Phytochemistry, 1974. Vol. 13, pp. 627 to 632. Pergamon Press. Printed in England.

7-DEHYDROAGAPANTHAGENIN AND 8(14)-DEHYDROAGAPANTHAGENIN, TWO NEW SPIROSTAN SAPOGENINS FROM *AGAPANTHUS AFRICANUS**

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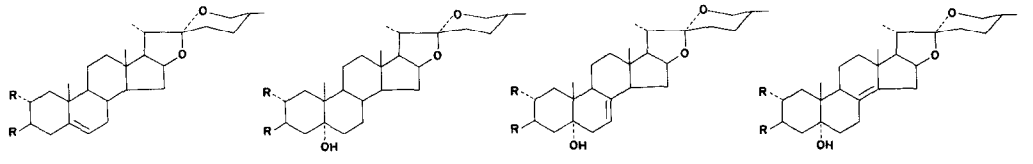
(*Received* 31 *July* 1973. *Accepted* 24 *September* 1973)

Key Word Index—*Agapanthus africanus*; Liliaceae; spirostan sapogenins; 7-dehydroagapanthagenin; 8(14)-dehydroagapanthagenin.

Abstract—Besides sitosterol, yuccagenin (**1a**) and agapanthagenin (**2a**), the two new spirostan sapogenins 7-dehydroagapanthagenin (**3a**) and 8(14)-dehydroagapanthagenin (**4a**) have been isolated from the rhizomes of *Agapanthus africanus* and their structures determined.

INTRODUCTION

Agapanthus africanus Hoffmnsg., a plant of South African origin, was first studied by Takeda *et al.*,[1] who isolated yuccagenin (**1a**). Later, Stephen and Mathew,[2,3] working with several unspecified species of *Agapanthus*, obtained **1a** and the new spirostan sapogenin agapanthagenin (**2a**). The present paper reports our results of the unhydrolysed ethanolic extract of the rhizomes of *A. africanus* cultivated on the Canary Isles. In addition to sitosterol, **1a** and **2a**, we isolated the two new spirostan sapogenins 7-dehydroagapanthagenin (**3a**) and 8(14)-dehydroagapanthagenin (**4a**) whose structures were established as (25*R*)-spirost-7-en-2α,3β,5α-triol and (25*R*)-spirost-8(14)-en-2α,3β,5α-triol respectively. This is the first time that spirostan sapogenins with Δ^7 and $\Delta^{8(14)}$ are found in nature.



RESULTS AND DISCUSSION

7-Dehydroagapanthagenin (**3a**), $C_{27}H_{42}O_5$ (by MS), was eluted together with **2a**, 8(14)-dehydroagapanthagenin (**4a**) and a spirostan sapogenin of still unknown structure, being

* Part XXIII in the series "New Sources of Steriod Sapogenins". For Part XXII see GONZÁLEZ, A. G., FREIRE, R., HERNÁNDEZ, R., SALAZAR, J. A. and SUÁREZ, E. (1973) *Anal. Quím.* **69**, 1031.

[1] TAKEDA, K., OKANISHI, T. and SHIMAOKA, A. (1955) *Ann. Rept. Shionogi Research Lab.* 107; (1956) *Chem. Abstr.* **50**, 15916b.

[2] STEPHEN, T. (1956) *J. Chem. Soc.* 1167.

[3] MATHEW, G. E. A. and STEPHEN, T. (1957) *J. Chem. Soc.* 262.

separated by preparative column chromatography of the acetates on silica gel and silica gel–$AgNO_3$. **3a** has three OH groups as inferred from its MS which shows the loss of 1, 2 and 3 H_2O molecules from the molecular ion. On mild acetylation, it gives the diacetate **3b**, $C_{31}H_{46}O_7$, which has an OH function (IR: 3580 cm^{-1}), but its PMR spectrum does not present any signals assignable to protons geminal to it. Hence, one of the OH groups in **3a** must be tertiary. The remaining two oxygens form part of a (20*S*, 22*R*, 25*R*)-spirostan ring; this is from the position and relative intensities of the bands at 982, 923, 900 and 865 cm^{-1} in the IR spectrum of **3b**,[4] and from the PMR signals ($CDCl_3$) at τ 6·55 (*m*, $W_{1/2}$ 12 Hz) and 8·39 (*s*, $W_{1/2}$ 5 Hz) characteristic of the 2H-C_{26} and 2H-C_{23} respectively.[5,6]

