action and since the product was isolated by dilution with water, the salt was effectively separated. When the product separated as a gum, it was taken into ethyl acetate. The ethyl acetate extract was washed with water and saturated sodium bicarbonate solution, then dried and evaporated. The products were recrystallized for analysis as indicated in Table II.

Hydroxymethylation of α-Dichloroacetamidomethyl Biaryl Ketone Intermediates (III).—The α-dichloroacetamidomethylaryl ketones described above were treated with two to three equivalents of 36–38% aqueous formaldehyde in 95% ethanol in the presence of a catalytic quantity of sodium bicarbonate. The reaction was allowed to proceed at 40° for 2 to 5 hours as described in other publications.[2,10]

Treatment of a 9.0-g. portion of 2-phenyl-5-dichloroacetamidoacetothienone in the above manner gave 980 mg. of a dihydroxymethylated compound in addition to the desired product. Similar dihydroxymethylation products have been described as by-products in the hydroxymethylation of α-dichloroacetamido-*p*-nitroacetophenone[16] and the corresponding *p*-methoxyacetophenone analog.[17] The dihydroxymethylated by-product in this case melted at 209–210° after two recrystallizations from ethanol. Hydroxyl absorption in the infrared also ruled out the possibility of a bis analog, another type of by-product which is sometimes obtained in such reactions.

Anal. Calcd. for $C_{16}H_{15}Cl_2NO_4S$: C, 49.49; H, 3.89; N, 3.61. Found: C, 49.70; H, 3.94; N, 3.41.

(16) F. Sorm, J. Gut, M. Suchy and D. Reichl, *Collection Czechoslov. Chem. Communs.*, 501 (1951); J. Sicher, J. Farkas and F. Sorm, *Chem. Listy* **46**, 483 (1952).

(17) M. C. Rebstock and E. L. Pfeiffer, THIS JOURNAL, **74**, 3207 (1952).

The monohydroxymethylation derivative II was the main product of the reaction. In certain of the above biaryl derivatives, the analytical differences between dihydroxymethylation, monohydroxymethylation and bis products do not satisfactorily distinguish between the three possibilities. For better identification, acetyl derivatives were prepared using either the ketone or the product obtained in the Meerwein-Verley-Ponndorf reduction of the ketone. Acetylations were carried out in pyridine in the presence of excess acetic anhydride. The products were isolated by removing the pyridine, excess acetic anhydride, and pyridine acetate on the vacuum pump and recrystallizing from a suitable solvent. 5-(α-Dichloroacetamido-β-acetoxypropionyl)-2-(5-bromo-2-thienyl)-thiophene was recrystallized for analysis from ethylene dichloride, then ethyl acetate, and finally ethanol (m.p. 168–169°).

Anal. Calcd. for $C_{15}H_{12}BrCl_2NO_4S_2$: C, 37.13; H, 2.49; N, 2.88. Found: C, 36.83; H, 2.76; N, 2.75.

1-(2-Methyl-5-phenylthienyl)-2-dichloroacetamido-1,3-propanediol diacetate was recrystallized for analysis from ethylene dichloride–low boiling petroleum ether mixture and finally from ethanol (m.p. 119–120°).

Anal. Calcd. for $C_{20}H_{21}Cl_2NO_5S$: C, 52.41; H, 4.62; N, 3.06; $COCH_3$, 18.8. Found: C, 52.56; H, 4.81; N, 3.04; $COCH_3$, 20.0.

Preparation of 1-Biaryl-2-dichloroacetamido-1,3-propanediols (I).—The β-hydroxy-α-dichloroacetamidopropionylbiaryl intermediates III were reduced in every case using Meerwein–Verley–Ponndorf conditions. The reaction was carried out and the products isolated in essentially the manner described in preceding publications.[2,3,10]

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Steroidal Sapogenins. XXIV. The Hydrochloric Acid Catalyzed Equilibration of 22ξ,25D- and 22ξ-25L-Spirostanes[2]

BY MONROE E. WALL, SAMUEL SEROTA AND LEE P. WITNAUER

RECEIVED DECEMBER 18, 1954

Prolonged heating of sarsasapogenin with ethanolic hydrochloric acid gives a mixture containing sarsasapogenin, smilagenin and the corresponding Δ^2- or Δ^3-desoxy analogs. On studying the reaction with desoxysarsasapogenin and desoxysmilagenin, it was found that an equilibration occurs in both cases in which formation of the more stable smilagenin isomer is favored. The significance of these results in relation to methods for acidic hydrolysis of saponins are discussed.

