Phytochemistry, 1975, Vol. 14, pp. 2257–2258. Pergamon Press. Printed in England.

27-HYDROXYRUSCOGENIN, A NEW SPIROSTAN SAPOGENIN FROM *SEMELE ANDROGYNA**

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(*Revised Received* 27 *February* 1975)

Key Word Index—*Semele androgyna*; Liliaceae; gibalbera; steroids; spirostan sapogenins; 27-hydroxyruscogenin.

Abstract—The new steroid sapogenin 27-hydroxyruscogenin has been isolated from stems and leaves of *Semele androgyna* L.; its structure was determined spectroscopically and by synthesis from 25(27)-dehydroruscogenin.

INTRODUCTION

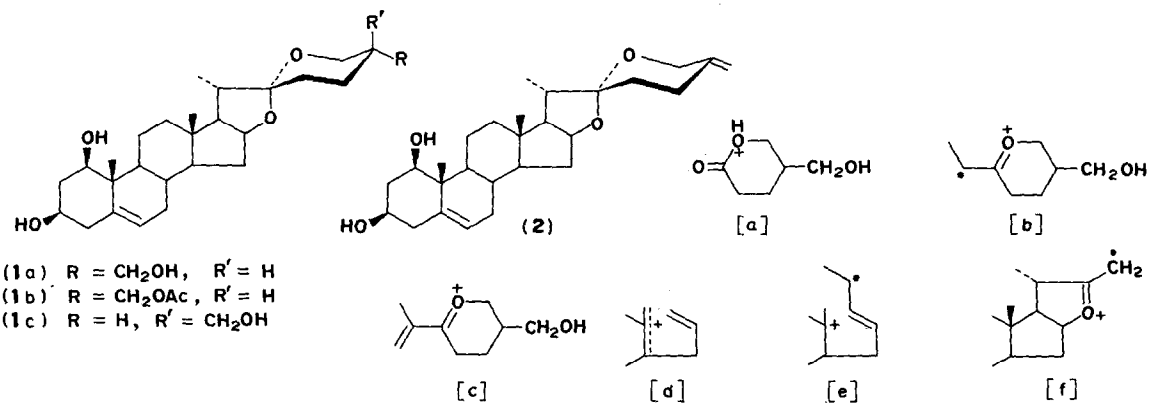
Recently we have isolated five new steroid sapogenins from stems and leaves of *Semele androgyna* L. endemic to the Canary Isles [1]. We now report the structure of 27-hydroxyruscogenin, a further constituent of this plant, obtained in very small quantity.

RESULTS AND DISCUSSION

27-Hydroxyruscogenin (**1a**), $C_{27}H_{42}O_5$, showed IR absorptions for hydroxyl groups (3400 cm^{-1}) and Δ^5 (3020, 2840 cm^{-1}) [2], the bands at 1015, 958, 908, 862 and 832 cm^{-1} indicating the presence of a 27-hydroxyspirostan sapogenin with 25*S* stereochemistry [3]. Its mass spectrum was that expected for spirostan sapogenins without electronegative substituents at C_{23} [4], but the fragments [**a**], [**b**] and [**c**] appeared 16 units higher which suggested an additional O atom in ring F.

Under mild conditions **1a** formed the triacetate **1b**, from whose chemical shifts for the protons at C-6, C-18 and C-19 we deduced that it had a 1β,3β-diacetylated androst-5-ene moiety as is present in ruscogenin acetate. The position and shape of the two multiplets corresponding to the protons at C_{26} and C_{27} (see Experimental) coin-

* Part 27 in the series New Sources of Steroid Sapogenins. For Part 26 see González, A. G., Francisco, C. G., Freire, R., Hernández, R., Salazar, J. A., Suárez, E. (1974) *Tetrahedron Letters* 4289.



(1a) R = CH_2OH, R' = H
(1b) R = CH_2OAc, R' = H
(1c) R = H, R' = CH_2OH

cided with those observed for the triacetates of igagenin [5] and crestagenin [6].

Selective oxidative hydroboration of 25(27)-dehydroruscogenin (**2**) gave an unseparable mixture of the isomeric 27-hydroxy compounds **1a** (25*S*) and **1c** (25*R*). This was treated with methanolic HCl obtaining the more stable 25*S* isomer which was identical with the natural product. The fact that the isomerization of the mixture only gave the 25*S* isomer casts doubt on whether one or both of them originally existed in the plant. It also might be that the two isomers came from a single furostanol precusor which, during the acid hydrolysis of the glycosides, would have suffered ring closure.