TABLE 1. CHEMICAL SHIFTS IN THE PMR SPECTRA OF SPIROSTAN SAPOGENINS (τ-scale, 60 MHz)

Compound	Solvent	H-$C_{2,3}$	H-C_7	2H-C_{26}	Me-C_{19}	Me-C_{21}	Me-C_{27}	Me-C_{25}	OAc
Agapanthagenin diacetate **3b**	$CDCl_3$	4·77 *m*[25]	—	6·55 *m*[13]	8·92 *s*	9·23 *s*	9·05 *d*(6)	~9·24	7·99 *s*
	C_6D_6	4·49 *m*[36]	—	6·44 *m*[13]	9·25 *s*	9·25 *s*	8·83 *d*(6)	~9·30	8·24, *s* 8·27, *s*
7-Dehydroagapanthagenin diacetate **3b**	$CDCl_3$	4·80 *m*[24]	4·90 *m*[24]	6·55 *m*[12]	8·96 *s*	9·33 *s*	~9·02	9·21 *d*(7)	7·98 *s*
	C_6D_6	4·50 *m*[36]	5·13 *m*[10]	6·42 *m*[12]	9·22 *s*	9·34 *s*	8·83 *d*(6)	~9·34	8·22 *s*
8(14)-Dehydroagapanthagenin diacetate **4b**	$CDCl_3$	4·78 *m*[26]		6·55 *m*[13]	9·02 *s*	9·02 *s*	~9·02	9·23 *d*(6)	7·99 *s*
	C_6D_6	4·50 *m*[30]		6·43 *m*[13]	9·00 *s*	9·24 *s*	8·85 *d*(6)	~9·31	8·23 *s*

* Coupling constants *J* in parentheses, $W_{1/2}$ in brackets (both in Hz).

The molecular formulae for **3a** and **3b** together with the IR absorptions at 3025, 1670 and 840 cm^{-1} of the diacetate indicate the presence of a double bond which must be tertiary since in the PMR spectrum (C_6D_6) of **3b** only one vinyl proton is observed (τ 5·13, *m*, $W_{1/2}$ 10 Hz). Taking into account that the chemical shifts and shapes of the signals for the protons geminal to the OAc groups in the PMR spectra of **3b** ($CDCl_3$ and C_6D_6) coincide with those observed for agapanthagenin diacetate (**2b**) (see Table 1), one may deduce that **3a** has a 2α,3β,5α-triol system.* On this basis the trisubstituted double bond can only be placed at C_7 as is inferred from PMR data: the theoretical values for the Me-C_{10} and Me-C_{13} of **3b** (τ 8·93 and 9·35)† agree with the experimental ones ($CDCl_3$, Table 1).

Structure **3a** was confirmed by the following reaction sequence: dehydration of **3b** with $SOCl_2$ in pyridine at 0° gave a mixture of 7-dehydroyuccagenin acetate (**5**) and 4,7-dehydrogitogenin acetate (**6**), no appreciable changes in their ratio being observed on modifying the temperature or $SOCl_2$ concentration. The structure of **5**, $C_{31}H_{44}O_6$, was established by spectral analysis: in the UV, typical absorptions were found at 261, 270, 281 and 292 nm,[8] and in the PMR spectrum ($CDCl_3$) the H-$C_{6,7}$ appear as an AB system; further-

* The strong deshielding observed for the H-$C_{2,3}$ (~0·36 ppm in $CDCl_3$ and C_6D_6) as compared with the chemical shifts of these protons in gitogenin acetate [(25*R*)-5α-spirost-2α,3β-diol acetate; τ 5·13 ($CDCl_3$) and 4·86 (C_6D_6)] is due to the presence of the 5α-OH group and is valid for characterizing this system.

† Contributions for the double bonds are taken from Ref. 7.

[4] Jones, R. N., Katzenellenbogen, E. and Dobriner, K. (1953) *J. Am. Chem. Soc.* **75**, 158.

