetoxyl absorption bands but lacks a hydroxyl absorption band. It shows a set of absorption bands at 981, 920, 899, and 864 cm^{-1} (the intensities at 899>920) which suggest the presence of a 25*R*-spirostane structure in **8a**.[7] The proton magnetic resonance (PMR) spectrum of **8a** supports the 25*R*-spirostane structure by two three-proton singlets at δ 0.79 (13-Me), and δ 1.24 (10-Me) and two three-proton doublets at δ 0.83 (25-Me) and δ 0.99 (20-Me). It also shows

6) I. Kitagawa, T. Nakanishi, Y. Morii, and I. Yosioka, *Tetrahedron Lett.*, **1976**, 1885 (preliminary account).
7) *a*) M.E. Wall, C.R. Eddy, M.L. McClennan, and M.E. Klumpp, *Analyt. Chem.*, **24**, 1337 (1952); *b*) R.N. Jones, E. Katzenellenbogen, and K. Dobriner, *J. Am. Chem. Soc.*, **75**, 158 (1953).

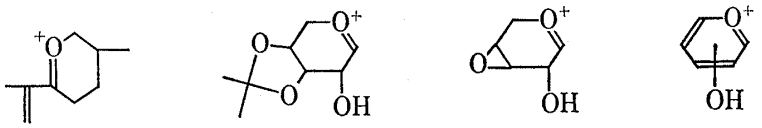


8 : R=H
8a : R=Ac

9



i : R=H
ia : R=Ac



v
m/e 139

Chart 2

the signals due to five acetoxyls. The signal intensity (six protons) between the range of δ 4.9 and δ 5.6 demonstrates the presence of a trisubstituted double bond in **8a**, since the range includes signals due to five methine protons which are geminal to five acetoxyls and one olefinic proton.

In the mass spectrum of **8a**, are observed a series of prominent fragment ion peaks of $C_{11}H_{15}O_7$[8] (53%, **ia**), $C_9H_{11}O_5$ (24%, **ii**), $C_7H_9O_4$ (51%, **iii**), and $C_7H_7O_3$ (**iv**)[9] which are derivable from a fully acetylated pentoaldopyranose moiety in **8a**.[1,10] The base peak observed at *m/e* 139 was shown by high resolution mass spectrometry to comprise two ions of $C_7H_7O_3$ (**iv**) and $C_9H_{15}O$ (**v**) as previously experienced in the mass spectrum of **6**.[1,11] The latter ion **v** is originated in the E and F rings of the spirostanol-type aglycone.

Based on the above mentioned evidence, it has become clear that **8a** is a pentaacetate of a pentoaldopyranoside of a spirostanol having one trisubstituted double bond, and among five acetoxyls three attach to its pentoaldose moiety and two to its aglycone part. In regard to the glycoside linkage in **8a**, a doublet (J=7 Hz) due to the anomeric proton is observed at δ 4.62 when the PMR spectrum was taken in a hexadeuterobenzene–hexadeuteroacetone

8) The elemental compositions of fragment ion peaks given with the chemical formulae were confirmed by high resolution mass spectrometry.
9) This ion constitutes a part of base peak along with an ion of $C_9H_{15}O$ (**v**) (*m/e* 139).
10) *a*) H. Budzikiewicz, C. Djerassi, and D.H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," vol. 2, Holden-Day Inc., San Francisco, 1964, p. 203; *b*) T. Kawasaki, T. Komori, Y. Ida, Y. Inatsu, K. Miyahara, and T. Nohara, International Conference on Mass Spectrometry, Kyoto, Sept., 1969, Abstract Papers, p. 221.
11) ref. 10*a*, p. 113.

(1:1) mixture, however the signal of anomeric proton is obscure in deuterochloroform because of overlap with a signal probably due to 16α-H.

On treatment with 0.5% sodium methoxide in methanol, **8a** was converted to the desacetyl derivative **8** which preserves no acetoxyl function as shown by its IR spectrum. The IR spectrum of **8** shows absorption bands ascribable to the 25*R*-spirostane skeleton and the presence of double bond in **8** is suggested by a positive tetranitromethane test.