EXPERIMENTAL

For experimental techniques see Ref. [1]. 27-Hydroxyruscogenin was isolated in low yield (2×10^{-4}%) from the more polar chromatographic fractions (EtOAc, Si gel 0·2–0·5 mm) of the acid hydrolyzed extract of *Semele androgyna* L. *27-Hydroxyruscogenin* (**1a**), mp 263–265° (MeOH), $[\alpha]_D$ −73° (*c* 0·188, C_6H_5N). (Found: C, 72·30; H, 9·35. $C_{27}H_{42}O_5$ requires: C, 72·61; H, 9·48%). ν_{max}^{KBr} cm^{-1}: 3400 (OH), 3020, 2840 (Δ^5), 1015, 958, 908, 862, 832 (spirostan ring). MS *m/e* (rel. int.): 446 (M^+, 5), 428 (76), 410 (9), 358 ([**f**], 3), 340 (8), 322 (2), 316 ([**e**], 5), 301 ([**e**] − Me, 5), 298 (28), 287 ([**d**], 6), 283 (4), 280 (6), 265 (5), 251 (4), 155 ([**c**], 100), 142 ([**b**], 9), 131 ([**a**], 14). *1,3,27-Triacetate* (**1b**), prepared as usual, mp 185–187° (MeOH), $[\alpha]_D$ − 66° (*c* 0·196, $CHCl_3$). (Found: C, 68·90; H, 8·13. $C_{33}H_{48}O_8$ requires: C, 69·20; H, 8·45%). $\nu_{max}^{CS_2}$ cm^{-1}: 3030, 2845 (Δ^5), 1740, 1235 (OAc), 1016, 970, 910, 862, 835 (spirostan ring). NMR ($CDCl_3$): τ 4·40 (1H, *m*, $W_{1/2}$ = 10 Hz, C-6), 5·50 (3H, *m*, $W_{1/2}$ = 37 Hz, C-1, C-3, C-16), 6·12 (2H, *m*, $W_{1/2}$ = 10 Hz, C-26 or C-27), 7·42 (2H, *m*, $W_{1/2}$ = 12 Hz, C-26 or C-27), 7·99 (9H, *s*, AcOat C-1, C-3, C-27), 8·86 (3H, *s*, C-19), 9·06 (3H, *d*, *J* 6 Hz, C-21), 9·23 (3H, *s*, C-18); (C_6D_6) τ 4·60 (1H, *m*, $W_{1/2}$ = 10 Hz, C-6), 5·35 (3H, *m*, $W_{1/2}$ 42 Hz, C-1, C-3, C-16), 6·25 (4H, *m*, $W_{1/2}$ 15 Hz, C-26, C-27), 8·27 (6H, *s*, AcO at C-1 and C-3), 8·35 (3H, *s*, AcO at C-27), 8·85 (3H, *d*, *J* 6 Hz, C-21), 8·95 (3H, *s*, C-19), 9·22 (3H, *s*, C-18).

27-Hydroxyruscogenin (**1a**) *from 25(27)-dehydroruscogenin.* To a soln of **2** (180 mg) in THF (10 ml) BH_3 (0·5 ml 0·3 M in THF) was added with stirring at 0° under N_2 and the mixture kept at room temp. for 1 hr. After destroying excess BH_3 with H_2O the soln was treated with 3 N NaOH (1 ml) and 30% H_2O_2 (1 ml) at 30–40° for 30 min. It was then poured into H_2O and extracted with EtOAc. The crude extract was dissolved in MeOH being 0·5 N in HCl and kept at room temp. overnight. Usual work-up gave **1a** (145 mg), mp 258–260° (MeOH), $[\alpha]_D$ −76° (*c* 0·228, C_6H_5N), which was identical with the natural product (mmp, TLC, IR). Its triacetate, mp 180–182° (MeOH), $[\alpha]_D$ − 66° (*c* 0·328, $CHCl_3$) was also identical with the acetate **1b** of the natural product (mmp, TLC, IR, PMR).

Acknowledgement—One of us (R.H.) thanks the C.S.I.C. for a postdoctoral fellowship.

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