

266. *Glucosides and Aglycones from Canary Scrophulariaceae. Part VI.*¹ *Structure of Two New Triterpenes from Scrophularia smithii Wydler.*²

By J. L. BRETON and A. G. GONZALEZ.

Two new triterpenes and a steroid have been isolated from the leaves of *Scrophularia smithii* W. The physical constants of the steroid suggest that it is α -spinasterol. The structures of the two triterpenes, A and B, have been elucidated. Triterpene A contained a diene system and oxidation gave a dienedione which formed a pyridazine derivative on treatment with hydrazine. Treatment of triterpene A with acid produces the second triterpene isolated, triterpene B. Triterpene A, on oxidation and subsequent reduction by the Huang-Minlon procedure, gives olean-11,13(18)-dien-3-ol. These facts, together with colour tests and infrared evidence which place hydroxyl groups at C-3 and C-23, determine the structure of triterpene A as olean-11,13(18)-diene-3,23,28-triol (V).

WE have isolated from the leaves of *Scrophularia smithii* W. two triterpenoids and a steroid, together with a wax. This wax was shown, by gas chromatography, to be a mixture of linear hydrocarbons containing from 27 to 33 carbon atoms.

The more abundant of the two triterpenes, triterpene A (we abandon our earlier name smithiandienol²) is a triol which readily forms a triacetate and a tribenzoate. Its molecular formula $C_{30}H_{48}O_3$ was confirmed by mass-spectrometric determination (for which we thank Dr. R. I. Reed, of Glasgow University). This gave a value of 457 ± 3 , and a prominent peak in the cracking pattern at a mass value of 424 indicated the ready loss of CH_2O . The ultraviolet spectrum [λ_{max} , 244, 253, and 262 $m\mu$ ($\log \epsilon$ 4.34, 4.38, and 4.17)] is very similar to that of olean-11,13(18)-dien-3-yl acetate,³ suggesting that the diene chromophores have similar environments in the two compounds. Chemical confirmation of this was obtained as follows.

Triterpene A absorbs one mol. of hydrogen on catalytic hydrogenation with Adams catalyst in acetic acid, and it consumes 1 mol. of perbenzoic acid. Therefore, one of the double bonds occupies a hindered position.

Oxidation of triterpene A (V) with selenium dioxide in benzyl acetate gave the dienedione (IV), identified by its spectral properties, λ_{max} 280 $m\mu$ ($\log \epsilon$ 4.0),⁴ and by its ready formation of the pyridazine derivative (VII), λ_{max} 230 and 280 $m\mu$ ($\log \epsilon$ 4.3 and 4.5). These transformations can only be accommodated by the formulation of triterpene A as 11,13(18)-unsaturated, as in (V).

Treatment of triterpene A with hydrogen chloride in methanol gives triterpene B, the second triterpene isolated from *S. smithii* W.; the analysis indicates loss of CH_2O in this reaction. Such ready loss can be rationalised by placing a primary hydroxyl function β to the diene system, *i.e.*, on C-28 of (V). The driving force of the change (V) \longrightarrow (II) presumably arises from the increased substitution of the new diene. That this is the correct structure of the second diene is shown by the near-identity of its ultraviolet spectrum, λ_{max} 238 and 245 $m\mu$ ($\log \epsilon$ 4.22 and 4.25), with that of 28-norolean-12,17(18)-dien-3-ol.⁵ With the latter compound, triterpene B also shares the property of aerial oxidation⁶ that produces a compound which, from its spectroscopic properties (ν_{max} 1665 cm^{-1} , λ_{max} 295 $m\mu$) appears to be a dienone.

¹ Part V, Delgado, González, Snatzke, and Tschesche, *Annalen*, in the press.

² Preliminary communication: Gonzalez and Munoz, *Anales real Soc. españ. Fis. Quím.*, 1960, **54**, B, 1001.

