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9(11)-DEHYDROAGAPANTHAGENIN, A NEW SPIROSTAN SAPOGENIN FROM *AGAPANTHUS AFRICANUS**

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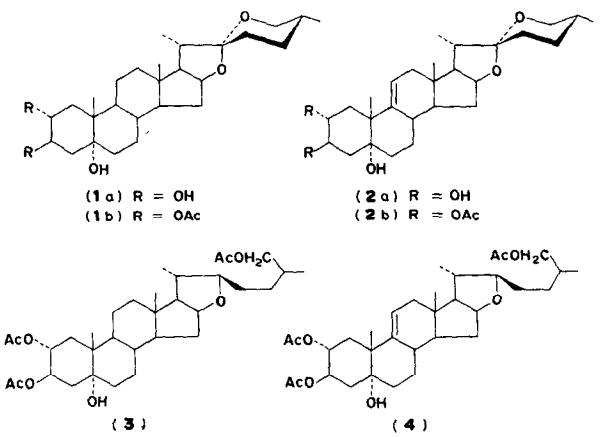
Key Word Index—*Agapanthus africanus*; Liliaceae; spirostan sapogenin; 9(11)-dehydroagapanthagenin.

Abstract—The structure of 9(11)-dehydroagapanthagenin, a new spirostan sapogenin isolated from the rhizomes of *Agapanthus africanus*, was determined on the basis of spectral and chemical evidence.

INTRODUCTION

In a previous paper [1] we reported the isolation of sitosterol, yuccagenin, agapanthagenin (**1a**) and the new spirostan sapogenins 7-dehydroagapanthagenin (**10a**) and 8(14)-dehydroagapanthagenin from the rhizomes of *Agapanthus africanus* Hoffmnsg. The structure of 9(11)-dehydroagapanthagenin (**2a**), a further spirostan sapogenin obtained in very small yield, has now been established as (25*R*)-spirost-9(11)-en-2α,3β,5α-triol.

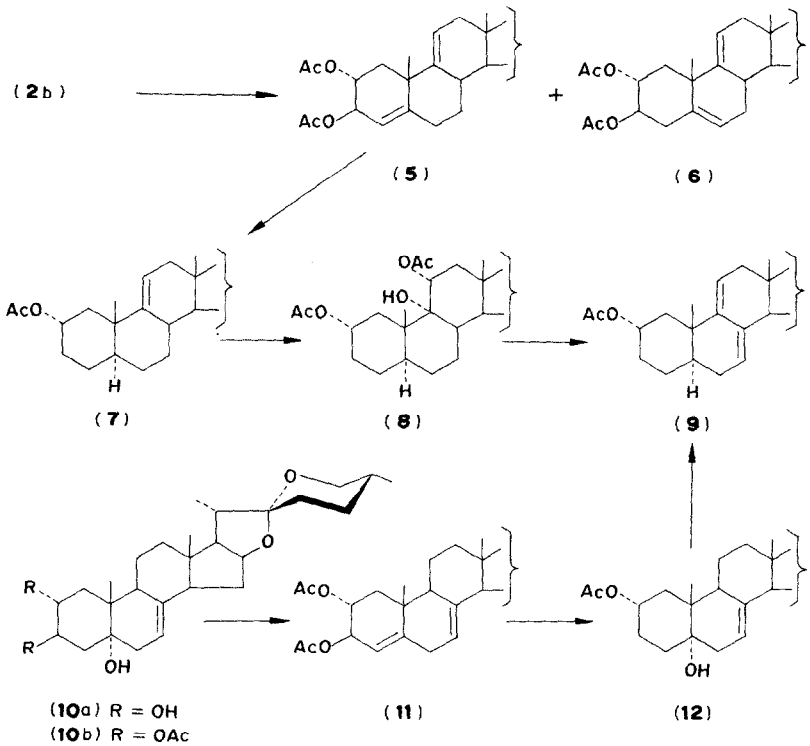


* Part 28 in the series "New Sources of Steroid Sapogenins". For Part 27 see González, A. G., Francisco, C. G., Freire, R., Hernández, R., Salazar, J. A. and Suárez, E. (1975) *Phytochemistry* **14**, 2257.

† In $CDCl_3$ if not otherwise specified.