In the mass spectrum of **8**, is observed an ion peak of $C_5H_9O_4$ (7.1%, **i**), wihch is again characteristic to a pentoaldopyranose moiety, in addition to a base peak of $C_9H_{15}O$ (**v**) derived from the spirostanol aglycone. In addition, are observed two fragment ions of $C_{27}H_{41}O_4$ (9.5%) and $C_{27}H_{41}O_5$ (1.0%), which are respectively presumed to be formed through **a** and **b** fissions (Chart 2), thus the molecular composition of the aglycone of **8** being demonstrated to be $C_{27}H_{42}O_5$, two hydrogen less than that of metagenin (**1**), and also the presence of one double bond in **8** being clarified.

On acid hydrolysis, **8** furnished in the excellent yields meteogenin (**3**)[3d] and arabinose.[12] Since the coupling constant of the anomeric proton in the PMR spectrum of **8a** is 7 Hz (*vide supra*), it follows therefore that **8** is an α-L-arabinopyranoside (C1 form) of an aglycone protometeogenin which, on acid treatment, is readily converted to meteogenin (**3**). It has also become clear that protometeogenin is a 25*R*-spirostanol possessing three hydroxyls and one trisubstituted double bond. Based on the ready conversion of protometeogenin to meteogenin (**3**) on acid treatment, it has been presumed that one hydroxyl of protometeogenin locates at C-11α and two in the A-ring (and/or less likely in the B-ring) while the double bond locates at C-4,5 or C-5,6.

Treatment of **8** with a dry acetone–dry cupric sulfate mixture furnished a diacetonide (**9**) as a sole product. In the mass spectrum of **9**, here again are observed a series of prominent ion peaks of $C_8H_{13}O_5$ (17%)(*via* **a** fission in **9**), $C_8H_{13}O_4$ (21%, **vi**), $C_5H_7O_3$ (23%, **vii**), and $C_5H_5O_2$ (17%, **viii**), all of which being derived from the monoisopropylidene-arabinose moiety.[14] On the other hand, three ion peaks of $C_{30}H_{45}O_5$ (1.4%, **b** fission in **9**), $C_{30}H_{45}O_4$ (2.1%, **a** fission in **9**), and $C_{27}H_{39}O_3$ (22%, $C_{30}H_{45}O_4$–$(CH_3)_2CO$)[14] are observed as fragment ions derived from the aglycone part along with a base peak at *m/e* 59 ($(CH_3)_2CO+H$), thus suggesting that two hydroxyls in the aglycone of **8** are involved in the acetonide formation in **9** and also showing that the arabinoside moiety in **8** is attached to 11α-hydroxyl of protometeogenin.

Finally, the location of two hydroxyls and one double bond in protometeogenin has been determined as shown in **8** on the basis of following circular dichroism (CD) examinations. In the CD spectrum of **8**, a strong negative maximum ($[\theta]_{200}$—70700) due to $\pi_x \rightarrow \pi_x^*$ transition of C=C[15a,b] is observed, whereas a similar maximum ($[\theta]_{200}$—88100) is observed in the case of **8a**. Applications of the octant rule for C=C and the inversed octant rule for C=C having an allylic oxygen function[15a,b] and comparison of the molar ellipticities of **8** and **8a** with those of several sterols (**10**, **11**, **12**, **13**, **14**),[15,16] have led us to assign a 3β-hydroxy-4-ene structure for **8**. The location of another hydroxyl in **8** may consequently be assigned as 2β since **i**) the hydroxyl joins readily in the acetonide formation with 3β-hydroxyl and ii) **8** gives meteogenin (**3**) on acid treatment (*cf.* mechanistic considerations[3d,e]).

The structure **8** has now become reasonable for a new prosapogenol which is designated as 11-O-α-L-arabinopyranosyl-protometeogenin. As for the increased molar ellipticities of **8** and **8a** as compared with those of **10**, the respective presence of 2β-hydroxyl and 2β-acetoxyl

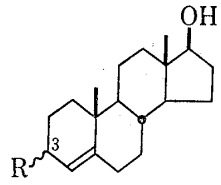
12) Presumed to be L-arabinose, since the plant has already been shown to contain rich amount of L-arabinoside derivatives.[1,13] Due to shortage of the material the optical rotation could not be taken.

