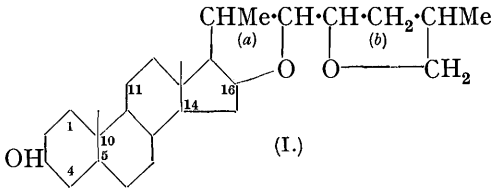
## 89. *Sapogenins. Part II. Sarsasapogenin and Smilagenin.*

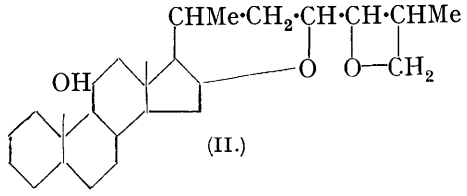
By Stanley N. Farmer and George A. R. Kon.

It has been pointed out in Part I (Askew, Farmer, and Kon, J., 1936, 1399) that measurements of unimolecular films support formula (I), assigned to tigogenin by Tschesche and Hagedorn (*Ber.*, 1935, **68**, 1412, 2247; 1936, **69**, 797), but cannot be reconciled with the structure (II), tentatively put forward for sarsasapogenin by Jacobs and Simpson (*J. Biol. Chem.*, 1935, **109**, 501), in which the hydroxyl group is at position $C_{11}$. The surface area of sarsasapogenin was found to be somewhat greater than that of the isomeric tigogenin and

consistent with a hydroxyl either at $C_2$ or $C_4$ if the compound belongs to the cholestane series, or at $C_3$ if it is a coprostane derivative.




(I.)

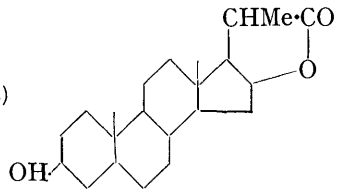



(II.)

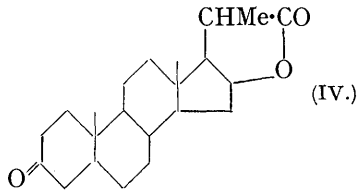
The experiments now recorded establish that sarsasapogenin is a coprostane derivative, and that smilagenin, also described in Part I, only differs from it as regards the side chain. The position of the hydroxyl at $C_3$ receives further support from dehydrogenation experiments, and it is hoped to adduce final proof of it shortly.

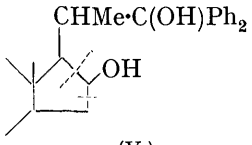
Sarsasapogenin acetate was oxidised with chromic acid to the *acetate* of the *lactone* (III); attempts to open the lactone ring with hydrogen bromide to afford a bromo-acid, which could be reduced to one of the known bile-acid derivatives, were unsuccessful, and we therefore carried out a degradation exactly analogous to that effected by Tschesche and Hagedorn (*Ber.*, 1935, **68**, 1412) on tigogenin. The lactone (III) was oxidised to the *keto-lactone* (IV), this reduced by Clemmensen's method to the deoxy-lactone, which was probably identical with the compound obtained by Jacobs and Simpson (*J. Biol. Chem.*, 1935, **110**, 565), and this treated with a large excess of phenylmagnesium bromide. The *diphenylcarbinol* (V) was oxidised to a mixture of the *acid* (VI) and ætiobilianic acid (VII), the latter in every way identical with a specimen kindly sent to us by Prof. H. Wieland.

(III.)

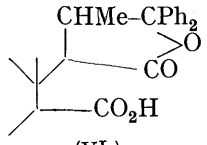



(IV.)

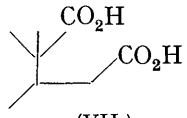



(V.)




(VI.)




(VII.)

The isolation of this acid proves that sarsasapogenin is a coprostane derivative; it also supplies an indication, though not a proof, that the hydroxyl cannot occupy position $C_4$, because the corresponding ketone would then be expected to undergo isomerisation with alkali. Treatment with acid causes degradation of the side chain, as found by Jacobs and Simpson, but the stability of the lactone (IV) under the conditions of the Clemmensen reduction is sufficient proof that this compound, in which the side chain has been shortened by oxidation, is stable to acids.