RESULTS AND DISCUSSION

9(11)-Dehydroagapanthagenin (**2a**) ($C_{27}H_{42}O_5$, microanalysis, MS) is a (20*S*,22*R*,25*R*)-spirostan sapogenin with three hydroxy groups as may be inferred from its IR, NMR and mass spectra. The MS showed the loss of 1, 2 and 3 water molecules from the molecular ion. The IR absorptions at 980, 920, 900 and 860 cm^{-1} indicated the presence of a (20*S*,22*R*,25*R*) spirostan ring [2], which was in accord with the MS fragmentation pattern [3] (see Experimental) and was confirmed by the NMR signals† at δ 3·45 (2H, *m*, $W_{1/2}$ = 13 Hz, C-26) and 1·60 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23) [4,5] of the diacetate **2b** ($C_{31}H_{46}O_7$) obtained by mild acetylation of **2a**. The tertiary nature of the third hydroxyl was deduced from the NMR spectrum of **2b** which showed no bands assignable to protons geminal to an OH group. The shape and position of the multiplet corresponding to the C-2 and C-3 protons (δ 5·3, $W_{1/2}$ = 26 Hz; C_6D_6: 5·5, $W_{1/2}$ = 30 Hz) established the hydroxyl system as 2α,3β,5α [1]. A further multiplet at δ 5·18 (C_6D_6: 1H, $W_{1/2}$ = 12 Hz) indicated the existence of a trisubstituted double bond which could only be located between C-9 and C-11 taking into account the energetic conditions necessary for its reduction and the chemical shifts of the C-10 and C-13 methyl groups (δ 1·25 and 0·70 respectively; theoretical values [6]: 1·22 and 0·70).



Hydrogenation of **2b** in HOAc over PtO_2 followed by mild acetylation gave a mixture of the tetrahydro derivative **3** and compound **4**.* The structure of **3** was established on the basis of its spectral data and by comparison with authentic material prepared by analogous treatment of agapanthagenin diacetate (**1b**). Thus, the structure proposed for **2a** is chemically confirmed except for the configuration at C-22 and the position of the trisubstituted double bond. These were determined by synthesizing the *trans*-diene **9** from **2b** on the one hand and from 7-dehydroagapanthagenin diacetate (**10b**) on the other (Scheme 1).

Dehydration of **2b** with $SOCl_2$ gave compounds **5** and **6** (both $C_{31}H_{44}O_6$), their spectral data being in accordance with the structures assigned (see Experimental). Hydrogenolysis of **5** over 10% Pd-C yielded **7** whose NMR spectrum showed the presence of only one acetate group (δ 2·00) and 1 vinyl proton (δ 5·28); the axial nature of the C-2 proton (δ 5·0, *m*, $W_{1/2}$ = 27 Hz) permitted the determination of the configuration of the C-5 proton as α. Osmylation of **7** followed by acetylation gave **8** ($C_{31}H_{48}O_7$) in whose NMR spectrum the axial C-11 proton appeared as the X part of an ABX system (δ 5·40, 5·30, 5·21 and 5·11). Dehydration of **8** with $SOCl_2$ and adsorption of the resulting 8-dehydro derivative on acid Al_2O_3 [8] afforded the diene **9** ($C_{29}H_{42}O_4$), the UV and NMR spectra of which were consistent with the structure proposed (see Experimental). On the other hand, dehydration of **10b** with $SOCl_2$ yielded **11** [1] which was hydrogenolized over 5% Pd-C in dry EtOAc to give **12**.† This was oxidized with $Hg(OAc)_2$ in HOAc to **9** which proved to be identical with the compound obtained from **2b**. Hence, 9(11)-dehydroagapanthagenin (**2a**) corresponds to (25*R*)-spirost-9(11)-en-2α,3β,5α-triol.

* The structure of **4** [NMR in C_6D_6: δ 5·22 (1H, *m*, $W_{1/2}$ = 12 Hz, C-11)] was proved by reducing it to **3**. Recently [7], the stereochemistry at C-22 of the (20*S*,25*R*)-furostan compounds was determined as *R*.

† The reaction conditions were chosen so that the best yield in **12** was obtained without contamination by its $\Delta^{8(14)}$ isomer [1], since the mixture of both could not be separated; 20% starting material was recovered.

EXPERIMENTAL

For experimental techniques see [1]. Chromatography was performed on Si gel (0·063–0·20 mm) dry columns. 9(11)-Dehydroagapanthagenin (**2a**), obtained in 0·004% yield from

air-dried rhizomes of the plant, was separated as the acetate from the other compounds in the way described previously [1].