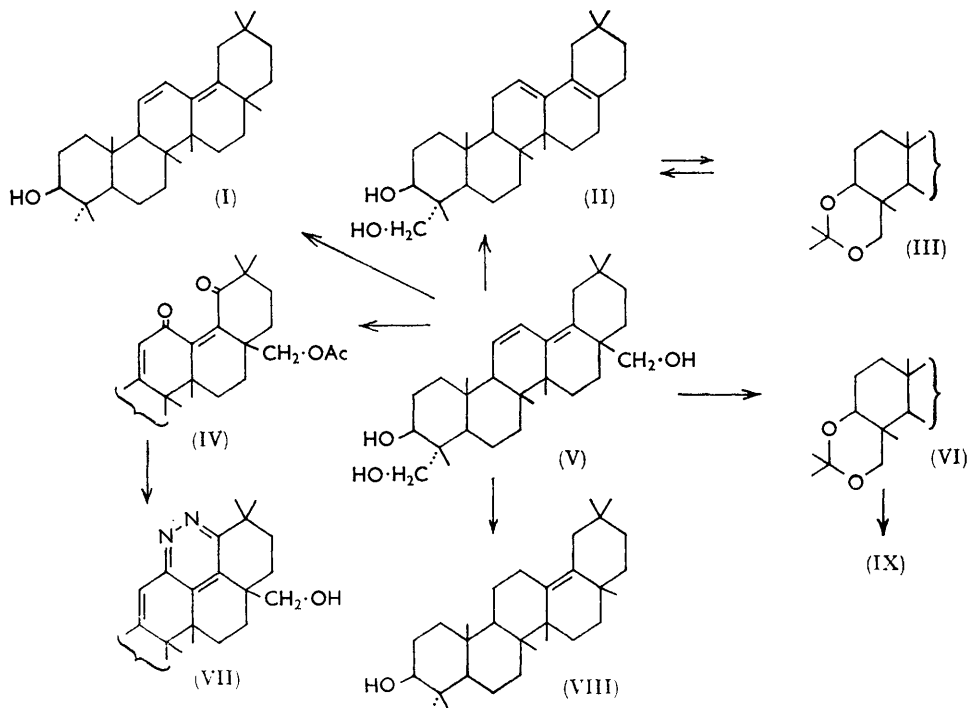
³ Beaton, Johnston, McKean, and Spring, *J.*, 1953, 3660.

⁴ Zimmerman, *Z. physiol Chem.*, 1935, **233**, 257; 1936, **245**, 47.

⁵ Barton and Brooks, *J.*, 1951, 257.

⁶ Carson and Noller, *J. Amer. Chem. Soc.*, 1941, **63**, 621.

Triterpene B readily forms a diacetate and a dibenzoate. An indication of the relative positions of the two surviving hydroxyl groups is provided by the ready formation of an isopropylidene derivative (VI). Since dihydro-triterpene A (the product of catalytic hydrogenation of triterpene A) with chromium trioxide in pyridine affords a ketone giving a positive Liebermann test,⁴ one of the hydroxyl groups is presumed to be at position 3.⁷ The resistance of compounds (V) and (IX) to periodate excludes position 2 as the site of the other hydroxyl group. When triterpene B (II) was heated at 270–290° in the presence of copper, traces of formaldehyde were produced and characterised by thin-layer and paper chromatography of the 2,4-dinitrophenylhydrazone. The presence of a 3,23-glycol is therefore indicated.⁸ The suggested stereochemistry of the glycol grouping depends on the close correspondence of the infrared spectrum of compound (IX) between 3700 and 3400 cm^{-1} with that of methyl hederagenin.⁹ As Cole and Muller⁹ have pointed out, the hydrogen-bonding effects which determine the form of the spectrum will be sensitive to the steric juxtaposition of the hydroxyl groups.



In order to relate triterpene A to a known triterpene, we oxidised it with chromium trioxide in pyridine and then reduced the product by the Huang-Minlon procedure.¹⁰ There resulted a small quantity of an alcohol which readily formed a benzoate. The physical constants of these compounds accord with those of olean-11,13(18)-dien-3-ol¹¹ (I) and its benzoate. Triterpene A is thus defined as olean-11,13(18)-diene-3,23,28-triol (V).