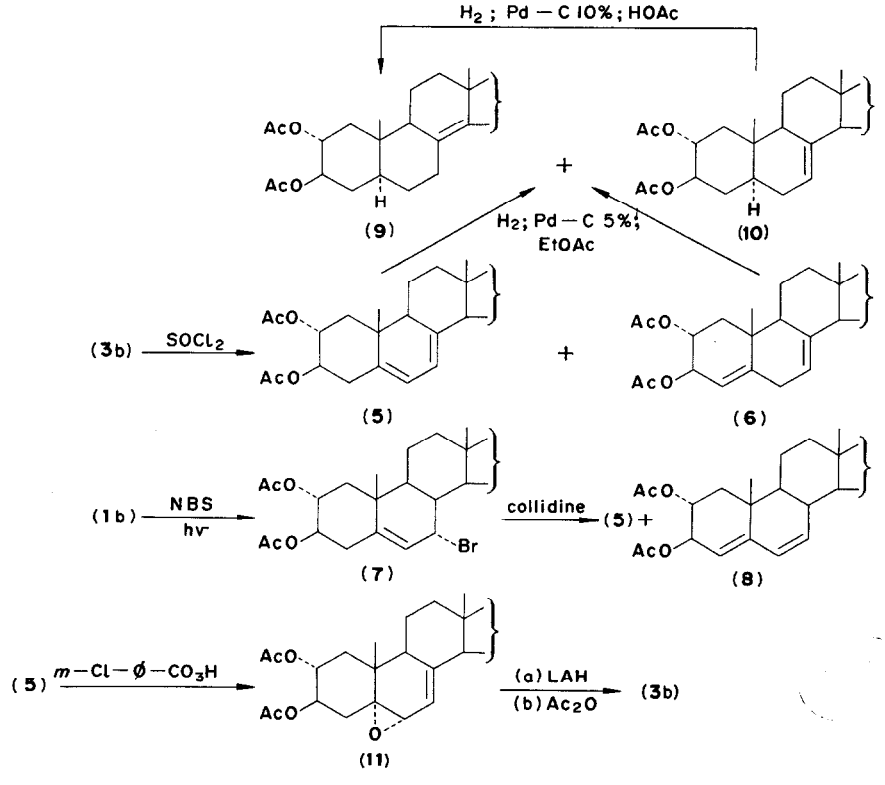
[5] Williams, D. H. and Bhacca, N. S. (1965) *Tetrahedron* **21**, 1641.

[6] Callow, R. K., James, V. H. T., Kennard, O., Page, J. E., Paton, P. N. and Riva de Sanseverino, L. (1966) *J. Chem. Soc.* **C**, 288.

[7] Bhacca, N. S. and Williams, D. H. (1964) *Application of NMR Spectroscopy in Organic Chemistry*, p. 19. Holden-Day, San Francisco.

[8] Rosenkranz, G., Romo, J. and Berlin, J. (1951) *J. Org. Chem.* **16**, 290.

more, the chemical shifts of the Me–C_{10} and Me–C_{13} (τ 8·94 and 9·28 in $CDCl_3$) coincide with the calculated ones (τ 8·94 and 9·27). **5** was also obtained by irradiating yuccagenin acetate (**1b**) in the presence of NBS,[8] yielding **7** which without further purification was refluxed in *o*-xylene–collidine to give the expected **5** and **8**. The latter compound shows UV absorptions at 233, 239 and 247 nm,[8] and in the PMR spectrum the H–$C_{6,7}$ and H–C_4 appear as an *ABX* and *AB* system respectively.



