Found: C, 59.32; H, 4.42. IR ν_{max}^{KBr} cm^{-1}: 3337 (OH), 1755 (lactol), 1614, 1603, 1592 (arom.). NMR ($CDCl_3$) τ: 6.00 (6H, s, $OC\underline{H}_3 \times 2$), 7.21 (2H, q, $J=7$ Hz, $-C\underline{H}_2CH_3$), 8.68 (3H, t, $J=7$ Hz, $-CH_2C\underline{H}_3$).

8-Ethyl-1,6,11-trihydroxynaphthacenequinone (I) (Bisanhydro-γ-rhodomycinone or Bisanhydrodecarbomethoxy-ε-rhodomycinone)——a) From IX: A mixture of H_3BO_3 (44 g) and H_2SO_4 (440 ml) was heated until a clear solution resulted, and then cooled to room temperature. To this was added 3.84 g of IX, and the mixture was heated with stirring at 110—140° for 10 min and at 140—150° for 20 min. During the reaction period, initial dark brown color of the mixture turned into dark reddish violet. The mixture was poured onto cracked ice to give red precipitates, which were collected, washed with H_2O, then with satd. $NaHCO_3$ and again with H_2O, and dried to give 2.4 g of dark red solid which showed a positive Beilstein test. This solid was heated in glycerol (100 ml) at 200° to get suspension. After cooling to 100°, KOH (15 g) was added, and the temperature was maintained at 170—175° for 0.5 hr. The reaction mixture was poured onto cracked ice and acidified with conc. HCl to give dark red precipitates, which showed a negative Beilstein test. Three recrystallizations from benzene gave 2.35 g (78.4%) of I, mp 205—206° (lit.[3] mp 206°). *Anal.* Calcd. for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: C, 71.84; H, 4.17. IR ν_{max}^{KBr} cm^{-1}: 1617 sh, 1592, 1581, 1561 sh, 1542 sh (arom.).

b) From XVII: A mixture of H_3BO_3 (16.7 g) and H_2SO_4 (167 ml) was heated with stirring until a clear solution resulted, and then cooled to 115°. To this was added 1.45 g of XVII, and the mixture was heated with stirring at 140—150° for 20 min, during which time, initial bluish violet color of the mixture turned into violet. The mixture was poured onto 500 g of cracked ice to give dark red precipitates, which were collected, washed with H_2O, then with satd. $NaHCO_3$, and again with H_2O, and dried to give 1.04 g of dark red crystals which showed a positive Beilstein test. Treatment of this crystals with KOH (6.1 g) in glycerol (34 ml) was carried out in a similar manner to that in a). The collected crystals (0.89 g, 84.0%) showed a negative Beilstein test and mp 204—206°. The sample was identical with that obtained in a).

c) From XVI: The cyclization of XVI (1.0 g) with H_2SO_4 (115 ml) in the presence of H_3BO_3 (11.5 g) was carried out in a similar manner to that in b). Resulting dark red crystals which indicated a positive Beilstein test were treated with KOH (4.1 g) in glycerol (27 ml) in a similar manner to that in a). The collected crystals (0.66 g, 89.0%) showed a negative Beilstein test. The sample was identical with that obtained in a).

[Chem. Pharm. Bull. 20(11)2506—2510(1972)]

UDC 547.92'457.1.04

Conversion of Steroid Saponins to the Corresponding Pregnane Glycosides

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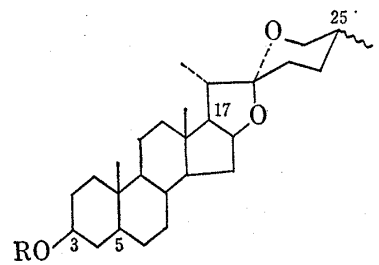
(Received July 18, 1972)

The steroid sapogenins (spirostanols) (Ia—c) are well known[2] as the most important starting material for the convenient preparation and production of pregnan-3β-ol-20-one (IIa, b) and pregn-5-en-3β-ol-20-one (IIc), from which a variety of steroid compounds of medicinal importance are derived.