Recently there have appeared a number of papers dealing with the stereochemistry of the spiroketal side chain[3a-i] Although the stereochemistry of carbon 20[3c,e] and the configuration of carbon 25[3a,b] seem well established, the question of the configuration of carbon 22 and the related matter of the conformation of the methyl group attached to carbon 25 are still unsettled (*cf.* references 3a, b, d, e, h and i).

In an attempt to obtain further information on the nature of the spiroketal side chain, we decided to study the effect of hydrochloric acid on sapogenins with 22ξ,25D- and 22ξ,25L-configurations.[4,5] Marker and Rohrmann[6] reported that sarsasapogenin (25L) was converted to smilagenin (25D) on prolonged heating with ethanolic hydrochloric acid. Other workers starting with the 25L-sapogenins neotigogenin[3f] and markogenin[7] reported similar conversions to the analogous 25D-sapogenins, tigogenin and samogenin.

When sarsaspogenin (I) 22ξ,25L-spirostan-3β-ol, was refluxed with hydrochloric acid under Marker's conditions[6] and the reaction product carefully chromatographed, surprisingly *four* sapogenins were obtained. In order of elution we found 2?-22ξ,25D-spirostene (II), 2?-22ξ,25L-spirostene (III), smilagenin (22ξ,25D-spirostan-3β-ol (IV) and sarsasapogenin (I). Of these II and IV were major con-

(1) A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture. Article not copyrighted.

(2) Paper XXIII, C. R. Eddy, M. A. Barnes, C. S. Fenske, accepted by *Anal. Chem.*

(3) (a) I. Scheer, R. B. Kostic and E. Mosettig, THIS JOURNAL, **75**, 4871 (1953); (b) V. H. T. James, *Chem. and Ind.*, 1388 (1953); (c) M. E. Wall, C. R. Eddy, and S. Serota, THIS JOURNAL, **76**, 2849 (1954); (d) M. E. Wall and S. Serota, *ibid.*, **76**, 2850 (1954); (e) M. E. Wall, S. Serota and C. R. Eddy, *ibid.*, **77**, 1230 (1955); (f) R. K. Callow and V. H. T. James, *Chem. and Ind.*, 691 (1954); (g) D. H. W. Dickson, *et al.*, *ibid.*, 692 (1954); (h) D. A. H. Taylor, *ibid.*, 1066 (1954); (i) J. B. Ziegler, W. E. Rosen and A. C. Shabica, THIS JOURNAL, **76**, 3865 (1954).

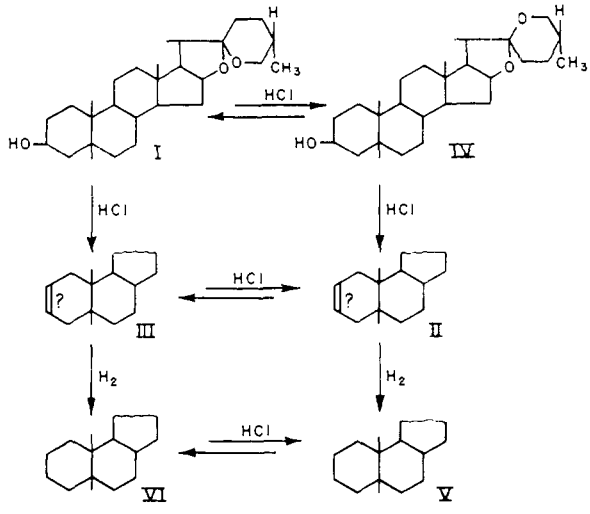
(4) As a result of the researches of Scheer, *et al.*,[3a] and of James,[3b] smilagenin and other 22 "iso" sapogenins have the D configuration at carbon 25, whereas sarsasapogenin and presumably other 22 "normal" sapogenins have the L configration.