Compound **6**, $C_{31}H_{44}O_6$, has two trisubstituted double bonds evidenced by two one-proton signals at τ 4·76 (*AB*, $W_{1/2}$ 5 Hz, H–C_4) and 5·04 (*m*, $W_{1/2}$ 10 Hz, H–C_7) in the PMR spectrum (C_6D_6). Its structure was established by partial hydrogenation over 5% Pd–C in dry EtOAc, giving 8(14)- and 7-dehydrogitogenin acetates (**9** and **10**; both $C_{31}H_{46}O_6$);* the PMR spectrum of **10** shows the presence of a vinyl proton (τ 4·84, *m*, $W_{1/2}$ 10 Hz). The same two compounds were also formed by reducing **5** under identical conditions. The fact that under these conditions the double bond in **10** is not isomerized to $C_{8(14)}$ indicates that **9** is produced directly from **5** and **6**. Transformation of **10** into **11** was achieved in

Chemical evidence for the α configuration of the OH at C_5 was obtained by treatment of **5** with 1·2 mol of *m*-chloroperbenzoic acid in dry benzene at 0–5°; the less hindered

*About 40% of hydrogenolysis products were also formed, which is in accord with the existence of an allylic acetate in **6**.

[9] MANCERA, O., BARTON, D. H. R., ROSENKRANZ, G. and DJERASSI, C. (1952) *J. Chem. Soc.* 1021.

double bond (Δ^5) is attacked and the epoxide enters from the α side giving **11**. Subsequent reduction with $LiAlH_4$ and acetylation yielded **3b**. Hence, the structure of 7-dehydroagapanthagenin (**3a**) is established as (25*R*)-spirost-7-en-2α,3β,5α-triol.

8(14)-Dehydroagapanthagenin (**4a**), $C_{27}H_{42}O_5$ (by MS), has three OH groups, as shown by MS. One of them must be tertiary because **4a** forms a diacetate (**4b**), $C_{31}H_{46}O_7$, with IR band at 3520 cm^{-1} but whose PMR spectrum displays no signals for protons geminal to the OH group. Again the three OH functions form a 2α,3β,5α-triol system (see Table 1) and the presence of a (20*S*, 22*R*, 25*R*)-spirostan ring is deduced from IR and PMR data as described for **3a**. The molecular formulae of **4a** and its diacetate indicate the existence of a double bond which must be tetrasubstituted because **4b** shows no PMR signals attributable to vinyl protons. The only position for this double bond compatible with the PMR data is $C_{8(14)}$: the calculated values for the Me–C_{10} (τ 9·04) and Me–C_{13} (9·05) agree with the observed ones in $CDCl_3$ (Table 1). Structure **4a** was confirmed by isomerizing the double bond in **3b** to $C_{8(14)}$. As has been observed,[10] a Δ^7 is hindered by a 5α-OH group; consequently, the isomerization conditions must be stronger than those required from the 5α-H series. In fact, the transformation of **3b** into **4b** was only achieved in HOAc with 10% Pd–C under H_2. Thus, **4a** is assigned the structure of (25*R*)-spirost-8(14)-en-2α,3β,5α-triol.

EXPERIMENTAL

M.ps. determined on a Kofler block, are uncorrected. If not otherwise stated compounds were recrystallized from MeOH. Optical rotations were measured in $CHCl_3$ and PMR spectra (60 MHz) with TMS as internal standard. The spray reagent for TLC was H_2SO_4–HOAc–H_2O (1:20:4). Column and dry column chromatography was performed on silica gel 0·2–0·5 and 0·063–0·20 mm, respectively. Acetylations were realized with Ac_2O in pyridine and saponifications with 2% KOH in MeOH, in both cases leaving the mixture at room temp. for 12 hr. Usual work-up was as follows: pour into H_2O, extract with organic solvent, wash with aq. HCl and H_2O, dry over Na_2SO_4 and evaporate *in vacuo*.

Isolation of the sapogenins. The air-dried rhizomes of the plant (5 kg), collected in La Laguna (Tenerife) in August 1972, were finely chopped and extracted several times with EtOH in a Soxhlet. After filtering the combined extracts in cold, they were concentrated *in vacuo* to *ca* 1 litre, diluted with an equal vol. of H_2O and defatted with C_6H_6 in a liquid–liquid extractor. Then conc. HCl was added to the aq. ethanolic soln till it was 2 N. It was refluxed for 4 hr, poured into H_2O, neutralized first with KOH and finally with $NaHCO_3$ and filtered. The precipitate was dissolved in EtOAc and washed several times with 10% aq. KOH and H_2O. Evaporation of the solvent afforded the crude mixture of sapogenins (27·6 g) which on column chromatography with $CHCl_3$ and $CHCl_3$–EtOAc as eluants gave sitosterol (0·9 g), yuccagenin (**1a**; 3·2 g) and a mixture of four spirostan sapogenins. This was acetylated and chromatographed on a dry column (C_6H_6–EtOAc, 4:1), obtaining the pure 2α,3β-diacetates of 8(14)-dehydroagapanthagenin (**4b**; 0·23 g) and agapanthagenin (**2b**; 0·41 g). The remaining mixture of the acetates of 7-dehydroagapanthagenin (**3b**; 3·9 g) and a spirostan sapogenin currently under study (0·20 g) was separated by dry column chromatography on silica gel–20% $AgNO_3$ eluting with C_6H_6–EtOAc (9:1).