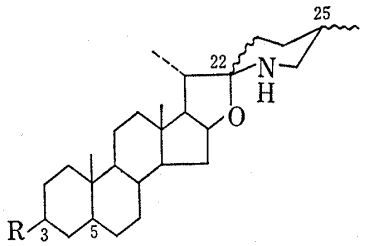
The spiroketal side chain at C-17 of I is degraded, through pseudomerization, oxidative cleavage of $\Delta^{20(22)}$ and hydrolysis of ester linkage, by the methods originally proposed by Marker and his collaborators.[2] A similar conversion of nitrogen analogs (spirosolane (IIIa) derivatives) of spirostanols has also been reported by Sato and his co-workers.[3]

1) Location: *1276 Katakasu, Fukuoka.*
2) J. Elks, "Rodd's Chemistry of Carbon Compounds," 2nd ed., Vol. II_E, ed. by S. Coffey, Elsevier Publishing Co., Amsterdam, 1971, pp. 9—11.
3) Y. Sato, "Chemistry of the Alkaloids," ed. by S.W. Pelletier, Van Nostrand Reinhold Co., New York, N.Y., 1970, pp. 613—615.

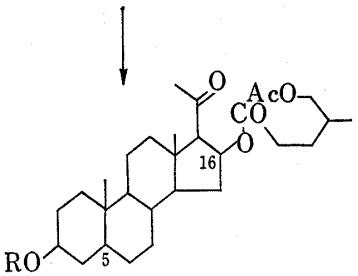
This paper describes the application of these methods to their parent glycosides (neutral and basic steroid saponins), trillin (Id),[4] timosaponin A-III (Ie),[5] gracillin (If),[6,7] desgalactotigonin (Ig),[8] and tomatine (IIIb),[9] to offer a method of preparation of pregnane glycosides



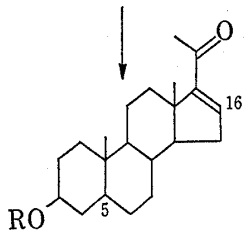
Ia : R=H, 5β-H
Ib : R=H, 5α-H
Ic : R=H, Δ^5
Id : R=β-D-glc. pyr, Δ^5, 25*R*
Ie : R=β-timobiose, 5β-H, 25*S*
If : R=β-gracillimatriose, Δ^5, 25*R*
Ig : R=β-lycotetraose, 5α-H, 25*R*



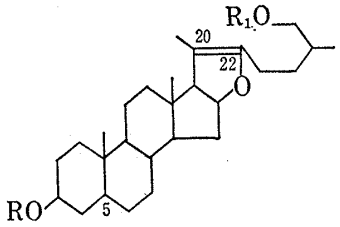
IIIa : R=H
IIIb : R=-O-β-lycotetraose, 5α-H, 22*S*, 25*S*



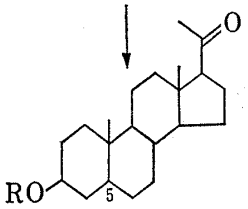
Va : R=β-D-glc. pyr(Ac), Δ^5
Vb : R=β-timobiose(Ac), 5β-H



VIa : R=β-D-glc. pyr(Ac), Δ^5
VIb : R=β-D-glc. pyr, Δ^5
VIc : R=β-timobiose(Ac), 5β-H
VId : R=β-timobiose, 5β-H
VIe : R=β-gracillimatriose(Ac), Δ^5
VIf : R=β-gracillimatriose, Δ^5
VIg : R=β-lycotetraose, 5α-H
VIh : R=H, 5β-H
VIi : R=H, 5α-H



IVa : R=β-D-glc. pyr(Ac), R_1=Ac, Δ^5
IVb : R=β-D-glc. pyr, R_1=Ac, Δ^5
IVc : R=β-timobiose(Ac), R_1=H, 5β-H
IVd : R=β-timobiose, R_1=H, 5β-H
IVe : R=β-gracillimatriose(Ac), R_1=Ac, Δ^5
IVf : R=β-gracillimatriose, R_1=H, Δ^5