Oxidation and subsequent reduction of dihydro-triterpene A as above afforded a compound whose physical constants, together with those of its derivatives, were in agreement with those of δ -amyrin¹² (VIII). A second substance, obtained with δ -amyrin, had λ_{max} .

⁷ Barton and de Mayo, *J.*, 1954, 887.

⁸ King, King, and Ross, *J.*, 1954, 3995; Tsuda and Kitagawa, *Ber.*, 1938, **71**, 1604.

⁹ Cole and Muller, *J.*, 1959, 1224.

¹⁰ Huang-Minlon, *J. Amer. Chem. Soc.*, 1949, **71**, 3301.

¹¹ Ruzicka, *Helv. Chim. Acta*, 1939, **22**, 767.

¹² Ames, Halsall, and Jones, *J.*, 1951, **450**, 453.

245 $m\mu$ (ϵ 600) and appeared from its infrared spectrum to be a hydrocarbon. Gas chromatography revealed the presence of two components in the proportion 97 : 3. The physical constants of the hydrocarbon (m. p. 146°, $[\alpha]_D^{20}$ -43°) do not accord with those of olean-12- or -13(18)-ene^{13a} and it is likely that our hydrocarbon is 23-norolean-13(18)-ene.

The steroid isolated from *S. smithii* W. has physical constants fully in accord with those of α -spinasterol.^{13b} It was accompanied by a small quantity of a second steroid, which had λ_{max} 244 $m\mu$ (ϵ 215) and appeared to be a conjugated diene.

EXPERIMENTAL

Rotations refer to chloroform solutions unless specified to the contrary. Ultraviolet spectra were measured, for ethanol solutions, on a Beckman D.V. spectrophotometer. Routine infrared spectra were obtained on a Perkin-Elmer model 137 spectrophotometer. The detailed infrared studies of the glycol group were performed in the laboratories of Professor Morcillo of the University of Madrid to whom we express our best thanks.

"Working up in the usual way" signifies addition of water, extraction with ether, washing with hydrochloric acid, aqueous sodium carbonate, and water, drying, and removal of the solvent.

Alumina of activity grade I was used unless otherwise stated. Gas chromatography was performed on a Pye argon instrument operated, with a gas flow of 30 c.c./min., by Mr. Bermejo of this Department. Microanalyses are by Dr. Calderon and his associates at the Micro-analytical Laboratories of the "Alonso Barba" Institute. To both these gentlemen we express our best thanks.

Extraction.—The dried leaves of *Scrophularia smithii* Wydler (12 kg.) were extracted several times with alcohol (20 l.). The alcoholic solution was evaporated to 6 l. and hydrolysed for 3 hr. with the same volume of 2*N*-sulphuric acid. The resulting solution was diluted to twice its volume with water and filtered. The residue was repeatedly extracted with ether. The ethereal solution was washed with 5% aqueous sodium hydroxide and then with water, dried (Na_2SO_4), and evaporated. The residue was leached with warm methanol. When the methanolic solution was cooled, the waxes and some of the α -spinasterol were precipitated. Filtration, removal of methanol, and extraction of the residue with cold benzene gave a crude mixture of the triterpenes and steroids (21 g.).

Waxes.—These had ν_{max} 1725, 1160 (ester), 715, and 730 (carbon chain) cm^{-1} . Saponification of the crude material (0.12 g.) with 2% potassium ethoxide solution (75 ml.) afforded an ether-insoluble substance with an infrared spectrum typical of an acid, and an ether-soluble portion. This ethereal solution was washed with aqueous sodium hydroxide and the neutral residue chromatographed on alumina. Elution with light petroleum afforded a hydrocarbon mixture; elution with ether gave more acidic material. All the acidic products were recombined and esterified with diazomethane. The neutral fraction had an infrared spectrum typical of long-chain hydrocarbons. It was analysed by gas chromatography (0.5% of Apiezon on Celite at 210°). C_{26} and C_{30} hydrocarbons were introduced as reference compounds. The chromatogram showed the presence of a series of hydrocarbons containing from 27 to 33 carbon atoms.