(5) G. Mueller and B. Riegel have proposed the use of 25D and 25L to denote configuration at carbon 25. We wish to thank Dr. Mueller for giving us this information prior to publication.

(6) R. E. Marker and E. Rohrmann, THIS JOURNAL, **61**, 846 (1939).

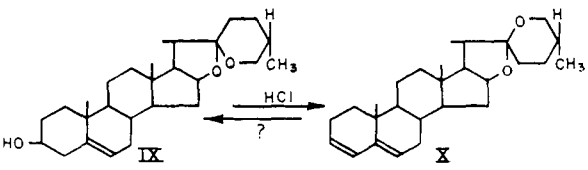
(7) M. E. Wall, *et al.*, *ibid.*, **75**, 4437 (1953).

stituents and I and III minor. The location of the double bond in II and III was not certain and the presence of Δ^3-unsaturation cannot be excluded. Both II and III gave strong positive color tests with tetranitromethane, indicating unsaturation. On catalytic hydrogenation in ether containing 5% acetic acid, II and III were converted to the known saturated analogs, desoxysmilagenin (22ξ,25D-spirostane (V)) and desoxysarsasapogenin (22ξ,25L-spirostane (VI).



The chromatographic separation of sarsaspogenin (I) and smilagenin (IV) was not sharp. Absolute purification of mixtures of I and IV was not feasible in the hydroxyl form. Of interest was the fact that presence of trace quantities of I in IV had little effect on the infrared spectra but depressed the melting point and completely changed the X-ray powder diffraction pattern. Acetylation of the impure "synthetic" smilagenin (IV) gave smilagenin acetate (VII) which after several crystallizations had properties identical in all respects, including X-ray patterns with the acetate of naturally occurring smilagenin. Similarly catalytic hydrogenation of "synthetic" IV gave dihydrosmilagenin (VIII), identical to VIII prepared from natural smilagenin.

Similar hydrochloric acid treatment of the rare diosgenin isomer, yamogenin (5-22ξ,25L-spirostene-3β-ol (IX)) resulted in formation of $\Delta^{3,5}$-desoxytigogenin (3,5-22ξ,25D-spirostadiene (X)). The identity of this compound was established by comparison with X prepared from diosgenin.[8] The infrared and ultraviolet spectra of the two preparations were essentially identical. Further confirmation was obtained by catalytic reduction of X to give the known desoxytigogenin (5α-22ξ, 25D-spirostane (XI)) identical in all respects including X-ray pattern with a sample prepared from natural tigogenin.[8] The yield of X from IX was low and no other crystalline products could be isolated from the resinous reaction mixture.



It now remained to be determined whether the 25L-sapogenins found in the previous experiments were unreacted products or produced by an equilibration from the 25D-analogs. Desoxysmilagenin (V) was refluxed with hydrochloric acid in the usual manner and the reaction product chromatographed. Sharp separation of the desoxysapogenins V and VI was achieved with V being the major product.

Repetition of the experiment starting with desoxysarsasapogenin (VI) gave similar results. An infrared study of the reaction products at various time intervals showed that conversion of VI to V began quickly and final equilibration took place in 48–72 hours. In another experiment, desoxysarsasapogenin was refluxed in absolute ethanol containing sufficient dry hydrogen chloride to make a 2 *N* solution. Equilibration again began rapidly and was virtually complete in 24 hours, the ratio of V to VI being 3:1. The data thus clearly demonstrated that the hydrochloric acid conversion of 25L- to 25D-sapogenins is reversible with the equilibrium greatly in favor of the 25D-component and does not require the presence of water.