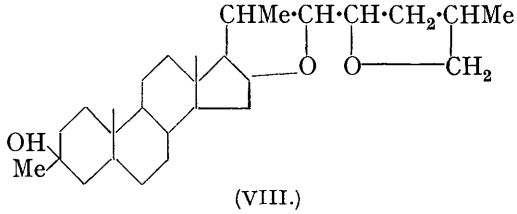
The opening of ring IV in the manner indicated shows that the oxide ring (*a*) must be attached to ring IV at $C_{16}$, as in tigogenin, and disposes of the alternative attachment to $C_{15}$, which was at one time regarded as a possibility by Jacobs and Simpson (*ibid.*).

We have established a connection between sarsasapogenin and smilagenin by oxidising the acetate of the latter to the acetate of the lactone (III), identical with that obtained from sarsasapogenin. It follows that the difference between these two aglucones must be confined to the last five carbon atoms of the side chain, which form part of the oxide ring (*b*) and are removed on oxidation to the lactone. It appears probable that the difference is one of configuration of the asymmetric carbon atom contained in this ring.

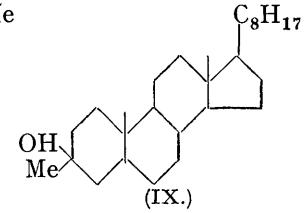
A by-product in the oxidation of smilagenin acetate is an acid, evidently analogous to the triketo-acid isolated by Jacobs and Simpson (*loc. cit.*) in their degradation of deoxysar-

sasapogenin. A similar, but apparently not identical, acid is also formed from sarsasapogenin acetate. In the formation of these acids the oxide rings are presumed to be broken and so the difference between the acids cannot be attributed to the steric configuration of the terminal oxide ring.

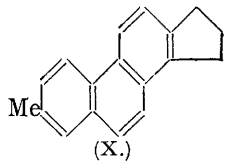
Apart, therefore, from the slight uncertainty regarding the nature of the side chain in these compounds, it only remains to establish the position of the hydroxyl group with certainty. It was hoped to do this by the selenium dehydrogenation of the methyl ether of sarsasapogenin to a methoxy-derivative of 3′-methyl*cyclo*pentenophenanthrene, but the required ether could not be prepared in sufficiently good yield. Sarsasapogenone was then treated with methylmagnesium iodide, and the resulting *methylsarsasapogenin* (VIII) dehydrogenated with selenium. The separation of the products, formed in poor yield, proved extremely difficult, but a hydrocarbon was eventually separated in the form of its *s*-trinitrobenzene *compound*, with the high m. p. of 174—175°, and this was in every way similar to a compound obtained by the same process starting with 3-*methylcholestan*-3-*ol* (IX), which was prepared for the sake of comparison. The identity of these compounds would establish the position of the methyl, and hence also the hydroxyl, group present in the starting materials.




(VIII.)




(IX.)




(X.)

The analysis of these derivatives appears to point to the parent hydrocarbon being a methyl*cyclo*pentenophenanthrene, presumably (X), in place of the expected dimethyl compound. However, the hydrocarbon regenerated from the apparently pure trinitrobenzene complex derived from methylcholestanol was not homogeneous, and a pure hydrocarbon has not yet been isolated. For this reason we prefer to leave the question of the nature of these dehydrogenation products open, pending the completion of synthetic experiments, now in progress together with a repetition of the dehydrogenation on a larger scale.

In our first experiment with methylcholestanol, the mixture of alcohol and selenium was gradually heated to 270°, then to 310—320°; hardly any dehydrogenation occurred under these conditions, and a saturated hydrocarbon, evidently *methylcholestane*, was recovered. This observation is analogous to that of Dorée and Petrov (J., 1934, 1129; 1935, 1391), who found that selenium could act as a hydrogenating catalyst in some cases. Methylcholestane was dehydrogenated by selenium at a higher temperature (350—360°).