IIa : R=H, 5β-H
IIb : R=H, 5α-H
IIc : R=H, Δ^5
IId : R=β-D-glc. pyr(Ac), Δ^5
IIe : R=β-D-glc. pyr, Δ^5
IIf : R=β-timobiose, 5β-H
IIg : R=β-gracillimatriose(Ac), Δ^5
IIh : R=β-gracillimatriose, Δ^5

4) T. Tsukamoto, T. Kawasaki, and T. Yamauchi, *Pharm. Bull.* (Japan), **4**, 35 (1956).
5) T. Kawasaki, T. Yamauchi, and N. Itakura, *Yakugaku Zasshi*, **83**, 892 (1963); T. Kawasaki and T. Yamauchi, *Chem. Pharm. Bull.* (Tokyo), **11**, 1221 (1963).
6) *a*) T. Tsukamoto and T. Kawasaki, *Yakugaku Zasshi*, **74**, 1127 (1954); *idem*, *Pharm. Bull.* (Japan), **4**, 104 (1956); *b*) T. Kawasaki and T. Yamauchi, *Chem. Pharm. Bull.* (Tokyo), **10**, 703 (1962).
7) T. Kawasaki, T. Yamauchi, and R. Yamauchi, *Chem. Pharm. Bull.* (Tokyo), **10**, 698 (1962).
8) T. Kawasaki and I. Nishioka, *Chem. Pharm. Bull.* (Tokyo), **12**, 1311 (1964).
9) R. Kuhn, I. Löw, and H. Trishmann, *Chem. Ber.*, **90**, 203 (1957).

which seem to be of interest from the therapeutic and biogenetic[10] view points but are not always easily accessible by the conventional way involving glycosidation.

Desgalactotigonin (Ig) which is known[8] to have a tetrasaccharide moiety, consisting of one mole each of D-galactose and D-xylose and two moles of D-glucose, combined with tigogenin (Ib, 25*R*) was converted to the corresponding 5α-pregn-16-en-3β-ol-20-one 3-O-oligoside (VIg), which was identified with that obtained from tomatine (IIIb), tomatidine 3-O-β-lycotetraoside.[9] Thus the structure of the sugar moiety of Ig is established and shown to be same as that of F-gitonin[8,11] which is coexistent with Ig in the leaves of *Digitalis purpurea* L.

Experimental[12]

Pregn-5-en-3β-ol-20-one 3-O-β-D-Glucopyranoside (IIe) from Trillin (Diosgenin 3-O-β-D-Glucopyranoside)[4] (Id)——Pseudomerization: One gram of Id tetraacetate,[4] mp 204—205°, $[\alpha]_D$ −67° (c=1.35, $CHCl_3$), was heated in a sealed tube with Ac_2O (2.5 ml) at 175° for 20 hr. A solid deposited on cooling was collected by filtration, washed with cold MeOH and the filtrate was poured into ice water. The precipitates were combined with the above solid and crystallized from MeOH to give pseudodiosgenin glucoside peracetate (IVa) as colorless prisms (0.45 g), mp 163—164°, $[\alpha]_D$ −35.2° (c=1.77, $CHCl_3$). IR ν_{max} cm^{-1}: 1761, 1709, no spiroketal absorptions. *Anal.* Calcd. for $C_{43}H_{62}O_{13}$: C, 65.63; H, 7.94. Found: C, 65.56; H, 7.94.

IVa (52.3 mg) was deacetylated with hot 5% KOH in MeOH for 1 hr to give crude crystals (38 mg) which were recrystallized from MeOH to afford free pseudo compound glucoside (IVb) as colorless plates (19 mg), mp 236—239° (decomp.), $[\alpha]_D$ −34.6° (c=1.37, pyridine). IR ν_{max} cm^{-1}: 3400, 1709, 1650. *Anal.* Calcd. for $C_{33}H_{52}O_8 \cdot H_2O$: C, 66.64; H, 9.15. Found: C, 66.56; H, 9.14.