The results thus presented suggest that methods for the isolation of sapogenins by acidic hydrolysis of saponins should be scrutinized carefully. Thus Marker[9] utilized for this purpose a solution of approximately 85% ethanol–15% water v./v. containing sufficient hydrochloric acid to give a 2 *N* solution. Marker[6] also used similar conditions for the conversion of I to IV. Under these conditions both the saponins and the sapogenins formed by hydrolysis remain in solution. Consequently there is a definite possibility of equilibration occurring with the production of artifacts. A procedure developed at this Laboratory[10] fortuitously employed an essentially aqueous medium (25% ethanol–75% water v./v.) in which saponins, but not sapogenins were soluble thus minimizing opportunities for equilibration. Thus sarsasapogenin can be routinely isolated in this manner without formation of smilagenin. This was demonstrated in surveys of more than 2000 plant samples[11a,b] and from the fact that enzymatic hydrolysis of saponins gave the same results as acid hydrolysis.[11c,d]

The fact that smilagenin is the favored isomer at equilibrium confirms previous assignments of structure[3e,h,i] in which the C_{26}-oxygen and C_{27}-methyl groups were given the most stable theoretical assignments. For reasons stated previously,[3e] we do not believe that data presently available permit a rigid assignment of the F ring configuration of sarsasapogenin.

(8) M. E. Wall, S. Serota and C. R. Eddy, Fifth Meeting-in-Miniature, Philadeophia Section, A. C. S., Jan. 29, 1953, abstracts of papers, page 12.

(9) R. E. Marker, *et al.*, THIS JOURNAL, **69**, 2167 (1947); see especially p. 2220.

(10) M. E. Wall, M. M. Krider, E. S. Rothman and C. Roland Eddy, *J. Biol. Chem.*, **198**, 533 (1952).

(11) (a) M. E. Wall, *et al.*, *J. Amer. Pharm. Assoc.*, **43**, 1 (1954); (b) **43**, 503 (1954); (c) M. M. Krider and M. E. Wall, THIS JOURNAL, **76**, 2988 (1954); (d) M. M. Krider, T. C. Cordon and M. E. Wall, *ibid.*, **76**, 3515 (1954).

Experimental

Physical Measurements.—Melting points were obtained with a Kofler micro hot-stage. Optical rotations were conducted in chloroform, concentration 8.0 g. per liter. Infrared spectra were conducted in CS_2 solution, concentration 10.0 g. per liter, using a Perkin–Elmer model 21 spectrophotometer. Calculation of the individual components of sarsasapogenin–smilagenin mixtures or similar mixtures of desoxy-analogs were approximated utilizing the peaks at 919 and 899 cm.$^{-1}$, or more accurately from graphical plots of known mixtures, using the ratio of the absorbance at these wave lengths. The X-ray diffraction patterns were recorded with a powder camera of 14.32 cm. diameter; CrKα radiation, λ = 2.2909 Å was used. Specimens were prepared for the camera by pressing a finely ground sample on a glass slide and cutting from it a narrow section, approximately 0.3 mm. thick.

Conversion of I to IV.—Twenty-five grams of sarsasapogenin (I)[12] was dissolved in 2500 ml. of hot 95% ethanol. While refluxing a mixture of 1670 ml. of 95% ethanol and 750 ml. of concentrated hydrochloric acid were added. Refluxing continued for 96 hours and then an additional 335 ml. of concentrated hydrochloric acid was added and heating resumed for 24 hours. The procedure was based on that of Marker and Rohrmann.[6] After cooling, two volumes of water were added, the precipitate filtered, washed and dried. The crude product was taken up in 400 ml. of benzene and chromatographed on 400 g. of Florosil.

DETAILS OF THE CHROMATOGRAPHY

Fraction	Volume, ml.	Eluate, g.	Infrared identification
		Hexane-benzene, 50/50	
1	550	0.0	.....
2	225	Trace	.....
3	450	4.5	Essent. similar to desoxysmilagenin
4	1000	2.8	Similar to 3 but desoxysarsasapogenin component
5	825	2.4	Smilagenin
6	1150	2.2	Smilagenin
7	650	1.0	Smilagenin
		Benzene	
8	1100	3.5	Smilagenin + minor sarsasapogenin
9	1000	2.4	Smilagenin + minor sarsasapogenin
		90% Benzene–10% chloroform	
10	1200	2.0	Smilagenin + *ca.* 20% sarsasapogenin
11	2000	1.3	Smilagenin + *ca.* 20% sarsasapogenin
		90% Benzene–10% ethanol	
12	2000	1.8	Amorphous
		23.9	

All the fractions except 12 were crystalline after chromatography so that approximately 90% of the total starting material was recovered in crystalline form. Fractions 3 and 4 had infrared spectra showing absence of hydroxyl in the region 3400–3600 cm.$^{-1}$.