Gas chromatography of the esterified acid fraction showed the presence of 7 components which have not been identified.

Separation of Steroids and Triterpenes.—The crude mixture of triterpenes and steroids, obtained as described above, was dissolved in benzene-chloroform (1 l.). There remained a residue which was mostly triterpene A and was purified by acetylation and chromatography on alumina. The portion soluble in benzene-chloroform was chromatographed on alumina. Waxes (330 g.) were eluted in benzene. Benzene-chloroform (4:1 v/v) eluted crude α -spinasterol (2 g.), m. p. 158—161°. Benzene-chloroform (1:2 v/v) eluted triterpene B (1.9 g.), m. p. 265—270°. Triterpene A (3.5 g.) appeared in chloroform-methanol (19:1 v/v).

Triterpene A.—The crude material, after frequent recrystallisation from methanol, gave hexagons, m. p. 295—299°, $[\alpha]_D^{20} + 65.4^\circ$ (c 1.5 in pyridine) (Found: C, 78.8; H, 10.2. $\text{C}_{30}\text{H}_{48}\text{O}_3$ requires C, 78.9; H, 10.5%). Treatment of *triterpene A* with acetic anhydride in pyridine

¹³ Elsevier's "Encyclopaedia of Organic Chemistry," ed. Radt, Elsevier, Amsterdam, 1952, Vol. 14, Suppl., pp. (a) 945, (b) 1795 *et seq.*

overnight afforded the *triacetate* as needles (from methanol, m. p. 180—181°, $[\alpha]_D^{20} - 85^\circ$ (c 1.0), λ_{\max} . 244, 252, and 262 $m\mu$ ($\log \epsilon$ 4.47, 4.5, and 4.33) (Found: C, 74.4; H, 9.4. $C_{36}H_{54}O_6$ requires C, 74.2; H, 9.3%). Treatment with benzoyl chloride in pyridine gave a *tribenzoate*, needles (from acetone), m. p. 229—230°, $[\alpha]_D^{20} - 9^\circ$ (c 0.82) (Found: C, 79.8; H, 7.7. $C_{51}H_{60}O_6$ requires C, 79.7; H, 7.8%).

Catalytic Reduction of Triterpene A.—Triterpene A (0.443 g.) in acetic acid (50 ml.) was shaken with Adams catalyst (0.12 g.) under hydrogen (absorption 51 c.c.; calc. for catalyst and 1 mol., 49.5 c.c.). The product was isolated by removal of solvent under reduced pressure, extraction of the residue with ether, evaporation of the ether, and crystallisation of the product from methanol. The dihydro-derivative, *olean-13(18)-ene-3,23,28-triol*, was obtained as needles m. p. 293°, $[\alpha]_D^{20} - 53^\circ$ (c 0.9 in pyridine) (Found: C, 76.7; H, 10.8. $C_{30}H_{50}O_3 \cdot H_2O$ requires C, 77.1; H, 10.9%). With acetic anhydride in pyridine it gave, as needles from methanol, the *triacetate*, m. p. 159—160°, $[\alpha]_D^{20} - 29.5^\circ$ (c 0.75) (Found: C, 73.7; H, 9.55. $C_{36}H_{56}O_6$ requires C, 74.0; H, 9.6%).

Oxidation with Perbenzoic Acid.—Triterpene A acetate (0.51 g.) in chloroform was treated with 0.1N-perbenzoic acid (50 ml.), and the excess of peracid was then estimated with sodium thiosulphate. 0.94 mol. of peracid was consumed.

Oxidation of Triterpene A Acetate with Selenium Dioxide.—The acetate (2.55 g.) was refluxed with selenium dioxide (2.55 g.) in benzyl acetate (50 ml.) for 22 hr. Removal of solvent and purification of the residue by passage through an alumina column in benzene solution afforded a resinous product, λ_{\max} . 244 $m\mu$ ($\log \epsilon$ 3.98), 252 $m\mu$ ($\log \epsilon$ 4.04), 262 $m\mu$ ($\log \epsilon$ 4.03) (starting material), and 281 $m\mu$ ($\log \epsilon$ 4.00) (dienedione).