Oxidative Cleavage of $\Delta^{20(22)}$ and Hydrolysis of Ester Linkage: To the solution of IVa (1.50 g) in AcOH (10 ml) containing 2% AcONa, 20% CrO_3 in 80% AcOH (2 ml) was added in dropwise in 20 min under stirring and cooling at 10°. After further stirring at room temperature for 2 hr, the mixture was diluted with water, the excess CrO_3 being decompsed with $NaHSO_3$, and extracted with ether. The extract was washed with water and $NaHCO_3$ solution, dried, evaporated and the residue was crystallized from MeOH to give 16β-(δ-acetoxy-γ-methyl valeroxy)-pregn-5-en-3β-ol-20-one glucoside peracetate (Va) as colorless needles (1.01 g), mp 143—145°, $[\alpha]_D$ −27.9° (c=1.79, $CHCl_3$). IR ν_{max} cm^{-1}: 1773, 1718. *Anal.* Calcd. for $C_{43}H_{62}O_{15}$: C, 63.06; H, 7.63. Found: C, 63.20; H, 7.66. Va (780 mg) in AcOH (8 ml) was refluxed for 16 hr, poured into a large amount of water and extracted with CH_2Cl_2. The organic layer was washed (water, $NaHCO_3$ solution), dried and evaporated and the residue was crystallized from MeOH to give pregna-5,16-dien-3β-ol-20-one glucoside tetraacetate (VIa) as colorless prisms (562 mg), mp 232—235°, $[\alpha]_D$ −45.3° (c=1.12, $CHCl_3$). UV λ_{max} nm(log ε): 238 (3.91). IR ν_{max} cm^{-1}: 1765, 1675, 1600. *Anal.* Calcd. for $C_{35}H_{48}O_{11}$: C, 65.20; 7.51. Found: C, 65.44; H, 7.48. VIa (65 mg) was deacetylated with hot 5% KOH in MeOH (1 ml) for 1 hr to give free glycoside (VIb) as a white powder (from dil. MeOH) (41 mg), mp 236—242° (decomp.). IR ν_{max} cm^{-1}: 3200, 1675, 1600. *Anal.* Calcd. for $C_{27}H_{40}O_7 \cdot H_2O$: C, 65.56; H, 8.56. Found: C, 65.51; H, 8.58.

Hydrogenation of Δ^{16}: VIa (100 mg) in ether (100 ml) was shaken under H_2 (3 kg/cm^2) with 5% Pd/$BaSO_4$ (500 mg) for 3.5 hr at room temperature. The product was crystallized from MeOH to give pregn-

10) Pregn-5-en-3β-ol-20-one and 5α-pregnan-3β-ol-20-one were found as their glycosides in Uzara root (R. Tschesche and G. Snatzke, *Ann.*, **636**, 105 (1960)) and the mono- and tri-glucosides and two di-glucosides of the former were recently isolated from *Nerium odorum* Sol. (T. Yamauchi, M. Hara, and K. Mihashi, *Phytochemistry*, in press).[a] Pregna-5,16-dien-3β-ol-20-one and its 3-O-β-chacotrioside were obtained respectively from *Solanum vespertilio* [A.G. Gonzarez, C. Garcia Francisco, R. Freire Barreira, and E. Suarez Lopez, *An. Quim.*, **67**, 433 (1971) [*C.A.* **75**, 115896 (1971)] and *Paris polyphylla* Sm. (R. Hida, T. Nohara, and T. Kawasaki, Abstracts of Papers, The 92nd Annual Meeting of the Pharmaceutical Society of Japan, Osaka, April 1972, p. 249).

11) T. Kawasaki, I. Nishioka, T. Komori, T. Yamauchi, and K. Miyahara, *Tetrahedron*, **21**, 299 (1956).

12) All melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured at 14—18°. Infrared (IR) spectra were obtained in Nujol with an IR Recording Spectrophotometer, Koken DS-201, ultraviolet (UV) spectra were measured in EtOH solution on a Shimadzu Automatic Recording Spectrophotometer and mass spectra were recorded on a JMS-0ISG mass spectrometer with an accelerating potential of 4.6 kV, an ionizing potential of 75 eV and a source temperature of 210—250°. Nuclear magnetic resonance (NMR) spectra were taken at 60 MHz on a JEOL-C-60H spectrometer and chemical shifts are given in δ scale with tetramethylsilane as internal standard. Thin-layer chromatography (TLC) of pregnane derivatives were carried out on Kieselgel G (E. Merck, A.G.) using hexane–AcOEt 3:1 as a solvent and H_2SO_4 (heating) as visualizing agent. In column chromatography, Kieselgel (E. Merck, A.G.) was used.