13) I. Kitagawa, K.S. Im, and Y. Morii, *Chem. Pharm. Bull.* (Tokyo), **24**, 3114 (1976).

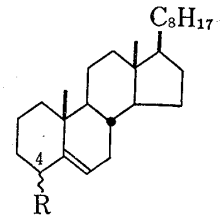
14) ref. 10*a*, p. 227.

15) *a*) A.I. Scott and A.D. Wrixon, *Tetrahedron*, **26**, 3695 (1970); *b*) *Idem*, *ibid.*, **27**, 4787 (1971); *c*) J. Hudec and D.N. Kirk, *Tetrahedron*, **32**, 2475 (1976).

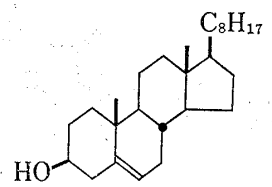
16) M. Legrand and R. Viennet, *C.R. Acad. Sci. Paris*, **C262**, 1290 (1966).



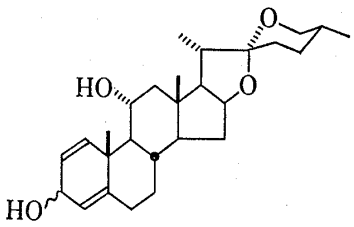
10 : R=β-OH
$[\theta]_{197}$ −33000
11 : R=α-OH
$[\theta]_{199}$ +13400



12 : R=β-OH
$[\theta]_{208}$ +1500
13 : R=α-OH
$[\theta]_{208}$ −7900



14 : $[\theta]_{200}$ +6600



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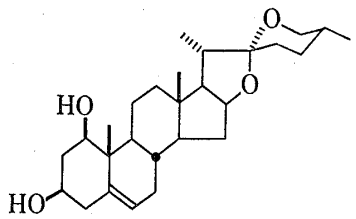


16 : ruscogenin

Chart 3

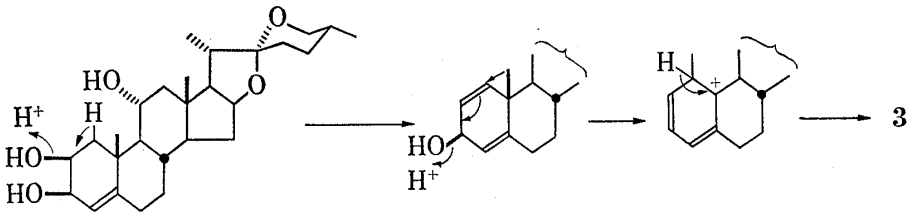
in **8** and **8a** is considered to be responsible since Dreiding model examinations in relation to the octant projection have shown that these residues occupy a negative octant.[15]

For the structure of a hypothetical genuine sapogenol of meteogenin (**3**), the one (**15**) having a 3-hydroxy-1,4-diene moiety was once proposed on the basis of mechanistic considerations (a dienol-benzene rearrangement[17]) and syntheses of related steroidal derivatives.[3d] It is interestingly pointed here that the structure of protometeogenin (aglycone of **8**) now elucidated includes a 2β,3β-dihydroxy-4-ene moiety which corresponds to a hydrated form of 3-hydroxy-1,4-diene structure.

Furthermore, since a furostanol 26-O-glucoside has been known to give a corresponding spirostanol aglycone even upon enzymatic hydrolysis[18] and since the presence of rich amount of furostanol glycosides has been suggested by TLC examinations (detection by the Ehrlich reagent[19]) of the total glycoside fraction of the plant material, the genuineness of **8** in regard to its spirostane skeleton (especially the E and F ring part) should be a subject of further investigation.

As far as we are aware, ruscogenin (**16**), possessing a 1β,3β-dihydroxy-5-ene moiety, has been an only example which, on acid treatment, is converted to luvigenin (**5**) having an A-ring aromatized skeleton.[20] In this case, the acid conditions were more severe as compared with those in the present conversion from protometeogenin 11-O-arabinoside (**8**) to meteogenin (**3**). In addition, although there have been some investigations on acid treatment of steroidal ene-diols giving A-ring aromatized sterols,[21] protometeogenin seems to be the first naturally occurring steroid which has a 2β,3β-dihydroxy-4-ene moiety and is readily converted to an A-ring aromatized steroid on acid treatment. The reaction pathway is presumed to proceed as shown in Chart 4 (**ix**→**x**→**xi**→**3**).