We have continued our survey of the occurrence of smilagenin and sarsasapogenin, and have extracted a variety of sarsaparilla known as Jamaica red, said to be derived from *Smilax ornata* Hook. Except for its brick-red colour, the drug is outwardly very similar to the Jamaica grey variety; the yield of pure aglucone from it was extremely poor, in agreement with the low hæmolytic power of extracts of this drug noted by Kobert (*Pharm. J.*, 1912, **88**, 779), and the compound proved to be sarsasapogenin. The latter also occurs in Honduras sarsaparilla, because van der Haar (*Rec. trav. chim.*, 1929, **48**, 726) has isolated the same glucoside, parillin, from this and from Vera Cruz (Mexican) sarsaparilla, and hydrolysed it to a high-melting aglucone; both these varieties of the drug may be derived from *Smilax medica* (" Encyclopædia Britannica," 11th Ed.).

## Experimental.

*Sarsasapogenin Methyl Ether.*—An attempt to methylate sarsasapogenin with diazomethane was unsuccessful; a very poor yield of the desired product was obtained by the method of Heilbron and Simpson (J., 1932, 268). 2·5 G. of the genin were boiled under reflux with 25 c.c. of methyl iodide, 26 g. of precipitated and dried silver oxide, and 25 mg. of sodium hydroxide. The solid was filtered off, the solution washed and evaporated, and the residue crystallised from

acetone. The major part of the genin was recovered, but in the most soluble fraction another *compound* was present; after crystallisation from rectified spirit, it melted at 153—155° (Found : OMe, 7·7. $C_{28}H_{46}O_3$ requires OMe, 7·2%).

*Oxidation of Sarsasapogenin Acetate.*—41 G. of chromic acid, 25 c.c. of water, and 125 c.c. of acetic acid were heated on the steam-bath in a three-necked flask equipped with a stirrer, reflux condenser, and dropping-funnel. A solution of 23 g. of sarsasapogenin acetate (Askew, Farmer, and Kon, *loc. cit.*) in 900 c.c. of acetic acid was run in with constant stirring in the course of 5 hours, the mixture being then heated and stirred for a further 3 hours. The cooled solution was poured into 2 l. of water and repeatedly extracted with a large volume of ether. The extract was thoroughly washed with water to remove most of the acetic acid, then with sodium carbonate (extract A), water, sodium hydroxide (extract B), again with water, dried over sodium sulphate, and evaporated. The *acetate* of the lactone (III) remained as a nearly colourless residue; it was recrystallised from alcohol (yield 3·8 g., m. p. 181—183°) and was then pure enough for the next step. After three crystallisations from alcohol it formed small plates, m. p. 184·5° (Found : C, 74·0; H, 9·4. $C_{24}H_{36}O_4$ requires C, 74·2; H, 9·3%); it had $[\alpha]_D^{25°}$ — 32°, $[\alpha]_{5461}^{25°}$ — 40°, $[\alpha]_{5461}/[\alpha]_D$ 1·25 ($c$ = 0·492 in chloroform).* The lactone dissolves in caustic alkali and is reprecipitated on acidification, but is evidently not extracted by alkali from its etheral solution.

The extract A was acidified with 10% sulphuric acid and extracted with ether. The dried extract gave on evaporation a gum; this was dissolved in ether and treated with a large excess of diazomethane. On removal of the ether a gum was obtained, which was dissolved in hot alcohol. Dense needles (590 mg.) were deposited on cooling in ice, m. p. 199—200° after another crystallisation from the same solvent. The compound was evidently the *methyl* ester of a triketo-acid (Found : C, 69·6; H, 8·9. $C_{30}H_{44}O_7$ requires C, 69·7; H, 8·6%), analogous to that isolated by Jacobs and Simpson (*J. Biol. Chem.*, 1935, **110**, 565). A quinoxaline could not be obtained by the action of *o*-phenylenediamine, but the addition of 4 : 5-diaminouracil sulphate to an alcoholic solution of the ester gave a yellow solution with a strong green fluorescence.