9(11)-*Dehydroagapanthagenin* 2α,3β-*diacetate* (**2b**). mp 247–248° (MeOH), $[\alpha]_D$ −100° ($CHCl_3$; *c* 0·426). (Found: C, 69·88; H, 8·84. $C_{31}H_{46}O_7$ requires: C, 70·16; H, 8·74%.) IR ν_{max}^{KBr} cm^{-1}: 3540 (OH), 3045 ($\Delta^{9(11)}$), 980, 925, 900, 865 (spirostan ring). NMR ($CDCl_3$): δ 5·3 (3H, *m*, $W_{1/2}$ = 26 Hz, C-2, C-3, C-11), 4·5 (1H, *m*, $W_{1/2}$ = 27 Hz, C-16), 3·45 (2H, *m*, $W_{1/2}$ = 13 Hz, C-26), 2·03, 2·00 (6H, *s*, OAc), 1·60 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23), 1·25 (3H, *s*, C-19), 0·95 (3H, *d*, *J* 6 Hz, C-21), ~0·78 (3H, *d*, C-27), 0·70 (3H, *s*, C-18); (C_6D_6): δ 5·5 (2H, *m*, $W_{1/2}$ = 30 Hz, C-2, C-3), 5·18 (1H, *m*, $W_{1/2}$ = 12 Hz, C-11), 4·5 (1H, *m*, $W_{1/2}$ = 26 Hz, C-16), 3·55 (2H, *m*, $W_{1/2}$ = 12 Hz, C-26), 1·79 (6H, *s*, OAc), 1·63 (2H, *s*, $W_{1/2}$ = 7 Hz, C-23), 1·13 (3H, *d*, *J* 6 Hz, C-21), 0·90 (3H, *s*, C-19), 0·70 (3H, *s*, C-18), ~0·65 (3H, *d*, C-27). Saponification gave 9(11)-*dehydroagapanthagenin* (**2a**), mp 262–265° (MeOH), $[\alpha]_D$ −77° ($CHCl_3$; *c* 0·370). (Found: C, 72·37; H, 9·57. $C_{27}H_{42}O_5$ requires: C, 72·61; H, 9·48%.) IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 3025 ($\Delta^{9(11)}$), 980, 920, 900, 860 (spirostan ring). MS (70 eV) *m/e* (rel. int.): 446 (M^+, 15), 428 (7), 410 (2), 392 (1·5), 387 (10), 374 (21), 359 (4), 332 (24), 314 (97), 139 (100).

Compounds **3** *and* **4** *from* 9(11)-*dehydroagapanthagenin* 2α,3β-diacetate. **2b** (230 mg) in HOAc (50 ml) was hydrogenated over PtO_2 (215 mg) at room temp. and atm pres for 28 hr. Acetylation and chromatographic separation (petrol–EtOAc, 4:1) gave **3** (170 mg) and **4** (33 mg). **3**, mp 129–130° (MeOH), $[\alpha]_D$ −42° ($CHCl_3$; *c* 0·184). (Found: C, 68·50; H, 9·16. $C_{33}H_{52}O_8$ requires: C, 68·72; H, 9·09%.) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590 (OH), 1730 (OAc). NMR ($CDCl_3$): δ 5·2 (2H, *m*, $W_{1/2}$ = 26 Hz, C-2, C-3), 4·3 (1H, *m*, $W_{1/2}$ = 26 Hz, C-16), 3·92 (2H, *d*, *J* 6 Hz, C-26), 3·3 (1H, *m*, $W_{1/2}$ = 24 Hz, C-22), 2·03, 2·00 (9H, *s*, OAc), 1·08 (3H, *s*, C-19), 0·96 (3H, *d*, *J* 6 Hz, C-27), 0·92 (3H, *d*, *J* 6 Hz, C-21), 0·77 (3H, *s*, C-18); (C_6D_6): δ 5·5 (2H, *m*, $W_{1/2}$ = 27 Hz, C-2, C-3), 4·3 (1H, *m*, $W_{1/2}$ = 26 Hz, C-16), 3·94 (2H, *d*, *J* 6 Hz, C-26), 3·3 (1H, *m*, $W_{1/2}$ = 22 Hz, C-22), 1·78, 1·76, 1·70 (9H, *s*, OAc), 0·97 (6H, *s*, C-19, C-18), 0·90 (3H, *d*, *J* 6 Hz, C-21 or C-27), ~0·83 (3H, *d*, C-27 or C-21). **4**, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3570 (OH), 1730 (OAc). NMR ($CDCl_3$): δ 5·3 (3H, *m*, $W_{1/2}$ = 33 Hz, C-2, C-3, C-11), 4·4 (1H, *m*, $W_{1/2}$ = 27 Hz, C-16), 3·92 (2H, *d*, *J* 6 Hz, C-26), 3·3 (1H, *m*, $W_{1/2}$ = 20 Hz, C-22), 2·02, 2·00 (9H, *s*, OAc), 1·25 (3H, *s*, C-19), 0·97 (3H, *d*, *J* 6 Hz, C-27), 0·92 (3H, *d*, *J* 6 Hz, C-21), 0·70 (3H, *s*, C-18); (C_6D_6): δ 5·6 (2H, *m*, $W_{1/2}$ = 28 Hz, C-2, C-3), 5·22 (1H, *m*, $W_{1/2}$ = 12 Hz, C-11), 4·3 (1H, *m*, $W_{1/2}$ = 28 Hz, C-16), 3·95 (2H, *d*, *J* 5 Hz, C-26), 3·3 (1H, *m*, $W_{1/2}$ = 20 Hz, C-22), 1·78, 1·70 (9H, *s*, OAc), 0·90 (3H, *s*, C-19), 0·90 (3H, *d*, *J* 6 Hz, C-21 or C-27), 0·83 (3H, *d*, *J* 6 Hz, C-27 or C-21), 0·72 (3H, *s*, C-18). By treating **4** as described for **2b** compound **3** was obtained which was identical with the above product (mmp. TLC, IR, NMR).