Yuccagenin **1a**, m.p. 248–249°, $[\alpha]_D$ −120° (*c* 0·302). *Acetate* **1b**, m.p. 179–181°, $[\alpha]_D$ −143° (*c* 0·214) (Found: C, 72·27; H, 8·74. Calc. for $C_{31}H_{46}O_6$: C, 72·34; H, 9·01%). $\nu_{max}^{CS_2}$: 3040, 2830 (Δ^5), 1745 (OAc), 980, 920, 900, 865 cm^{-1} (spirostan ring). PMR ($CDCl_3$): τ 4·53 (1H, *m*, $W_{1/2}$ 11 Hz, H–C_6), 5·08 (2H, *m*, $W_{1/2}$ 30 Hz, H–$C_{2,3}$), 6·57 (2H, *m*, $W_{1/2}$ 13 Hz, 2H–C_{26}), 7·98 (6H, *s*, OAc), 8·88 (3H, *s*, Me–C_{19}), 9·03 (3H, *d*, *J* 6 Hz, Me–C_{20}), 9·21 (3H, *s*, Me–C_{18}), ~9·21 (3H, *d*, Me–C_{25}). Hydrogenation of **1b** (0·2 g) in HOAc (30 ml) over 10% Pd–C (0·1 g) for 8 hr at room temp. and atm. pres. gave gitogenin acetate (0·15 g), identical with an authentic sample (m.m.p., TLC, IR spectra superimposable).

Agapanthagenin 2α,3β-*diacetate* **2b**, m.p. 298–300°, $[\alpha]_D$ −100° (*c* 0·676) (Found: C, 70·03; H, 8·90. Calc. for $C_{31}H_{48}O_7$: C, 69·89; H, 9·08%). ν_{max}^{KBr}: 3490 (OH), 1740 (OAc), 980, 920, 900, 865 cm^{-1} (spirostan ring). PMR: Table 1.

Conversion of **1b** *in* **2b**. **1b** (0·46 g) in $CHCl_3$ (10 ml) was treated with *m*-chloroperbenzoic acid (0·52 g) in $CHCl_3$ (25 ml) at 0°. After 4 hr the soln was poured into H_2O, washed with aq. KOH and H_2O and the solvent evaporated *in vacuo*. The resulting crude 5α,6α-epoxy derivative (0·41 g) was dissolved in Et_2O (17 ml) and poured dropwise into a stirred suspension of $LiAlH_4$ (0·25 g) in Et_2O (13 ml). After 2 hr at reflux the excess $LiAlH_4$ was destroyed with some drops of H_2O. Usual work-up gave a residue which was acetylated and purified by dry column

[10] Bladon, P., Clayton, R. B., Greenhalgh, C. W., Henbest, H. B., Jones, E. R. H., Lovell, B. J., Silverstone, G., Wood, G. W. and Woods, F. (1952) *J. Chem. Soc.* 4883.

chromatography (C_6H_6–EtOAc, 4:1), yielding **2**b (0·21 g), identical with the natural product (m.m.p., TLC, IR spectra superimposable).

7-Dehydroagapanthagenin 2α,3β-diacetate **3**b, m.p. 223–225°, $[\alpha]_D$ −88° (*c* 0·212) (Found: C, 69·91; H, 8·65. $C_{31}H_{46}O_7$ requires: C, 70·16; H, 8·74%). $\nu_{max}^{CS_2}$: 3580 (OH), 3025, 1670, 840 (Δ^7), 1745 (OAc), 982, 923, 900, 865 cm^{-1} (spirostan ring). PMR: Table 1. Saponification gave **3**a, m.p. 276–278° (Me_2CO); *m/e* (%) 446 (M^+, 0·5), 428 (74), 410 (2), 392 (0·6).