The extract B was acidified and extracted with ether and a solid was obtained on evaporation of the extract, forming long slender needles, m. p. 220° after two crystallisations from alcohol; it appeared to be a fairly acidic *lactone* (Found : C, 71·9; H, 9·3. $C_{20}H_{30}O_4$ requires C, 71·8; H, 9·1%).

*Action of Hydrogen Bromide on the Acetoxy-lactone.*—1·5 G. of the lactone, dissolved in 60 c.c. of alcohol, were kept ice-cold and saturated with dry hydrogen bromide (4 hours). The product was liberated by pouring into water, and taken up in ether, the extract being washed with water, sodium bicarbonate, dried and evaporated, a red-brown gum being obtained. As this did not solidify, a 4% solution of it in benzene was allowed to percolate through a column of activated alumina. A much lighter-coloured product (800 mg.) was recovered on evaporation, and 200 mg. of colourless crystals were obtained on elution of the alumina with ether and evaporation of the ether. The crystals were readily soluble in the usual organic solvents except benzene, from which they separated in needles, m. p. 201°. These were free from halogen and saturated to bromine and permanganate, but developed a yellow colour with tetranitromethane in chloroform, and dissolved in alkali, being reprecipitated by acids; the compound was thus a *lactone* differing from the original acetoxy-lactone by one molecule of water (Found : C, 77·8; H, 9·3. $C_{24}H_{34}O_3$ requires C, 77·8; H, 9·3%).

The bromine-containing gum (800 mg.) in boiling acetic acid was treated with small quantities of zinc dust in the course of 5 hours. Water was then added, and the product taken up in ether, the extract freed from acid with bicarbonate, dried, and evaporated. The residue solidified on rubbing with methyl alcohol, and was recrystallised from this solvent, then twice from ethyl alcohol, forming microscopic needles, m. p. 99°. It was a *lactone* and apparently saturated (Found : C, 80·2; H, 10·0. $C_{22}H_{32}O_2$ requires C, 80·4; H, 9·9%).

*Hydroxy-lactone* (III).—The acetoxy-lactone (1·27 g.) in 105 c.c. of alcohol was boiled for 50 minutes with 280 c.c. of 5% alcoholic potassium hydroxide, the solution then poured into water and extracted with ether. The aqueous layer was acidified with 10% sulphuric acid and re-extracted with ether, the extract washed, dried, and evaporated, yielding 900 mg. of *hydroxy-lactone*, long needles, m. p. 202° after two crystallisations from alcohol [a better solvent is acetone–petroleum (b. p. 60—80°)] (Found : C, 75·9; H, 9·5. $C_{22}H_{34}O_3$ requires C, 76·2; H, 9·5%). It had $[\alpha]_D^{25°}$ — 36·2, $[\alpha]_{5461}^{25°}$ — 44·2, $[\alpha]_D/[\alpha]_{5461}$ 1·22 ($c$ = 0·733 in chloroform); Dr. R. K. Callow informs us that the compound showed no progestin-like activity when tested on a rabbit.

*Keto-lactone* (IV).—900 Mg. of the hydroxy-lactone (III) in 65 c.c. of acetic acid were treated dropwise and with constant shaking with 720 mg. of chromic acid in 9 c.c. of acetic acid in the

* We are again indebted to Dr. R. K. Callow for determining the rotations recorded in this work.

course of 30 minutes. The solution was kept for 2½ hours, poured into water, and repeatedly extracted with a large volume of ether. The extract was shaken three times with water, then with 5% sodium carbonate solution, again with water, dried, and evaporated; 730 mg. of the *keto-lactone* were obtained, forming short glassy needles, m. p. 184·5° after one crystallisation from rectified spirit (the m. p. is depressed 30° by the acetoxy-lactone) (Found: C, 76·7, 76·4; H, 9·0, 9·3. $C_{22}H_{32}O_3$ requires C, 76·7; H, 9·4%).