Compound **3** *from agapanthagenin* 2α,3β-*diacetate*. **1b** (74 mg) was treated as indicated for **2b**, yielding **3** (50 mg), mp 128–130° (MeOH), identical with the above product (mmp, TLC, IR, NMR). (Found: C, 68·72; H, 9·03. $C_{33}H_{52}O_8$ requires: C, 68·72; H, 9·09%).

Compounds **5** *and* **6** *from* 9(11)-*dehydroagapanthagenin* 2α,3β-*diacetate*. **2b** (495 mg) in dry Py (20 ml) was treated with $SOCl_2$ (0·25 ml) at 0° for 40 min. Chromatography (C_6H_6) on $AgNO_3$–Si gel (1:4) gave **5** (270 mg) and **6** (148 mg). **5**, mp 179–181° (MeOH), $[\alpha]_D$ −129° ($CHCl_3$; *c* 0·176). (Found: C, 72·39; H, 8·61. $C_{31}H_{44}O_6$ requires: C, 72·63; H, 8·65%.) IR ν_{max}^{KBr} cm^{-1}: 3040 ($\Delta^{4,9(11)}$), 1740 (OAc), 985, 927, 902, 870 (spirostan ring). NMR ($CDCl_3$): δ ~5·6–4·9 (2H, *m*, C-2, C-3), 5·33 (1H, *m*, $W_{1/2}$ = 10 Hz, C-11), 5·09 (1H, *s*, $W_{1/2}$ = 6 Hz, C-4), 4·4 (1H, *m*, $W_{1/2}$ = 30 Hz, C-16), 3·43 (2H, *m*, $W_{1/2}$ = 14 Hz, C-26), 2·02 (6H, *s*, OAc), 1·59 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23), 1·31 (3H, *s*, C-19), 0·94 (3H, *d*, *J* 6 Hz, C-21), ~0·75 (3H, *d*, C-27), 0·70 (3H, *s*, C-18); (C_6D_6): δ ~5·9–4·9 (2H, *m*, C-2, C-3), 5·66 (1H, *s*, $W_{1/2}$ = 5 Hz, C-4), 5·19 (1H, *m*, $W_{1/2}$ = 12 Hz, C-11), 4·5 (1H, *m*, $W_{1/2}$ = 30 Hz, C-16), 3·55 (2H, *m*, $W_{1/2}$ = 12 Hz, C-26), 1·75 (6H, *s*, OAc), 1·61 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23), 1·14 (3H, *d*, *J* 6 Hz, C-21), 1·13 (3H, *s*, C-19), 0·73 (3H, *s*, C-18), 0·65 (3H, *d*, *J* 6 Hz, C-27). **6**, mp 147–149° (MeOH), $[\alpha]_D$ −107° ($CHCl_3$; *c* 0·216). (Found: C, 72·89; H, 8·47. $C_{31}H_{44}O_6$ requires: C, 72·63; H, 8·65%.) IR $\nu_{max}^{CS_2}$ cm^{-1}: 3040 ($\Delta^{5,9(11)}$), 1740 (OAc), 980, 925, 900, 865 (spirostan ring), NMR ($CDCl_3$): δ 5·50 (2H, *m*, $W_{1/2}$ = 12 Hz, C-5, C-11), ~5·5–4·7 (2H, *m*, C-2, C-3), 4·5 (1H, *m*, $W_{1/2}$ = 26 Hz, C-16), 3·43 (2H, *m*, $W_{1/2}$ = 12 Hz, C-26), 2·00 (6H, *s*, OAc), 1·58 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23), 1·24 (3H, *s*, C-19), 0·94 (3H, *d*, *J* 6 Hz, C-21), ~0·75 (3H, *d*, C-27), 0·71 (3H, *s*, C-18); (C_6D_6): δ ~5·7–4·8 (2H, *m*, C-2, C-3), 5·29 (2H, *m*, $W_{1/2}$ = 12 Hz, C-5, C-11), 4·5 (1H, *m*, $W_{1/2}$ = 30 Hz, C-16), 3·55 (2H, *m*, $W_{1/2}$ = 13 Hz, C-26), 1·75, 1·73 (6H, *s*, OAc), 1·61 (2H, *s*, $W_{1/2}$ = 7 Hz, C-23), ~1·14 (3H, *d*, C-21), 1·08 (3H, *s*, C-19), 0·74 (3H, *s*, C-18), 0·64 (3H, *d*, *J* 6 Hz, C-27).