17) D.N. Kirk and M.P. Hartshorn, "Steroid Reaction Mechanism," Elsevier, London, 1968, p. 283.
18) H. Ripperger, H. Budzikiewicz, and K. Schreiber, *Chem. Ber.*, **100**, 1725 (1967).
19) S. Kiyosawa, M. Hutoh, T. Komori, T. Nohara, I. Hosokawa, and T. Kawasaki, *Chem. Pharm. Bull.* (Tokyo), **16**, 1162 (1968).
20) G.A. Gonzalez, R. Freire, M.G. Garcia-Estrada, J.A. Salazer, and E. Saurez, *Tetrahedron*, **28**, 1289 (1972).
21) *a*) D. Baldwin, J.R. Hanson, and A.M. Holtom, *J. Chem. Soc. Perkin I*, **1973**, 1704; *b*) J.R. Hanson, *Tetrahedron Lett.*, **1972**, 4501.



ix (protometeogenin) x xi

Chart 4

As mentioned in the isolation procedure of **8a** (*vide supra*), the total ether extractive of the soil bacterial hydrolysate contains **8** as its partially acetylated derivative, and as was pointed in our previous paper,[1] the glycoside fraction from the titled plant is rich in a mixture of variously acetylated glycosides and this seems to result in formation of a complex mixture of the glycoside ingredients.

Experimental[22]

Isolation of Glycoside Mixture (R-BEC)——A syrup (720 g) was obtained by extraction of the subterranean part of the titled plant (air dried, cut, 3 kg) with warm MeOH (6 hr, three times) and evaporation of the solvent. The syrupy extractive was partitioned into *n*-BuOH–water mixture and the *n*-BuOH soluble portion was evaporated under reduced pressure to give a residue (445 g). The residue (325 g) was then treated repeatedly with ether and the insoluble portion (165 g) was dissolved in MeOH and subjected to column chromatography using active charcoal (Seisei-shirasagi, Takeda Chem. Ind., 300 g) and Celite 545 (Wako Pure Chem. Ind., 250 g). Successive elution with MeOH and MeOH–acetone (1: 1) gave the glycoside mixture (R-BEC) (72.3 g).

Soil Bacterial Hydrolysis of Glycoside Mixture (R-BEC)——A suitable soil bacterial strain (YSB-26, unidentified yet) was selected from many soil samples (collected at Toneyama, Toyonaka, Osaka) by the method described before[4] (R-BEC as a sole carbon source, however, dil. HCl was not used for adjusting pH and pH of the medium in the present case was neutral), and the selected microorganism was cultivated stationarily for 21 days at 31—33° on the synthetic medium (15 flasks, each one flask contained 2 g of R-BEC in one liter of medium). In order to avoid thermal decomposition, the synthetic medium was prepared by innoculating a mixture of aqueous inorganic material first and afterwards, by adding the glycoside mixture to the medium aseptically as undertaken in our previous case.[23] The total culture broth was then extracted successively with ether and *n*-BuOH. The ether extract was washed with water, dried over $MgSO_4$, and evaporated to dryness to give a residue (17.1 g, TLC in Fig. 1). Similar treatment of the *n*-BuOH extract gave 3.4 g of a residue.