*Deoxy-lactone.*—380 Mg. of the above lactone in 69 c.c. of alcohol were boiled for 7½ hours with a large excess of amalgamated zinc, whilst 13 c.c. of hydrochloric acid were added in small portions during that time. The solution was poured into water and extracted with ether, the extract being well washed, dried, and evaporated. The residue was a light brown oil (370 mg.) which solidified on rubbing with methyl alcohol. After one crystallisation from this solvent it formed flattened needles, m. p. 133·5°, but after melting and resolidification it melted at 128°, the figure given by Jacobs and Simpson (*loc. cit.*) for the compound prepared from deoxysarsasapogenin (Found: C, 79·9; H, 10·2. Calc.: C, 79·9; H, 10·4%).

*Degradation of the Deoxy-lactone.*—A solution of 9·2 g. of the deoxy-lactone in 450 c.c. of ether was run dropwise (30 mins.) into a mechanically stirred solution of Grignard reagent prepared from 36 g. of bromobenzene, 4·95 g. of magnesium, and 135 c.c. of ether. The solution was boiled under reflux for 6 hours, the ether then distilled off, and the dark residue treated with ice and dilute sulphuric acid. The product was taken up in ether, the extract washed, dried, and evaporated, yielding a brown syrup which partly solidified on keeping. It was warmed with 100 c.c. of acetic acid, an almost colourless solid being deposited (8·7 g.); this was insoluble in acetic acid and practically so in methyl alcohol, but freely soluble in benzene. After two crystallisations from methyl alcohol–acetone, it formed glistening needles, m. p. 205·5°, evidently containing acetone of crystallisation (Found: in air-dry material, C, 81·2; H, 10·0; after drying at 130° in a high vacuum, C, 83·5; H, 9·3. $C_{34}H_{46}O_2,C_3H_6O$ requires C, 81·6; H, 9·6%. $C_{34}H_{46}O_2$ requires C, 83·9; H, 9·5%); it was therefore the *diphenylcarbinol* (V).

8·6 G. of the crude carbinol were suspended in 215 c.c. of acetic acid in a three-necked flask (see p. 417), and heated on a steam-bath. 12·9 G. of chromic acid in 30 c.c. of 80% acetic acid were dropped in during 30 minutes, and the stirring continued for a further 3 hours. The solution was diluted with 750 c.c. of water made just acid with sulphuric acid, repeatedly extracted with much ether, and the extract washed free from acetic acid with the same slightly acid water, and finally with distilled water; emulsions tended to form at first. The extract was now shaken three times with 2*N*-sodium hydroxide; a dark brown, viscous sodium salt separated between the two layers. The clear alkaline solution was acidified with sulphuric acid, and the acid isolated by means of ether as a yellow-brown oil. This was taken up in a little warm acetic acid, and water was added until a slight turbidity appeared. After some time, the solution deposited crude ætiobilianic acid (180 mg.); this was recrystallised four times from dilute acetic acid (charcoal) and formed dense prisms, m. p. 226·5°. A sample of the acid kindly sent by Prof. H. Wieland melted at 225·5° and a mixture of the two had an intermediate m. p. (Found: C, 70·9; H, 9·7. Calc. for $C_{19}H_{34}O_4$: C, 70·8; H, 9·4%). A small amount was sublimed in a vacuum, giving the anhydride, m. p. 203° (Wieland, Schlichting, and Jacobi, *Z. physiol. Chem.*, 1926, **161**, 80, give m. p. 206°).