The infrared spectra of both fractions resembled that of desoxysmilagenin although it was apparent that fraction 4 had some of the sarsasapogenin analog. Both fractions gave a strong yellow color test with tetranitromethane and hence were assigned structures II and III, although presence of a Δ^3-isomer is not excluded. The fractions 3 and 4 were combined and catalytically hydrogenated in the presence of PtO_2 in ether containing 5% acetic acid at room temperature and 45 pounds pressure for six hours.[13] After removing the catalyst, the solvent was evaporated, the residue taken up in petroleum ether, b.p. 30–60°, and the solution chromatographed on Florosil. Elution with petroleum ether resulted in a sharp separation of the two components V and VI. Desoxysmilagenin V was eluted with petroleum ether and accounted for 85% of the weight of fractions 3 and 4. Crystallization of V from methanol gave plates, m.p. 139–140°, $[\alpha]^{25}D$ −69.0° (lit.[6] m.p. 140°). The infrared spectrum and X-ray diffraction powder pattern of V was identical to those of an authentic sample prepared from smilagenin *via* Wolff–Kishner reduction of smilagenone.[8] Desoxysarsasapogenin (VI) was eluted with benzene. Crystallization from ethyl acetate gave plates, m.p. 216–218°, $[\alpha]^{25}D$ −84° (lit.[14] 216–217°). The infrared spectrum and X-ray powder diffraction patterns were identical to those of a reference sample prepared from Wolff–Kishner reduction of sarsasapogenone.[8]

Returning to the main chromatogram, fractions 5–11 were identified from their infrared spectra as consisting essentially of smilagenin (IV) with a minor admixture of sarsasapogenin (I). Compound I was adsorbed to a slightly greater extent than IV so that the later fractions, particularly 10 and 11, were richer in I. The infrared spectrum of I had among other features a strong doublet in the region 1220–1225 cm.$^{-1}$ and very weak absorption near 1250 cm.$^{-1}$ whereas IV had a strong, sharp single peak near 1250 cm.$^{-1}$ and no absorption in the 1220–1225 cm.$^{-1}$ region. Consequently mixtures of the two components could be recognized readily by the infrared spectra in this region as well as by the ratio of the absorbancies 900 cm.$^{-1}$/920 cm.$^{-1}$ which are markedly different for I and IV.

Repeated crystallizations of the fractions low in sarsasapogenin, 5, 6 and 7, from acetone, or aqueous acetone failed to bring the melting point above 182–185° whereas the best samples of IV from natural sources had m.p. 188–189°. The infrared spectra of "synthetic" IV and natural IV were identical but as shown in Table I, the X-ray powder diffraction patterns of the two were totally different, indicating the pronounced effect of traces of I on certain properties of IV which depend on crystal structure.

Acetylation of synthetic IV in pyridine–acetic anhydride at room temperature gave smilagenin acetate (VII), crystallized from methanol, m.p. 150°, identical in all respects with the acetate of natural IV including infrared spectrum and X-ray diffraction pattern.

Catalytic hydrogenation of IV in glacial acetic acid using PtO_2 catalyst, room temperature and 45 pounds pressure for 12 hours gave dihydrosmilagenin (VIII), crystals from acetone, m.p. 163–164°, $[\alpha]^{25}D$ +2° (lit.[3a] m.p. 164–166, $[\alpha]^{25}D$ +3°). The infrared spectrum and X-ray powder pattern, Table I, were identical with a sample prepared from natural IV. Fractions 10 and 11 were crystallized from acetone and the mother liquors evaporated. The residue was then crystallized from ethanol–water. The crystals thus obtained had m.p. 180–184° with infrared spectrum resembling sarsasapogenin (I), but showing presence of 20–30% IV. Further attempts at purification by crystallization were unsuccessful.