5-en-3β-ol-20-one glucoside tetraacetate (IId) as colorless prisms (65 mg), mp 222—224°, $[\alpha]_D$ −26.6° (c=0.52, $CHCl_3$). IR ν_{max} cm^{-1}: 1757, 1706. *Anal.* Calcd. for $C_{35}H_{50}O_{11}$: C, 65.00; H, 7.79. Found: C, 64.84; H, 7.74. IId (141 mg) was deacetylated with 5% KOH in MeOH and a crude product (85 mg) was crystallized from MeOH to give the free glucoside (IIe) as colorless leaflets (65 mg), mp 273—275° (decomp.), $[\alpha]_D$ −14.9° (c=0.75, pyridine) [lit.,[10a] mp 270—271° (decomp.), $[\alpha]_D$ −13.2° (pyridine)]. IR ν_{max} cm^{-1}: 3450, 1706. *Anal.* Calcd. for $C_{27}H_{42}O_7$: C, 67.75; H, 8.84. Found: C, 67.42; H, 8.82. Hydrolysis of IIe with boiling 1N H_2SO_4 in 60% acetone yielded glucose (paper chromatography (PC)) and pregn-5-en-3β-ol-20-one (IIe), mp 190.5—191.5°, identified with authentic sample (mp 191—192.5°) by mixed melting point determination and comparison of IR spectra and *Rf* values on thin-layer chromatogram (TLC).

5β-Pregnan-3β-ol-20-one 3-O-β-D-Glucopyranosyl-(1→2)-β-D-galactopyranoside (β-Timobioside) (IIf) from Timospaponin A-III (Sarsasapogenine 3-O-β-Timobioside)[5] (Ie)——Pseudomerization: Ten grams of Ie heptaacetate prepared in an usual way, white powder (from ether–hexane), mp 123—126°, $[\alpha]_D$ −93.2° (c=2.41, $CHCl_3$), no hydroxyl absorptions on IR spectra and single spot on TLC,[13] was heated in a sealed tube with Ac_2O (20 ml) at 170° for 6 hr. The reaction mixture was poured into ice-water (500 g) and the precipitates were collected, washed, dried and crystallized from ether–hexane to give psuedosarsasapogenin glycoside peracetate (IVc) as a white powder (9.7 g), mp 108°, UV λ_{max} nm(log ε): 214 (3.78). IR ν_{max} cm^{-1}: 1761, 1701, no spiroketal absorptions. IVc (1.0 g) was deacetylated as IVa and the product was crystallized from dil. EtOH to give the free glycoside (IVd) as colorless plates (610 mg), mp 265—270° (decomp.), $[\alpha]_D$ −14.2° (c=1.0, pyridine). IR ν_{max} cm^{-1}: 3460, 1698. *Anal.* Calcd. for $C_{39}H_{64}O_{13}\cdot 2H_2O$: C, 60.29; H, 8.82. Found: C, 60.29; H, 8.86.

Oxidative Cleavage of $\Delta^{20(22)}$ and Hydrolysis of Ester Linkage: IVc (1.0 g) was oxidized with CrO_3 in the same manner as in IVa to give the ketoester glycoside peracetate (Vb) as a white powder (0.9 g) (ether–hexane), IR ν_{max} cm^{-1}: 1770, 1720. Vb (600 mg) was hydrolyzed with AcOH as Va to yield 5β-pregnan-3β-ol-20-one timobioside heptaacetate (VIc) as a white powder (420 mg) (ether–hexane), IR ν_{max} cm^{-1}: 1761, 1669, 1592. Deacetylation of VIc (100 mg) as VIa gave the free glycoside (VId) as colorless plates (32 mg) (dil. EtOH), mp 243—248° (decomp.), $[\alpha]_D$ −6.9° (c=1.04, pyridine), IR ν_{max} cm^{-1}: 3500, 1669, 1596. *Anal.* Calcd. for $C_{33}H_{52}O_{12}$: C, 61.86; H, 8.18. Found: C, 61.18; H, 8.34. Acid hydrolysis of VId gave glucose, galactose (PC) and 5β-pregn-16-en-3β-ol-20-one (VIh), mp 185.5—187.5° $[\alpha]_D$ +48.8° (c=0.72, $CHCl_3$) (lit.[14] mp 188—190°, $[\alpha]_D$ +49°).