Compound **7** *from* **5**. **5** (260 mg) in EtOH (100 ml) was hydrogenated over 10% Pd-C (250 mg) at room temp. and atm pres for 3 hr. Chromatography (C_6H_6–EtOAc, 19:1) yielded **7** (200 mg), mp 214–216° (Me_2CO–MeOH), $[\alpha]_D$ −82° ($CHCl_3$; *c* 0·634). (Found: C, 76·16; H, 9·65. $C_{29}H_{44}O_4$ requires: C, 76·27; H, 9·71%.) IR ν_{max}^{KBr} cm^{-1}: 3040 ($\Delta^{9(11)}$), 1730 (OAc), 980, 922, 900, 865, (spirostan ring). NMR ($CDCl_3$): δ 5·28 (1H, *m*, $W_{1/2}$ = 13 Hz, C-11), 5·0 (1H, *m*, $W_{1/2}$ = 27 Hz, C-2), 4·4 (1H, *m*, $W_{1/2}$ = 26 Hz, C-16), 3·44 (2H, *m*, $W_{1/2}$ = 12 Hz, C-26), 2·00 (3H, *s*, OAc), 1·59 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23), 0·96 (3H, *s*, C-19), 0·95 (3H, *d*, *J* 6 Hz, C-21), 0·76 (3H, *d*, *J* 6 Hz, C-27), 0·68 (3H, *s*. C-18).

Compound **8** *from* **7**. To **7** (160 mg) in dry C_6H_6 (9 ml) a soln of OsO_4 (100 mg) in dry Py–C_6H_6 (1:2; 1·5 ml) was added and the mixture left at room temp. for 96 hr. After adding Na_2SO_3 (710 mg) and $KHCO_3$ (710 mg) in H_2O–MeOH (3:2; 11·5 ml) the soln was stirred for 5 hr. Usual work-up, acetylation and chromatographic purification (C_6H_6–EtOAc, 4:1) gave **8** (132 mg), mp 243–245° (MeOH), $[\alpha]_D$ −94° ($CHCl_3$; *c* 0·490). (Found: C, 69·67; H, 8·86. $C_{31}H_{48}O_7$ requires: C, 69·89; H, 9·08%.) IR ν_{max}^{KBr} cm^{-1}: 3487 (OH), 1730 (C-2 OAc), 1705 (C-11 OAc), 985, 925, 902, 865 (spirostan ring). NMR ($CDCl_3$): δ 5·40, 5·30, 5·21, 5·11 (1H, *ABX*, C-11), ~4·8 (1H, *m*, $W_{1/2}$ ≃ 24 Hz, C-2), 4·5 (1H, *m*, $W_{1/2}$ = 24 Hz, C-16), 3·43 (2H, *m*, $W_{1/2}$ = 13 Hz, C-26), 1·97 (6H, *s*, OAc), 1·59 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23), 1·02 (3H, *s*, C-19), ~0·94 (3H, *d*, C-21), 0·85 (3H, *s*, C-18), ~0·76 (3H, *d*, C-27).