Conversion of IX to X.—Yamogenin,[15] 1.0 g. was refluxed 96 hours in a solution of 170 ml. of 95% ethanol to which were added 34.1 ml. of concentrated hydrochloric acid. After working up the reaction product as described under I → IV, the product was dissolved in petroleum ether, b.p. 30–60°, and chromatographed on Florosil. Elution with petroleum ether gave 0.4 g., which on crystallization from acetone yielded 0.15 g. of plates, m.p. 130–140°. The product was identified as $\Delta^{3,5}$-desoxytigogenin (X). Ultraviolet absorption spectra showed maxima at 228, 234.5 and 243 mμ with 234.5 having strongest absorption. Both the ultraviolet and infrared spectrum of X were essentially identical to those of a somewhat purer sample prepared from diosgenin.[8] Catalytic hydrogenation of X in ether–5% acetic acid gave desoxytigogenin (XI), crystals from acetone, m.p. 172°, with infrared spectrum and X-ray powder patterns identical with XI prepared by Wolff–Kishner reduction of tigogenone.[8] No other crystalline components could be isolated from the acid catalyzed conversion of IX to X.

(12) Isolated from *Yucca schidigera* obtained near McConnico, Arizona, m.p. 196–198°, infrared spectrum identical with that of an authentic specimen.

(13) Under these conditions we have found that most nuclear double bonds can be hydrogenated without affecting the spiroketal side chain.

(14) J. C. E. Simpson and W. A. Jacobs, *J. Biol. Chem.*, **110**, 565 (1935).

(15) Yamogenin was isolated from a sample of *Dioscorea composita* from Vera Cruz province, Mexico. Repeated crystallizations from acetone removed diosgenin leaving a soluble residue which on crystallization from ether gave yamogenin, m.p. 195–200° (lit.[9] 200°), with infrared spectrum essentially identical with that published by Jones, *et al.*[16]

(16) R. N. Jones, E. Katzenellenbogen and K. Dobriner, Collected Infrared Absorption Spectra of Steroid Sapogenins, N.R.C. No. 2929, 1953, Ottawa, Canada.

Conversion of V to VI.—Desoxysmilagenin (V), 10.0 g., was dissolved in 1 liter of refluxing 95% alcohol to which was added a solution of 670 ml. of 95% ethanol and 300 ml. of concentrated hydrochloric acid. After refluxing 72 hours an additional 135 ml. of hydrochloric acid was added followed by 24 hours further heating. The usual work-up and chromatography on Florosil gave 5.57 g. of V and 1.0 g. of VI, the two components being cleanly separated as described previously.

Conversion of VI to V.—Desoxysarsasapogenin (VI) was relatively insoluble in 85% ethanol. In one experiment carried out using this solvent in the usual manner the conversion of VI to V was only 50%. Use of isopropyl alcohol overcame solubility problems. Thus, 0.6 g. of VI in 120 ml. of refluxing isopropyl alcohol to which were added 130 ml. of isopropyl alcohol and 45 ml. of concentrated hydrochloric acid was refluxed 72 hours. Aliquots were removed at various time intervals. The proportion of desoxysmilagenin (V) and of desoxysarsasapogenin (VI) was calculated from the ratios of the corrected absorbancies 900 $cm.^{-1}$/920 $cm.^{-1}$. A standard curve was prepared from known mixtures of V and VI from which the proportions present in various unknown samples could be calculated. A similar experiment starting with VI was carried out under anhydrous conditions. VI, 0.75 g., was refluxed in 250 ml. of absolute ethanol containing dry hydrogen chloride (2 *N*). The results for both the aqueous and anhydrous experiments are shown below.

Time, hr.	Desoxysarsasapogenin, % Aqueous	Anhyd.	Time, hr.	Desoxysarsasapogenin, % Aqueous	Anhyd.
0.5	100	100	12	..	40
1	95	95	24	20	30
3	85	75	48	10	30
5	70	60	72	5	25
8	50	55	120	5	..

Acknowledgment.—We should like to acknowledge the assistance of H. W. Jones, R. F. Mininger, C. S. Fenske and D. R. Killen in various phases of this investigation. Infrared spectroscopy was under the direction of C. R. Eddy. The plant samples from which various sapogenins were prepared were collected by D. S. Correll and H. S. Gentry, Plant Introduction Section, Horticultural Crops Research Branch, Beltsville, Maryland.