Hydrogenation of Δ^{16}: VIc (210 mg) was hydrogenated as VIa to give a white powder (205 mg) (ether–hexane), IR ν_{max} cm^{-1}: 1757, 1709, which was deacetylated to yield (IIf) as colorless plates (135 mg) (dil. MeOH), mp 244—248° (decomp.), $[\alpha]_D$ −20.1° (c=1.29, $CHCl_3$), IR ν_{max} cm^{-1}: 3270, 1695. *Anal.* Calcd. for $C_{33}H_{54}O_{12}\cdot H_2O$: C, 59.98; H, 8.54. Found: C, 60.51; H, 8.78.

Pregn-5-en-3β-ol-20-one 3-O-β-D-Glucopyranosyl-(1→3)-[α-L-Rhamnopyranosyl-(1→2)]-β-D-Glucopyranoside (β-Gracillimatrioside) (IIh) from Gracillin (Diosgenin 3-O-β-Gracillimatrioside)[6] (If)——Pseudomerization: Two grams of If nonaacetate,[6a,7] was heated in a sealed tube with Ac_2O (5 ml) and AcOH (0.1 ml) at 175° for 20 hr. Subsequent treatment as in Ie gave the pseudodiosgenin glycoside peracetate (IVe) as a white powder (2.03 g) (ether–hexane), mp 108°, IR ν_{max} cm^{-1}: 1757, 1712, no spiroketal absorptions. IVe (530 mg) was deacetylated as IVc to give the free glycoside (IVf) as colorless plates (128 mg) (dil. MeOH), mp 235—240° (decomp.), $[\alpha]_D$ −43.0° (c=1.30, pyridine). IR ν_{max} cm^{-1}: 3390, 1709. *Anal.* Calcd. for $C_{45}H_{72}O_{17}\cdot H_2O$: C, 59.85; H, 8.26. Found: C, 59.40; H, 8.31.

Oxidative Cleavage of $\Delta^{20(22)}$ and Hydrolysis of Ester Linkage: IVe (600 mg) was oxidized as IVc and the product was crystallized from ether–hexane to give a white powder (570 mg), which was refluxed with AcOH and treated as Ve to give pregna-5,16-dien-3β-ol-20-one gracillimatrioside nonaacetate (VIe) as a white powder (423 mg) (ether–hexane), mp 141—143°. IR ν_{max} cm^{-1}: 1750, 1667, 1592. VIe (65 mg) was deacetylated as VIc and a crude product (35 mg) was passed through a silica gel (2.5 g) column by using $CHCl_3$–MeOH (4:1) as a solvent. The eluate was evaporated to dryness and the residue was crystallized from dil. MeOH to give the free glycoside (VIf) as colorless needles (15 mg), mp 273—275° (decomp.), $[\alpha]_D$ −35.1° (c=1.1, pyridine). IR ν_{max} cm^{-1}: 3390, 1647, 1592. *Anal.* Calcd. for $C_{39}H_{60}O_{16}\cdot H_2O$: C, 57.06; H, 7.36. Found: C, 57.13; H, 7.66.