The resin (0.9 g.) was heated at 200° with anhydrous hydrazine (6 ml.) in diethylene glycol (30 ml.) for 8 hr. After cooling, the solution was diluted with water. There was precipitated a solid which, after crystallisation from methanol, melted at 299° and was identified as triterpene A. From the mother-liquors of the above crystallisation, there separated a yellow solid, m. p. 257°, which was partly soluble in concentrated hydrochloric acid. Extraction of the hydrochloric acid solution with ether, basification with sodium hydroxide, re-extraction of the aqueous solution with ether, and removal of solvent yielded the *pyridazine derivative* as colourless needles (from acetone), m. p. 250—252° (with softening), $[\alpha]_D^{20} + 256.7^\circ$ (c 0.2) (Found: N, 5.9, 5.6. $C_{30}H_{44}N_2O_2$ requires N, 5.9%).

Isopropylidene Derivative of Triterpene A.—Triterpene A (6 g.) was left in ether (2 l.) and acetone (500 ml.) containing concentrated sulphuric acid (20 ml.) at room temperature for 65 hr. The solution was then washed with sodium hydrogen carbonate solution and water, dried, and evaporated. The product was chromatographed in light petroleum on alumina (200 g.). The *isopropylidene derivative* was eluted in benzene and benzene-chloroform (19 : 1 v/v). Crystallised from heptane, it had m. p. 259—261° (4.8 g.), $[\alpha]_D^{20} + 56.7^\circ$, λ_{\max} . 245, 254, and 263 $m\mu$ ($\log \epsilon$ 4.46, 4.5, and 4.31), ν_{\max} . 3500, 1170, 1110, 1075, and 860 cm^{-1} (in Nujol) (Found: C, 79.7; H, 10.6. $C_{33}H_{52}O_3$ requires C, 79.9; H, 10.5%).

Triterpene B.—Triterpene A acetate (0.3 g.) was refluxed in methanol (35 ml.) with concentrated hydrochloric acid (10 ml.) for 1 hr. Solvent was removed under reduced pressure, water was added, the suspension filtered, and the residue crystallised from methanol. There resulted needles of *triterpene B* (II), m. p. 170°, which became yellow on standing. The pure material had $[\alpha]_D^{20} + 88.3^\circ$, ν_{\max} . 3638, 3624 (shoulder), and 3534 cm^{-1} (in CCl_4). Gas chromatography (4% of silicone on Celite at 240°) demonstrated the purity of the material, only one peak, of retention time 40 min., being observed (Found: C, 78.0; H, 10.35. $C_{29}H_{46}O_2 \cdot H_2O$ requires C, 78.3; H, 10.8%). Its *diacetate* formed needles (from methanol), m. p. 170—171°, $[\alpha]_D^{20} + 60.7^\circ$, λ_{\max} . 238 and 245 $m\mu$ ($\log \epsilon$ 4.36 and 4.31) (Found: C, 77.9; H, 9.9. $C_{33}H_{60}O_4$ requires C, 77.7; H, 9.9%). The saponification number of the acetate accorded with its formulation as a diacetate. Treatment of triterpene B with benzoyl chloride in pyridine gave the *dibenzoate* as needles (from acetone), m. p. 210°, $[\alpha]_D^{20} + 97^\circ$ (c 0.2) (Found: C, 80.8; H, 8.3. $C_{43}H_{54}O_4$ requires C, 81.4; H, 8.5%). The physical constants of triterpene B and its acetate and benzoate accord with those of the product obtained directly from the plant. No m. p. depressions were observed on admixture of the alcohols or their derivatives.