8(14)-*Dehydroagapanthagenin 2α,3β-diacetate* **4**b, m.p. 272–273°, $[\alpha]_D$ −64° (*c* 0·208) (Found: C, 69·95; H, 8·52. $C_{31}H_{46}O_7$ requires: C, 70·16; H, 8·74%). ν_{max}^{KBr}: 3520 (OH), 1740 (OAc), 980, 920, 900, 865 cm^{-1} (spirostan ring). PMR: Table 1. Saponification gave **4**a, m.p. 264–267°; *m/e* (%) 446 (M^+, 0·3), 428 (100), 410 (3), 392 (1).

7-Dehydroyuccagenin and 4,7-dehydrogitogenin acetates **5** *and* **6** *from* **3**b. **3**b (0·4 g) in dry pyridine (10 ml) was treated with $SOCl_2$ (0·3 ml) at 0° for 1·5 hr. Dry column chromatography of the product (0·35 g) on silica gel–20% $AgNO_3$ (C_6H_6–EtOAc, 19:1) gave **5** (0·11 g) and **6** (0·14 g).

5, m.p. 178–182°, $[\alpha]_D$ −147° (*c* 0·200) (Found: C, 72·67; H, 8·84. $C_{31}H_{44}O_6$ requires: C, 72·63; H, 8·65%). $\nu_{max}^{CS_2}$: 3040, 2800, 1655, 840 ($\Delta^{5,7}$), 1745 (OAc), 985, 925, 900, 865 cm^{-1} (spirostan ring). λ_{max}^{EtOH}: 261, 270, 281, 292 nm ($\Delta^{5,7}$). PMR ($CDCl_3$): τ 4·34, 4·44, 4·58, 4·68 (2H, AB, H–$C_{6,7}$), 5·07 (2H, *m*, $W_{1/2}$ 27 Hz, H–$C_{2,3}$), 6·57 (2H, *m*, $W_{1/2}$ 12 Hz, 2H–C_{26}), 7·97 (6H, *s*, OAc), 8·94 (3H, *s*, Me–C_{10}), ~9·01 (3H, *d*, Me–C_{20}), ~9·23 (3H, *d*, Me–C_{25}), 9·28 (3H, *s*, Me–C_{13}); (C_6D_6): τ 4·7 (4H, *m*, $W_{1/2}$ 36 Hz, H–$C_{2,3,6,7}$), 6·43 (2H, *m*, $W_{1/2}$ 12 Hz, 2H–C_{26}), 8·20 (6H, *s*, OAc), 8·82 (3H, *d*, *J* 6 Hz, Me–C_{20}), 9·08 (3H, *s*, Me–C_{10}), 9·28 (3H, *s*, Me–C_{13}), ~9·28 (3H, *d*, Me–C_{25}).

6, m.p. 200–202°, $[\alpha]_D$ −119° (*c* 0·382) (Found: C, 72·43; H, 8·53. $C_{31}H_{44}O_6$ requires: C, 72·63; H, 8·65%). $\nu_{max}^{CS_2}$: 3030, 2830, 1670, 840 ($\Delta^{4,7}$), 1745 (OAc), 981, 922, 900, 865 cm^{-1} (spirostan ring). PMR ($CDCl_3$): τ 4·52, 4·64 (1H, *mm*, $W_{1/2}$ 5 Hz, H–C_3), 4·83 (3H, *m*, $W_{1/2}$ 12 Hz, H–$C_{2,4,7}$), 6·56 (2H, *m*, $W_{1/2}$ 13 Hz, 2H–C_{26}), 7·94 (6H, *s*, OAc), 8·80 (3H, *s*, Me–C_{10}), 9·00 (3H, *d*, *J* 6 Hz, Me–C_{20}), 9·21 (3H, *d*, *J* 6 Hz, Me–C_{25}), 9·32 (3H, *s*, Me–C_{13}); (C_6H_6): τ 4·17, 4·31 (1H, *mm*, $W_{1/2}$ 5 Hz, H–C_3), 4·56 (1H, *m*, $W_{1/2}$ ~24 Hz, H–C_2), 4·76 (1H, *AB*, $W_{1/2}$ 5 Hz, H–C_4), 5·04 (1H, *m*, $W_{1/2}$ 10 Hz, H–C_7), 5·36 (1H, *m*, $W_{1/2}$ 22 Hz, H–C_{16}), 6·42 (2H, *m*, $W_{1/2}$ 12 Hz, 2H–C_{26}), 8·21 (6H, *s*, OAc), 8·81 (3H, *d*, Me–C_{20}), 8·98 (3H, *s*, Me–C_{10}), 9·33 (3H, *s*, Me–C_{13}), ~9·33 (3H, *d*, Me–C_{25}).