Compound **9** *from* **8**. To a soln of **8** (100 mg) in dry Py (3 ml) $SOCl_2$ (0·1 ml) was added at 0° and the mixture kept at 0–5° for 13 hr. After usual work-up the product was dissolved in C_6H_6–petrol (1:1; 20 ml), adsorbed on acid Al_2O_3 (act. II) for 30 min and then eluted with $CHCl_3$. Purification by chromatography (C_6H_6–EtOAc, 19:1) yielded **9** (40 mg), mp 179–182° (Me_2CO–MeOH), $[\alpha]_D$ −42° ($CHCl_3$; *c* 0·290). (Found: C, 76·82; H, 8·93. $C_{29}H_{42}O_4$ requires: C, 76·61; H, 9·31%.) IR ν_{max}^{KBr} cm^{-1}: 3035 ($\Delta^{7,9(11)}$), 1735 (OAc), 980, 925, 900, 865 (spirostan ring). UV λ_{max}^{EtOH} nm (log ε): 236 (4·19), 243 (4·25), 251 (4·07). NMR ($CDCl_3$): δ 5·44 (2H, *m*, $W_{1/2}$ = 15 Hz, C-7, C-11), 5·0 (1H, *m*, $W_{1/2}$ = 24 Hz, C-2), 4·5 (1H, *m*, $W_{1/2}$ = 26 Hz, C-16), 3·45 (2H, *m*, $W_{1/2}$ = 12 Hz, C-26), 2·00 (3H, *s*, OAc), 1·59 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23), ~0·94 (3H, *d*, C-21), 0·90 (3H, *s*, C-19), 0·75 (3H, *d*, *J* 6 Hz, C-27), 0·58 (3H, *s*, C-18). MS (70 eV) *m/e* (rel. int.): 454 (M^+, 15), 395 (5), 340 (69), 139 (100).

Compound **12** *from* **10**b. Dehydration of **10**b (900 mg) in dry Py (20 ml) with $SOCl_2$ (0·7 ml) at 0° and separation of the $\Delta^{5,7}$ isomer by chromatography on $AgNO_3$–Si gel (1:4) [1] gave **11** (330 mg) which was dissolved in dry EtOAc (150 ml) and hydrogenated over 5% Pd-C (170 mg) at room temp. and atm pres for 2 hr. Chromatography (C_6H_6–EtOAc, 19:1) gave starting material **11** (66 mg) and **12** (201 mg), mp 219–222° ($CHCl_3$–MeOH), $[\alpha]_D$ −89° ($CHCl_3$; *c* 0·476). (Found: C, 76·16; H, 9·66. $C_{29}H_{44}O_4$ requires: C, 76·27; H, 9·71%.) IR ν_{max}^{KBr} cm^{-1}: 3020 (Δ^7), 1735 (OAc), 980, 925, 900, 865 (spirostan ring). NMR ($CDCl_3$): δ 5·16 (1H, *m*, $W_{1/2}$ = 11 Hz, C-7), ~4·9 (1H, *m*, $W_{1/2} \simeq$ 24 Hz, C-2), ~4·5 (1H, *m*, $W_{1/2} \simeq$ 24 Hz, C-16), 3·43 (2H, *m*, $W_{1/2}$ = 12 Hz, C-26), 1·98 (3H, *s*, OAc), 1·58 (2H, *s*, $W_{1/2}$ = 6 Hz, C-23), 0·95 (3H, *d*, *J* 6 Hz, C-21), 0·82 (3H, *s*, C-19), ~0·76 (3H, *d*, C-27), 0·62 (3H, *s*, C-18).

Compound **9** *from* **12**. To **12** (170 mg) in $CHCl_3$ (3 ml) a soln of $Hg(OAc)_2$ (302 mg) in HOAc (7 ml) was added and the mixture stirred at 25–30° for 24 hr. After filtering in the cold and washing the ppt. with $CHCl_3$–HOAc (3:7; 10 ml), the soln was refluxed for 3 hr. Extraction with $CHCl_3$ and purification by chromatography on $AgNO_3$–Si gel (1:4) (C_6H_6) gave **9** (86 mg) which was identical with the compound synthesized from **2**b (mmp, TLC, IR, UV, NMR).

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