The viscous sodium salt obtained as a by-product gave on acidification a gummy acid, which was isolated by means of ether (450 mg.); it solidified after some months and crystallised from dilute alcohol in needles, m. p. 212—213°. It was probably the *acid* (VI) analogous to the product obtained by Tschesche and Hagedorn (*Ber.*, 1935, **68**, 1412) from tigogenin (Found: C, 78·8; H, 8·8. $C_{37}H_{42}O_4$ requires C, 79·3; H, 8·2%).

*Oxidation of Smilagenin Acetate.*—This was carried out exactly as described on p. 417, 1·5 g. of acetoxy-lactone being obtained from 9·2 g. of smilagenin acetate. The compound melted at 184·5° after one crystallisation from alcohol, and did not depress the m. p. of the corresponding compound from sarsasapogenin; it had $[\alpha]_D^{25°}$ — 32·0, $[\alpha]_{5461}^{25°}$ — 37·8, $[\alpha]_D/[\alpha]_{5461}$ = 1·18 ($c$ = 0·972 in chloroform) (these values are regarded as more accurate than those given on p. 417) (Found: C, 74·4, 74·3; H, 9·3, 9·4. Calc. for $C_{24}H_{36}O_4$: C, 74·2; H, 9·3%).

3-*Methylcholestan*-3-*ol.*—β-Cholestanone was obtained by the method of Vavon and Jakubowicz (*Bull. Soc. Chim. biol.*, 1933, **53**, 581) as modified by Callow (private communication). 194 G. of the ketone in 2 l. of ether were added in a rapid stream to a Grignard reagent prepared from 336 g. of methyl iodide, 47·8 g. of magnesium activated by heating with iodine, and 1 l. of ether. The solution, which did not deposit a solid addition compound, was boiled under reflux for 2 hours, the solvent distilled off, the grey semi-solid residue decomposed with ice and dilute sulphuric acid, and the product taken up in ether. The extract was washed with caustic soda,

water, dried, and evaporated, the residue being crystallised from acetic acid, giving plates, m. p. about 97° (195 g.); these were rather soluble in the usual organic solvents and evidently consisted of a mixture of two isomerides. One of these was obtained pure after repeated crystallisation from acetic acid and had the constant m. p. 147° (Found : C, 84·2; H, 12·5. $C_{28}H_{50}O$ requires C, 83·9; H, 12·1%).

*3-Methyl-$\Delta^{3(?)}$-cholestene.*—An attempt to dehydrate the above carbinol with thionyl chloride in pyridine (Darzens, *Compt. rend.*, 1911, **152**, 601) was unsuccessful; the product, obtained in poor yield, formed clusters of needles, m. p. 98°, from alcohol, and contained halogen. The carbinol could be distilled unchanged in a high vacuum, but when distilled in the presence of a little aniline hydrobromide it lost water; the distillate was unsaturated to bromine and tetranitromethane and crystallised from acetone in fine prisms, m. p. 81—82° (Found : C, 87·6; H, 12·4. $C_{28}H_{48}$ requires C, 87·8; H, 12·2%).

*Dehydrogenation of 3-Methylcholestan-3-ol.*—50 G. of the carbinol were heated with 75 g. of selenium in a stream of nitrogen, a bath of sodium and potassium nitrates being used to maintain a constant temperature. In the first experiment a certain amount of frothing was experienced, possibly due to incomplete removal of solvents, and the temperature of the bath was raised gradually; it was kept at 270° for 3 hours, at 310—320° for 15 hours, and at 340° for 3 hours. The products were then extracted with ether, and the filtered solution evaporated, the residue being distilled at 1·2 mm. A few drops boiled below 200°, 5·7 g. at 200—225° (this contained much selenium), and 35 g. of a yellow, slightly fluorescent oil were collected at 225—235° (mainly 229—231°). This solidified almost completely overnight, and was purified by rubbing with acetone and successive recrystallisation from acetone, alcohol, and acetone, flattened needles, m. p. 96—97°, being obtained; they were evidently *3-methylcholestane* (Found : C, 86·9; H, 13·2. $C_{28}H_{50}$ requires C, 86·9; H, 13·1%).