Hydrogenation of Δ^{16}: VIe (500 mg) was hydrogenated as VIc and a crude product (white powder, 490 mg) was chromatographed over Al_2O_3 (Woelm, neutral, grade 1, 15 g). Ether fraction was crystallized from hexane (or MeOH) to give pregn-5-en-3β-ol-20-one gracillimatrioside nonaacetate (IIg) as colorless needles (380 mg), mp 229—231°, $[\alpha]_D$ −38.8° (c=1.20, $CHCl_3$). IR ν_{max} cm^{-1}: 1745, 1700. *Anal.* Calcd. for $C_{57}H_{80}O_{25}$: C, 58.75; H, 6.92. Found: C, 58.55; H, 6.88. IIg (90 mg) was deacetylated with 5% KOH–MeOH and the product was crystallized from dil. MeOH to give the free glycoside (IIh) as colorless needles (38 mg), mp 231—236° (decomp.), $[\alpha]_D$ −37.2° (c=1.52, pyridine). IR ν_{max} cm^{-1}: 3400, 1706. *Anal.* Calcd. for $C_{39}H_{62}O_{16}\cdot 2H_2O$: C, 56.92; H, 8.08. Found: C, 57.01; H, 8.18. Acid hydrolysis of IIh gave glucose

13) T. Kawasaki and K. Miyahara, *Chem. Pharm. Bull.* (Tokyo), **11**, 1546 (1963).
14) M.E. Wall and H.A. Walens, *J. Am. Chem. Soc.*, 77, 5661 (1955).

and rhamnose (2:1, PC[6a]) and IIc, mp 188—189.5°. $[\alpha]_D$ +29.6° (c=1.03, $CHCl_3$), identified with an authentic sample, mp 189—191°. $[\alpha]_D$ +28.2° (c=1.32, $CHCl_3$), by direct comparison (mixed mp, IR, TLC).

5α-Pregn-16-en-3β-ol-20-one 3-O-β-D-Glucopyranosyl-(1→2)-[β-D-Xylopyranosyl-(1→3)]-β-D-Glucopyranosyl-(1→4)-β-D-Galactopyranoside (β-Lycotetraoside)——From Tomatine[9] (IIIb): IIIb (490 mg) was acetylated with Ac_2O (4 ml) and pyridine (8 ml) for 2 days at room temperature. The mixture was poured into ice-water, the precipitates were collected and dried. The procuedure was repeated four times to yield tridecaacetate (no hydroxyl absorptions on IR and single spot on TLC[13]) as a white powder (ether–hexane) (740 mg), mp 135—142°, $[\alpha]_D$ −14.5° (c=1.2, $CHCl_3$). The acetate was added in portionwise to boiling AcOH (20 ml) and the solution was refluxed for 30 min and then cooled with running water. CrO_3 (110 mg) in 80% AcOH (10 ml) was added in dropwise (in 15 min) to the above solution under stirring at 10—15°, and the mixture was stirred at 25° for another 1 hr. Diluted with water, excess CrO_3 was decomposed with $NaHSO_3$ and the solution was saturated with NaCl, extracted with CH_2Cl_2 and the extract was washed, dried and evaporated. The residue was dissolved in AcOH (25 ml), refluxed for 2 hr and AcOH was removed *in vacuo*. The residue was extracted with ether and the extract was washed (water, $NaHCO_3$ solution), dried and evaporated to give the crude peracetate of 5α-pregn-16-en-3β-ol-20-one lycotetraoside (VIg) (554 mg), IR ν_{max} cm^{-1}: 1740, 1665, 1595. It was deacetylated with 2.5% KOH in 90% *tert*-BuOH (70 ml) at 90° for 12 hr and the reaction mixture was concentrated to 20 ml, neutralized with AcOH, diluted with water (50 ml) and extracted with BuOH saturated with water. The BuOH layer was evaporated, the residue (300 mg) was passed through a silica gel column using $CHCl_3$–MeOH–water (7:3:1) and crystallized from dil. MeOH to give the pure free glycoside (VIg) as colorless needles (170 mg), 286—288° (decomp.), $[\alpha]_D$ −14.8° (c=1.2, pyridine). IR $\nu_{max}$$cm^{-1}$: 3380, 1615, 1587. *Anal.* Calcd. for $C_{44}H_{68}O_{21}\cdot 2H_2O$: C, 54.54; H, 7.50. Found: C, 54.90; H, 7.65. Acid hydrolysis gave xylose, glucose, galactose (1:2:1, PC[8]) and 5α-pregn-16-en-3β-ol-20-one (VIi), mp 205—207° (MeOH), $[\alpha]_D$ +49.8° (c=1.18, EtOH), identical with an authentic sample, mp 206—207.5°, $[\alpha]_D$ +50.1° (c=1.01, EtOH) (lit.[15] mp 209—209.5°, $[\alpha]_D$ +50.4° (EtOH)) (mixed mp, IR, TLC). VIg was acetylated as IIIb to give the peracetate as a white powder (ether–hexane), mp 126—129°. $[\alpha]_D$ −11.2° (c=1.02, $CHCl_3$). mass spectrum[16] m/e: 259 ($C_{11}H_{15}O_7^+$, peracetylated terminal pentose residue), 299 ($C_{21}H_{31}O^+$), 331 ($C_{14}H_{19}O_9^+$, peracetylated terminal hexose residue), 835 ($C_{35}H_{47}O_{23}^+$, peracetylated trisaccharide (hexose-(pentose-)-hexose) residue). NMR ($CDCl_3$) ppm: 0.83 (3H, singlet), 0.87 (3H, singlet), 1.97—2.25 (broad doublet, AcO×12), 6.68 (1H, singlet).