PHILADELPHIA 18, PENNA.

[CONTRIBUTION FROM THE PHARMACEUTICAL INSTITUTE, MEDICAL FACULTY, UNIVERSITY OF KYUSHU]

Cholesterol and Related Compounds. III. Conversion of Phenanthrene to Anthracene Ring System in $\Delta^{5,7}$-, $\Delta^{6,8(9)}$- and $\Delta^{5,8(9)}$-Cholestadienol

BY KYOSUKE TSUDA AND RYOICHI HAYATSU[1]

RECEIVED JULY 7, 1954

The irradiation of alcoholic solutions of 7-dehydrocholesterol (I), isodehydrocholesterol (II) and $\Delta^{5,8(9)}$-cholestadienol (III) with mercuric acetate and *p*-toluenesulfonic acid, in a nitrogen stream, yielded the same substance IV in each case; the ultraviolet absorption spectrum of IV showed the bands of a benzenoid type compound. The structure of IV was established by nitric acid oxidation to methylpyromellitic acid and by selenium dehydrogenation which yielded a hydrocarbon VI. The latter showed the ultraviolet absorption curve typical of anthracene hydrocarbons.

When 7-dehydrocholesterol and ergosterol are irradiated with visible light, peroxide is formed in the presence of oxygen and bis-(ergostadienol) in the absence of oxygen.[2] In the present experiments, the irradiation of mixtures of a sterol (7-dehydrocholesterol (I), isodehydrocholesterol (II) or $\Delta^{5,8(9)}$-cholestadienol (III)[3]) *p*-toluenesulfonic acid and mercuric acetate with a mercury and an incandescent lamp, in the absence of air, yielded a common product (IV) with a cyclopentanoanthracene nucleus. This product (m.p. 153–154°) is a trienol with the empirical formula $C_{27}H_{42}O$; the ultraviolet absorption data suggest that it has a benzenoid structure.

Crystals of m.p. 153–154° also were obtained by the irradiation of III (in acetic anhydride and *p*-toluenesulfonic acid) with sunlight under somewhat different conditions in the absence of mercuric acetate. This method is superior to the general procedure described above in that chromatography is unnecessary for the purification of the desired product (IV) which precipitates as the acetate and is pure after one recrystallization. However, we found that this reaction proceeds satisfactorily only in the summer in the presence of strong sunlight.

When the common product (m.p. 153–154°) was oxidized with nitric acid and the resulting acid methylated, an ester (V) was obtained which was identical with the tetramethyl methylpyromellitate[3,4] obtained by the nitric acid oxidation and subsequent methylation of 7-dehydrocholesterol or $\Delta^{5,8(9)}$-cholestadienol. The product of the skeletal conversion reaction was, therefore, tentatively assigned the structure represented by formula IV.

The following results furnished confirmatory evidence: The selenium dehydrogenation of IV give a hydrocarbon, $C_{19}H_{18}$, the melting point of which was difficult to determine. The picrate was identical with the picrate of the hydrocarbon, $C_{19}H_{18}$, obtained by the selenium dehydrogenation of the phenol formed by the dienone–phenol rearrangement of 7-keto-$\Delta^{5,8(9)}$-cholestadienol.[3] As was pointed out previously,[3] this hydrocarbon, $C_{19}H_{18}$, shows an ultraviolet absorption curve which is characteristic of anthracene rather than phenanthrene compounds. These facts can be explained if formula IV is assigned to the reaction product of the skeletal conversion and formula VI, 3′-methyl-1,2-cyclopentano-10-methylanthracene, to the hydrocarbon.

The nitric acid oxidation of a steroid possessing two double bonds in the B-ring results in the forma-

(1) Takamine Research Laboratory, Sankyo Co., Ltd., Tokyo, Japan.

(2) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 163.

(3) K. Tsuda, K. Arima and R. Hayatsu, THIS JOURNAL, **76**, 2933 (1954).

(4) Reference 2, p. 169.