Isolation of Peracetate (8a)——The ether extract (16.7 g) obtained above was subjected to column chromatography using silicic acid (800 g) and developing successively with $CHCl_3$, $CHCl_3$–AcOEt, and AcOEt–MeOH. The combined fraction obtained by elution with $CHCl_3$–AcOEt (1: 1) mixture gave a prosapogenol mixture (2.35 g) which was shown by TLC to contain rich amount of a prosapogenol giving spot A (Fig. 1). Acetylation of the prosapogenol mixture (2.3 g) with Ac_2O (6 ml)–pyridine (10 ml) at 16° overnight followed by the usual work-up gave a peracetate mixture (2.3 g) which was purified by column chromatography (silicic acid, 125 g, AcOEt–*n*-hexane=1: 1) and preparative TLC (silica gel, AcOEt–*n*-hexane=2: 3, developing twice) to give **8a** (35 mg). Crystallization of **8a** was failed and purified by repeated precipitation using *n*-hexane–EtOH. **8a** (amorphous), IR $\nu_{max}^{CS_2}$ cm^{-1}: 1757, 1750 (sh), 1742 (sh), 1245, 1220 (OAc), 981, 920, 899, 864 (intensity at 899>920). PMR ($CDCl_3$) δ: 0.79 (3H, s, 13-Me), 0.83 (3H, d, J=*ca.* 7 Hz, 25-Me), 0.99 (3H, d, J=6 Hz, 20-Me), 1.24 (3H, s, 10-Me), 1.99 (6H, s), 2.02, 2.04, 2.17 (3H each, all s) (AcO×5), 3.1—4.2 (6H, unresolved m), 4.4 (2H, broad d, anomeric H and presumably 16α-H), 4.9—5.6 (6H, m, CHOAc×

22) The following instruments were used for obtaining the physical data: mp (Yanagimoto Micro-melting-point Apparatus, recorded uncorrected); IR spectra (Hitachi IR Spectrometer EPI-G3); mass spectra and high resolution mass spectra (JEOL JMS-01SG Mass Spectrometer, direct inlet); PMR spectra (Hitachi R-22 NMR Spectrometer, 90 MHz, tetramethylsilane as an internal standard); CD spectra (JASCO UV/ORD-6 Spectrometer). Silica gel (Camag D-5) and Kieselgel G (Merck) were used for TLC and detection by 1% $Ce(SO_4)_2$ in 10% H_2SO_4 with heating. On preparative TLC, detection was made by spraying dist. water. For column chromatography, silicic acid (Mallinckrodt, 100 mesh) and Kieselgel 60 (Merck, 70—230 mesh) were used.

23) I. Yosioka, T. Sugawara, K. Yoshikawa, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 2450 (1972).

5 and olefinic H); (C_6D_6–$(CD_3)_2CO$=1: 1) δ: 4.4 (1H, m, 16α-H), 4.62 (1H, d, J=7 Hz, anomeric H), 4.9—5.4 (5H, m), 5.47 (1H, t-like, J=4 Hz) (CHOAc×5 and olefinic H). CD (c=0.068, MeOH): $[\theta]_{245}$ 0, $[\theta]_{200}$ −88100 (neg. max.). MS *m/e* (%): 788 (M^+, 0.1), 729 (M^+−AcO, 0.4), 728 (M^+−AcOH, 0.3), 686 (M^+−AcOH−C_2H_2O, 0.6), 668 (M^+−2AcOH, 1.3), 259 (**ia**, 53), 199 (**ii**, 24), 157 (**iii**, 51), 139 (**iv**, **v**, 100), 97 (62). High Resolution MS: Found: 788.398, 729.384, 728.379, 259.082, 199.059, 157.051, 139.115, 139.039. Calcd. for $C_{42}H_{60}O_{14}$ (M^+)=788.398, $C_{40}H_{57}O_{12}$=729.385, $C_{40}H_{56}O_{12}$=728.377, $C_{11}H_{15}O_7$ (**ia**)=259.082, $C_9H_{11}O_5$ (**ii**)=199.061, $C_7H_9O_4$ (**iii**)=157.050, $C_9H_{15}O$ (**v**)=139.112, $C_7H_7O_3$ (**iv**)=139.040.