7-Dehydroyuccagenin and 4,6-dehydrogitogenin acetates (**5** *and* **8**) *from* **1**b. **1**b (0·15 g) in dry CCl_4 (10 ml) was refluxed with NBS (0·075 g) for 5 min, irradiating with a W lamp (60 W). The soln was poured into H_2O, $CHCl_3$ extracted and the organic layer washed with aq. $NaHCO_3$ and H_2O. Evaporation *in vacuo* gave the 7α-bromo derivative **7** (0·15 g) which without further purification was dissolved in *o*-xylene (5 ml) and collidine (0·5 ml) and refluxed for 30 min. Dry column chromatography of the product on silica gel–20% $AgNO_3$ (C_6H_6–EtOAc, 19:1) yielded pure **5** (61 mg) and **8** (42 mg).

5, m.p. 179–183°, $[\alpha]_D$ −142° (*c* 0·184) (Found: C, 72·37; H, 8·81. $C_{31}H_{44}O_6$ requires: C, 72·63; H, 8·65%). Identical with compound **5** obtained from **3**b (m.m.p., TLC, UV, IR and PMR spectra superimposable).

8, m.p. 204–207°, $[\alpha]_D$ −225° (*c* 0·276) (Found: C, 72·85; H, 8·68. $C_{31}H_{44}O_6$ requires: C, 72·63; H, 8·65%). $\nu_{max}^{CS_2}$: 3025, 1655, 855 ($\Delta^{4,6}$), 1745 (OAc), 982, 920, 900, 865 cm^{-1} (spirostan ring). λ_{max}^{EtOH}: 233, 239, 247 nm ($\Delta^{4,6}$). PMR($CDCl_3$): τ 3·94, 4·11 (1H, *ABX*, J_{AX} 4 Hz, H–C_7), 4·22, 4·38 (1H, *ABX*, $W_{1/2}$ 4 Hz, H–C_6), 4·52 (1H, *AB*, $W_{1/2}$ 6 Hz, H–C_4), 4·76 (2H, *m*, $W_{1/2}$ 20 Hz, H–$C_{2,3}$), 6·56 (2H, *m*, $W_{1/2}$ 12 Hz, 2H–C_{26}), 7·96 (6H, *s*, OAc), 8·88 (3H, *s*, Me–C_{10}), 9·03 (3H, *d*, *J* 6 Hz, Me–C_{20}), 9·16 (3H, *s*, Me–C_{13}), ~9·21 (3H, *d*, Me–C_{25}).

8(14)- *and 7-dehydrogitogenin acetates* (**9** *and* **10**) *from* **6**. **6** (90 mg) in EtOAc (50 ml) was hydrogenated for 3 hr over 5% Pd–C (47 mg) at room temp. and atm. pres. Separation of the residue by dry column chromatography (silica gel–20% $AgNO_3$; C_6H_6) gave hydrogenolysis products (34 mg) and pure **9** (11 mg) and **10** (17 mg).