The compound was again subjected to dehydrogenation for 46 hours at 350—360°. After extraction with ether and evaporation of the solvent, a thick dark oil with a green fluorescence was obtained; it was dissolved in petroleum (b. p. 60—80°), filtered from some insoluble material, and the solution (approximately 1%) allowed to percolate through a 30-cm. column of Merck's activated alumina (compare Gamble, Kon, and Saunders, J., 1935, 644); this was followed by an equal volume of the pure solvent. The yellow oil recovered on evaporation was treated with *s*-trinitrobenzene, a brownish-orange compound being formed. This melted at about 150° after two crystallisations from alcohol; the hydrocarbon regenerated from it by means of stannous chloride was not homogeneous, as the m. p. altered with every crystallisation; a preparation melting at about 165° gave analytical figures corresponding to a *dimethylcyclopentenophenanthrene* (Found : C, 92·6; H, 7·4. $C_{19}H_{18}$ requires C, 92·6; H, 7·4%).

In another experiment the carbinol was carefully dried, and the temperature of the bath maintained at 330—340° for 16 hours and at 355—360° for a further 24 hours. The dehydrogenation proceeded smoothly. The products were extracted as before, and purified with alumina without previous distillation, 18 g. of reddish oil being recovered. This was treated with 12 g. of *s*-trinitrobenzene dissolved in benzene and a little alcohol. 9·5 G. of crude complex separated overnight, and a further 10 g. were obtained on concentrating the mother-liquor and rubbing the resulting red oil with petroleum (b. p. 40—60°). The total solid was purified by rubbing with this solvent, and the hydrocarbon was regenerated from it by dissolving in alcohol (750 c.c.) and adding a hot solution of 50 g. of stannous chloride in a little hydrochloric acid. After boiling for a short time, the alcohol was removed under reduced pressure, and the hydrocarbon recovered by adding water and extraction with ether; persistent emulsions were formed. The hydrocarbon was purified once more by the alumina process, and was recovered in two portions, 2·3 g. (*A*) representing the more soluble, less easily adsorbed and nearly colourless solid, and 2·6 g. (*B*), which was pale yellow and was recovered from the later runnings; *A* was almost completely soluble in alcohol, and crystallised in iridescent plates (1·1 g.), m. p. 90—100 (*A'*), and the mother-liquor on concentration gave an oil. The latter was reconverted into the trinitrobenzene compound, and this recrystallised from alcohol, but a compound of definite m. p. could not be obtained in this way (see below), and the same applies to the complex prepared from *A'*. Similarly, *B* was crystallised from alcohol, but a compound of definite m. p. was not obtained from it, the m. p. rising gradually to over 210°; this gave a trinitrobenzene complex, m. p. about 165° after one crystallisation.

As the result of the experience on the dehydrogenation of methylsarsasapogenin (p. 420), *cyclo*hexane was employed for the crystallisation of the *trinitrobenzene complex*; in this way fine silky needles, m. p. 174—175°, were obtained after a long series of crystallisations; these were apparently derived from a methyl*cyclo*pentenophenanthrene (Found : C, 64·6, 64·6, 64·5; H, 4·1,

4·1, 4·0. $C_{24}H_{19}O_6N_3$ requires C, 64·7; H, 4·3%). The hydrocarbon regenerated from it was purified by the alumina method, but it was not homogeneous, as the least soluble fraction obtained in minute amount by crystallisation from alcohol melted at about 165°, whilst the bulk formed flattened needles melting at about 120°; a hydrocarbon of constant m. p. has not yet been obtained. The portions of low m. p. gave a *picrate*, orange-red needles from alcohol, m. p. 145—146° (Found: C, 62·3; H, 4·45. $C_{24}H_{19}O_7N_3$ requires C, 62·5; H, 4·2%), a *s*-trinitrobenzene *compound*, yellow needles from alcohol, m. p. 181—182° (Found: C, 64·3; H, 4·1%), and a *styphnate*, aggregates of yellow needles from alcohol, m. p. 175—176° (Found: C, 60·8; H, 4·45. $C_{24}H_{19}O_8N_3$ requires C, 60·4; H, 4·0%). It is noteworthy that these derivatives are all stable to hot alcohol.