From Desgalactotigonin[8] (Ig): Ig (100 mg) was acetylated three times with Ac_2O (1 ml) and pyridine (1 ml) on a boiling water-bath for 3 hr and the mixture was evaporated *in vacuo* to give a resinous mass. The resin was chromatographed over silica gel using hexane–AcOEt as a solvent to afford Ig dodecaacetate as a white powder (ether–hexane) (92 mg), mp 129—130.5°, $[\alpha]_D$ −36.3° (c=1.02, $CHCl_3$), no hydroxyl absorptions on IR and single spot on TLC.[13] Mass Spectrum m/e: 259 ($C_{11}H_{15}O_7^+$), 331 ($C_{14}H_{19}O_9^+$), 399 ($C_{27}H_{43}O_2^+$), 835 ($C_{35}H_{47}O_{23}^+$). The peracetate (740 mg) was dissolved in Ac_2O (15 ml), heated in a sealed tube at 180° for 22 hr, and then Ac_2O was removed *in vacuo* to a resin (705 mg). The resin in 80% AcOH (10 ml) was oxidized with CrO_3 (300 mg) in 80% AcOH (10 ml) and treated as in the case of IIIb. The reaction mixture was shaken with ether (300 ml) and the organic layer was washed with water, dried and evaporated. A solution of the product in AcOH (15 ml) was refluxed for 2 hr and evaporated *in vacuo* to dryness (a resin, 485 mg). The residue was treated with 2.5% KOH in 90% *tert*-BuOH and worked up in the same way as in VIg to give a crude product (396 mg). It was chromatographed over silica gel using $CHCl_3$–MeOH–water (7:3:1) as a solvent to afford a free glycoside as colorless fine needles (90 mg) (dil. MeOH), mp 285—288° (decomp.), $[\alpha]_D$ −15.3° (c=1.0, pyridine). IR ν_{max} cm^{-1}: 3375, 1653, 1598. *Anal.* Calcd. for $C_{44}H_{68}O_{21}\cdot 2H_2O$: C, 54.54; H, 7.50. Found: C, 54.36; H, 7.56. Acid hydrolysis gave xylose, glucose, galactose (1:2:1, PC[8]) and VIi. The glycoside was identified with VIg derived from IIIb by direct comparison (mixed mp, IR, TLC). Peractate, mp 127—129.5°, $[\alpha]_D$ −11.0° (c=1.07, $CHCl_3$) was also identical with VIg peracetate on NMR and mass spectra.

Acknowledgement The authors express their gratitudes to the late Dr. Y. Sato of National Institutes of Health in U.S.A. for tomatine as a starting material, and Prof. T. Yamauchi of Fukuoka University for the information concerning pregnenolone glycosides in *Nerium odorum* prior to publication. Thanks are also due to Miss M. Kawamura for the mass spectra and to the members of the Central Analysis Room of this University for microanalysis.

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