Isopropylidene Derivative of Triterpene B.—The triterpene (0.3 g.) was left in ether (225 ml.) and acetone (45 ml.) containing concentrated sulphuric acid (1.5 ml.). Working up as before yielded the isopropylidene derivative as needles (from benzene), m. p. 203°, $[\alpha]_D^{20} + 37.7^\circ$ (c 1.2), ν_{\max} . 1170, 1130 and 1110 cm^{-1} (in Nujol). The compound gradually acquired a yellow colour

which appears to be due to partial oxidation [λ_{\max} . 238, 245, and 292 μ ($E_{1\text{cm}}^{1\%}$. 285, 651, and 98)]. The analysis more closely approximates to $\text{C}_{32}\text{H}_{48}\text{O}_3$ than to $\text{C}_{32}\text{H}_{50}\text{O}_3$ (Found: C, 80.6; H, 10.2. Calc. for $\text{C}_{32}\text{H}_{48}\text{O}_3$: C, 80.0; H, 10.0. Calc. for $\text{C}_{32}\text{H}_{50}\text{O}_3$: C, 82.6; H, 10.7%). Hydrolysis of this compound and crystallisation of the product from methanol afford the original triterpene B.

Treatment of Triterpene B with Sodium Periodate.—The triterpene (8 mg.) was treated in ethanol (1 ml.) with ethanolic sodium periodate (8.4 mg. in 3 ml.). No consumption of periodate was observed.

Pyrolysis of Triterpene B with Copper.—The triterpene (0.14 g.) was heated with copper powder (0.5 g.) at 280–290° for 1 hr. The gases evolved were led into an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride. The solution, in which a small precipitate was formed, was extracted with ether and the extract was washed with dilute hydrochloric acid and water. The product remaining on removal of solvent was dissolved in benzene and spotted on to silica gel chromatoplates. Authentic formaldehyde 2,4-dinitrophenylhydrazone was also spotted on to these plates and they were developed with chloroform and with chloroform–benzene (3 : 1 v/v). The material from the reaction showed 5 spots, the most intense of which corresponded to that of the authentic formaldehyde 2,4-dinitrophenylhydrazone. On paper, in heptane saturated with methanol, 3 spots were observed the R_F of one of them coinciding with that of formaldehyde 2,4-dinitrophenylhydrazone.

Oxidation of Triterpene A with Chromium Trioxide in Pyridine.—Triterpene A (2.2 g.) in pyridine (25 ml.) was treated with chromium trioxide (2.2 g.) and pyridine (20 ml.) and left at room temperature overnight. The mixture was worked up in the usual way and afforded 2 g. of product. This was dissolved in diethylene glycol (17 ml.), and refluxed with sodium hydroxide (1.1 g.) and anhydrous hydrazine (1.1 ml.) for 1 hr.; the condenser was then removed and the temperature was raised to 200°. The condenser was then replaced and the mixture refluxed for a further 3 hr. After cooling, dilute hydrochloric acid was added and the mixture extracted with benzene. The product (1.4 g.) was chromatographed on alumina. Benzene eluted crystalline material, m. p. 225° (0.1 g.), $[\alpha]_D^{20}$ -67° (c 0.6), λ_{\max} . 243, 252, and 262 μ ($\log \epsilon$ 4.3, 4.36, and 4.16), giving a benzoate, m. p. 225°. Crystals (0.17 g.) of m. p. 265° were eluted with benzene–chloroform (2 : 3 v/v); chloroform–methanol (1 : 1 v/v) afforded starting material, m. p. 290°. The remainder of the product was non-crystalline and resinous.