3-*Methylsarsasapogenin.*—5 G. of sarsasapogenone (Jacobs and Simpson, *J. Biol. Chem.*, 1935, **109**, 501) in 400 c.c. of ether were added to a Grignard reagent prepared from 15·6 g. of methyl iodide as described on p. 418. The crude *carbinol* was obtained in almost quantitative yield and had m. p. 185° (not depressed by the addition of the parent ketone); it was clearly homogeneous, as the m. p. remained constant after crystallisation from *cyclo*hexane and from acetone; it formed flattened needles (Found: C, 78·1, 78·2; H, 10·8, 10·8. $C_{28}H_{46}O_3$ requires C, 78·1; H, 10·8%).

*Dehydrogenation.* 86 G. of the carbinol were dehydrogenated with 130 g. of selenium at a bath temperature of 350° for 33 hours, and the product worked up as described on p. 419. The greater part of this was insoluble in petroleum, and was a dark brown gum which gradually solidified and is still under investigation. After the first treatment with alumina, 8·5 g. of an amber oil (*A*) and 3·8 g. of a yellow solid (*B*) were obtained, corresponding roughly to *A* and *B* above. These were separately treated with *s*-trinitrobenzene, but the solid obtained in each case contained much of the reagent, from which it had to be separated by repeated extraction with *cyclo*hexane and could then be recovered by evaporation of the extract. As a compound of constant m. p. could not be obtained by crystallisation from alcohol, the crude complex was once recrystallised from this solvent, and the hydrocarbon regenerated from it and fractionally crystallised from alcohol; the m. p. of this rose steadily until it reached 215—216°, but the process could not be continued owing to lack of material. The *hydrocarbon* formed iridescent plates corresponding in composition to the formula $C_{19}H_{16}$ (Found: C, 93·4; H, 6·6. $C_{19}H_{16}$ requires C, 93·4; H, 6·6%). The hydrocarbon was dissolved in alcohol (it was very sparingly soluble) and a little benzene and treated with *s*-trinitrobenzene. The orange solution did not deposit the complex until it had been concentrated, whereupon a deep brownish-orange complex, m. p. 157—158°, was obtained. On dissolving this in alcohol and cooling, the hydrocarbon separated out, but the complex was re-formed on adding more trinitrobenzene; it now had m. p. 164—166°, not depressed by admixture of the complex of similar m. p. from methylcholestanol. It is evident that this complex decomposes very readily in alcoholic solution, and this may account for the difficulties experienced when this solvent is employed for the crystallisation of mixtures. From the more soluble portions of the hydrocarbon mixture, a *s*-trinitrobenzene complex was prepared and crystallised from *cyclo*hexane, orange needles, m. p. 174—175°, being obtained; these were in every way identical with the complex described on p. 419 (mixed m. p.) (Found: C, 64·7, 64·6, 64·8; H, 4·1, 4·3, 4·2. Calc.: C, 64·7; H, 4·3%).

From a portion of the trinitrobenzene complex which could not be crystallised to a constant m. p., a hydrocarbon mixture was obtained; after repeated crystallisation from alcohol, a material melting rather indefinitely at about 220° was produced, giving a *s*-trinitrobenzene *complex*, m. p. 161—163° after one crystallisation from *cyclo*hexane. It formed dark orange needles, and its m. p. was depressed by admixture of the foregoing compound (Found: C, 60·3; H, 3·7. $C_{19}H_{13}O_6N_3$ requires C, 60·3; H, 3·5%); it could not be further examined owing to lack of material.

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