Alkaline Hydrolysis of 8a giving 8——To a solution of **8a** (33 mg) in dry MeOH (1 ml) was added 1% NaOMe–MeOH (1 ml) and the total solution was kept stirring at 25° for 1 hr and 45 min, poured into ice-water, and extracted with AcOEt. The AcOEt extract was washed with water, dried over $MgSO_4$, and evaporated under reduced pressure. Crystallization of the product from MeOH gave **8** as colorless needles of mp 265.5—267°, which colored yellow with tetranitromethane in EtOH. IR ν_{max}^{KBr} cm^{-1}: 3385 (br, OH), 982, 920, 900, 867 (900>920). CD (c=0.072, MeOH): $[\theta]_{218}$ 0, $[\theta]_{200}$ −70700 (neg. max.), $[\theta]_{197}$ −62800!. MS *m/e* (%): 578 (M^+, 0.2), 542 (M^+−$2H_2O$, 0.2), 524 (M^+−$3H_2O$, 0.3), 445 (**b** fission in **8**, 1), 429 (**a** fission in **8**, 9.5), 411 (21.4), 149 (9.5), 139 (**v**, 100), 133 (**i**, 7.1), 115 (14), 97 (9.5). High Resolution MS: Found: 578.344, 542.324, 524.312, 445.294, 429.299, 139.112, 133.053. Calcd. for $C_{32}H_{50}O_9$ (M^+)=578.345, $C_{32}H_{46}O_7$=542.324, $C_{32}H_{44}O_6$=524.314, $C_{27}H_{41}O_5$=445.295, $C_{27}H_{41}O_4$=429.300, $C_9H_{15}O$ (**v**)=139.112, $C_5H_9O_4$ (**i**)=133.051.

Acetonidation of 8 giving 9——A solution of **8** (4 mg) in dry acetone (20 ml) was treated with anhydrous cupric sulfate (700 mg) and the total mixture was kept stirring at 40° for 8 hr and at 30° overnight, and filtered. Evaporation of the filtrate gave **9** (3 mg). Colorless solid (amorphous) from MeOH. MS *m/e* (%): 658 (M^+, 0.5), 643 (M^+−CH_3, 1.5), 583 (0.5), 525 (0.5), 485 (**b** fission in **9**, 1.4), 469 (**a** fission in **9**, 2.1), 453 (1.1), 428 (4), 411 (469−$(CH_3)_2CO$, 22), 393 (5), 189 (**a** fission in **9**, 17), 173 (**vi**, 21), 139 (**v**, 77), 115 (**vii**, 23), 97 (**viii**, 17), 69 (37), 59 ($(CH_3)_2CO$+H, 100). High Resolution MS: Found: 658.406, 643.382, 485.325, 469.329, 411.291, 189.076, 173.081, 139.112, 115.037, 97.030. Calcd. for $C_{38}H_{58}O_9$ (M^+)=658.408, $C_{37}H_{55}O_9$=643.385, $C_{30}H_{45}O_5$=485.327, $C_{30}H_{45}O_4$=469.332, $C_{27}H_{39}O_3$ ($C_{30}H_{45}O_4$−$(CH_3)_2CO$)=411.290, $C_8H_{13}O_5$=189.076, $C_8H_{13}O_4$ (**vi**)=173.081, $C_9H_{15}O$ (**v**)=139.112, $C_5H_7O_3$ (**vii**)=115.040, $C_5H_5O_2$ (**viii**)=97.029.

Acid Hydrolysis of 8 giving Meteogenin (3) and Arabinose——A solution of **8** (14 mg) in a mixture of conc. HCl–MeOH (1: 4, 6 ml) was heated under reflux for 4 hr, poured into ice-water, and extracted with ether. After the usual work-up, a product obtained from the ether extract was purified by preparative TLC (silica gel and Kieselgel G, $CHCl_3$–AcOEt=10: 1) and the aglycone (7 mg) thus obtained was crystallized from MeOH to give colorless prisms of mp 152—154° (high mass: Found: 410.282; Calcd. for $C_{27}H_{38}O_3$ (M^+)=410.282), which were identified with authentic meteogenin (3) by mixed mp, IR (CS_2), MS, and TLC (three different solvent systems). The aqueous layer was neutralized with Amberlite IR 45 (10 g) and concentrated under reduced pressure to give a syrupy residue which was identified with L-arabinose by paper partition chromatography (PPC) (Toyo Filter Paper, No. 50, iso-PrOH–*n*-BuOH–H_2O=7:1:2, detection with aniline hydrogen phthalate) and by TLC (Avicel cellulose, AcOEt–pyridine–AcOH–H_2O=5:5:1:3, detection as for PPC).

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