Oxidation of Dihydro-triterpene A.—This compound (1.5 g.) was oxidised with chromium trioxide in pyridine, and the product reduced with hydrazine (0.7 ml.) as described above. The product was chromatographed on alumina (21 g.; activity grade II). The first 4 fractions, eluted in light petroleum–benzene (2 : 1 v/v), were resins (0.267 g.) which crystallised on treatment with acetone and on recrystallisation from acetone and ethyl acetate afforded plates, m. p. 146°, $[\alpha]_D^{20}$ -43° (c 0.27). This substance, λ_{\max} . 237 and 245 μ ($\log \epsilon$ 2.77), ν_{\max} . 2950, 1370, 1365, 1170w, and 978w cm^{-1} (Found: C, 85.6; H, 11.6. Calc. for $\text{C}_{29}\text{H}_{48}, \frac{1}{2}\text{H}_2\text{O}$: C, 85.9; H, 12.1%), was shown to be a mixture of two components present in the proportion 97 : 3 by gas chromatography. Elution with light petroleum–benzene (1 : 1 v/v) gave needles, m. p. 202–205° (0.284 g.), $[\alpha]_D^{20}$ -48° (c 0.9). These gave a red-violet colour in the Liebermann–Burchard reaction and a yellow colour with green fluorescence on treatment with concentrated sulphuric acid. The crystals were pure since gas chromatography (0.75% of silicone on Celite at 224°) exhibited only one peak (retention time of 10 min.). The infrared spectrum showed max. at 3640, 2924, 1450, 1370, 1365, and 1033 cm^{-1} (in CCl_4); there was no ultra-violet maximum above 215 μ . The acetate, prepared in the usual way, crystallised as plates, m. p. 202–204°, $[\alpha]_D^{20}$ -33° (c 0.9). The presence of some alcohol as impurity in the acetate was revealed by gas chromatography. The benzoate obtained by use of benzoyl chloride in pyridine crystallised as plates, m. p. 215–216°, $[\alpha]_D^{20}$ -6° (c 0.77).

α -Spinasterol.—The steroid, m. p. 158–161°, isolated by chromatography from the crude steroids from the plant, melted, after frequent recrystallisation from methanol, at 165° and had $[\alpha]_D^{20}$ -2° (c 0.2). A small quantity of impurity was disclosed by gas chromatography. The ultraviolet spectrum, λ_{\max} . 244 μ ($E_{1\text{cm}}^{1\%}$. 9) makes it probable that the impurity is of the ergosterol type. The infrared spectrum had max. at 3640, 1655, 1375, 1360, 1018, and 970 cm^{-1} (in CCl_4). In the Salkowsky reaction, an orange colour was observed in the sulphuric acid layer, and in the Liebermann–Burchard reaction the colour series violet–dark blue–green was produced. The steroid was precipitated with digitonin, and gave a positive Tortelli–Jaffe reaction and a yellow colour on treatment with tetranitromethane (Found: C, 81.3; H, 12.0).

Calc. for $C_{29}H_{46}O, H_2O$: C, 80.9; H, 11.6%. The acetate (prepared by acetic anhydride and pyridine) had m. p. 175—178°, $[\alpha]_D^{20} - 2^\circ$ (*c* 1.2) (Found: C, 81.5; H, 11.8. Calc. for $C_{31}H_{58}O_2$: C, 81.9; H, 11.1%). α -Spinasterol was recovered on saponification of the acetate. The benzoate formed plates (from methanol-acetone), m. p. 195—197°, $[\alpha]_D^{20}$ (*c* 1.88) (Found: C, 83.7; H, 10.4. Calc. for $C_{36}H_{52}O_2$: C, 83.7; H, 10.1%). The ketone obtained by oxidation of the alcohol with chromium trioxide in pyridine gave a violet colour in the Zimmerman reaction and crystallised as needles (from acetone), m. p. 170—172°, $[\alpha]_D^{20} + 23^\circ$ (*c* 1.72) (Found: C, 84.3; H, 10.9. Calc. for $C_{29}H_{46}O$: C, 84.8; H, 11.2%). Hydrogenation of the acetate (Adams catalyst; acetic acid) produced the dihydro-acetate, m. p. 113—115° (methanol), $[\alpha]_D^{20} + 12$ (*c* 4.5).

We thank the Juan March Foundation for generous assistance. We are most grateful to Dr. Sventenius for his help in the botanical classification of *S. smithii* and to Professor E. P. Machado and Mr. R. P. M. Bond for the English version of this paper.

DEPARTMENT OF ORGANIC CHEMISTRY, UNIVERSITY OF LA LAGUNA,
CANARY ISLANDS.

[Received, August 27th, 1962.]