9, m.p. 214–216°, $[\alpha]_D$ −56° (*c* 0·132) (Found: C, 72·20; H, 9·11. $C_{31}H_{46}O_6$ requires: C, 72·34; H, 9·01%). $\nu_{max}^{CS_2}$: 1740 (OAc), 982, 925, 900, 865 cm^{-1} (spirostan ring). PMR ($CDCl_3$): τ 5·08 (2H, *m*, $W_{1/2}$ 24 Hz, H–$C_{2,3}$), 6·56 (2H, *m*, $W_{1/2}$ 13 Hz, 2H–C_{26}), 8·00 (6H, *s*, OAc), 9·04 (3H, *s*, Me–C_{10}), ~9·04 (3H, *d*, Me–C_{20}), 9·20 (3H, *s*, Me–C_{13}), ~9·21 (3H, *d*, Me–C_{25}).

10, m.p. 221–225°, $[\alpha]_D$ −103° (*c* 0·216) (Found: C, 72·08; H, 8·89. $C_{31}H_{46}O_6$ requires: C, 72·34; H, 9·01%). $\nu_{max}^{CS_2}$: 3030, 1710, 845 (Δ^7), 1745 (OAc), 982, 925, 900, 865 cm^{-1} (spirostan ring). PMR ($CDCl_3$): τ 4·84 (1H, *m*, $W_{1/2}$ 10 Hz, H–C_7), 5·11 (2H, *m*, H–$C_{2,3}$), 6·56 (2H, *m*, $W_{1/2}$ 12 Hz, 2H–C_{26}), 8·00 (6H, *s*, OAc), ~9·03 (3H, *d*, Me–C_{20}), 9·08 (3H, *s*, Me–C_{10}), 9·22 (3H, *d*, *J* 6 Hz, Me–C_{25}), 9·36 (3H, *s*, Me–C_{13}).

9 *and* **10** *from* **5**. **5** (75 mg) in EtOAc (25 ml) was hydrogenated for 3 hr over 5% Pd–C (40 mg) as described for **6**. Dry column chromatography (silica gel–20% $AgNO_3$; C_6H_6) of the residue gave **9** (18 mg), m.p. 217–218°, and **10** (47 mg), m.p. 221–225°, identical with the compounds obtained above (m.m.ps, TLC, IR, PMR spectra superimposable).

9 *from* **10**. A soln of **10** (30 mg) in HOAc (30 ml) was stirred for 20 hr with 10% Pd–C (20 mg) under H_2 at room temp. and atm. pres. Purification of the residue by preparative TLC (silica gel $PF_{254+366}$, thickness 0·5 mm; C_6H_6–EtOAc, 19:1) gave **9** (20 mg) which proved to be identical with the compound obtained from **5** and **6** (m.m.p., TLC, IR, PMR spectra superimposable).

3b *from* **5**. A soln of **5** (51 mg) in dry C_6H_6 (14 ml) was treated with *m*-chloroperbenzoic acid (22 mg) in C_6H_6 (4 ml) at 0–5° for 4 hr. The resulting 5α,6α-epoxide **11** was recovered as described for the conversion of **1**b in **2**b, dissolved in Et_2O (14 ml) and reduced with $LiAlH_4$ (40 mg) in Et_2O (10 ml) at reflux for 2 hr. After usual work-up the residue was acetylated and purified by dry column chromatography (C_6H_6–EtOAc, 17:3) obtaining

3b (23 mg), m.p. 222–224°, $[\alpha]_D$ −88° (*c* 0·230), identical with the acetate of the natural product (m.m.p., TLC, IR, PMR spectra superimposable).

4b *from* **3b**. **3b** (100 mg) in HOAc (30 ml) was isomerized over 10% Pd–C (200 mg) for 24 hr as described for **9**. Dry column chromatography (C_6H_6–EtOAc, 17:3) of the residue gave starting material (10 mg) and **4b** (30 mg), m.p. 272–273°, $[\alpha]_D$ −70° (*c* 0·112) (Found: C, 70·28; H, 8·72. $C_{31}H_{46}O_7$ requires: C, 70·16; H, 8·74%). It showed to be identical with the acetate of the natural product (m.m.p., TLC, IR, PMR spectra superimposable).

Acknowledgements—The authors are obliged to Dr. J. Seibl (Organic Chemistry Department, ETH, Zürich) for the MS. One of us (C. G. F.) thanks the Ministerio de Educación y Ciencia for a fellowship "Formación de Personal Investigador". This work was realised within the Programme of Chemistry 1971 conceded by the Foundation "Juan March".