Steroids and Walden Inversion. Part XXV. A Kinetic Study of the Methanolysis of Cholesteryl Toluene-*p*-sulphonate in the Presence of Methoxide Ions.*

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Methanolysis of cholesteryl toluene-*p*-sulphonate in the presence of methoxide ions gives cholesteryl methyl ether, 6β-methoxy-3 : 5-*cyclo*-cholestane, and cholesta-3 : 5-diene, unaccompanied by *epi*cholesteryl methyl ether. A kinetic study shows that the reaction is of the first order with respect to the toluene-*p*-sulphonate with $k_1 = 0{\cdot}0043$ min.$^{-1}$; since the rate of methanolysis under identical conditions but in the absence of methoxide ions has been found to be $k_1 = 0{\cdot}0046$ min.$^{-1}$ (Pearson, King, and Langer, *J. Amer. Chem. Soc.*, 1951, **73**, 4149), these solvolyses occur by a unimolecular mechanism (S_N1). The methoxide ion, in contrast to ions of type NR_2^-, is too weakly nucleophilic to compete by an S_N2 substitution process with the π-electron-facilitated S_N1 substitution.

Nucleophilic substitution at $C_{(3)}$ in saturated steroids usually proceeds with inversion of configuration at $C_{(3)}$ and therefore by a bimolecular mechanism (S_N2). Thus, cholestan-3β-yl toluene-*p*-sulphonate (I ; *p*-$C_6H_4Me{\cdot}SO_2{\cdot}O$ equatorial) by methanolysis at 65° gives

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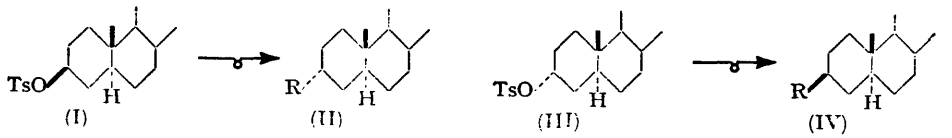
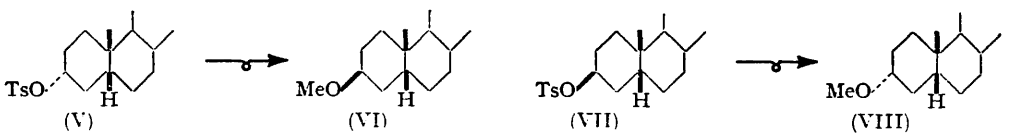
3α-methoxycholestane (II; R = MeO) (73%), together with a mixture of cholest-2- and -3-ene (17%), but unaccompanied by the 3β-epimeride (Stoll, *Z. physiol. Chem.*, 1932, **207**, 147; Nace, *J. Amer. Chem. Soc.*, 1952, **74**, 5937), whilst use of pyridine or piperidine at 100° affords *N*-cholestan-3α-ylpyridinium toluene-*p*-sulphonate (II; R = $C_5H_5N^+$} *p*-$C_6H_4Me{\cdot}SO_2{\cdot}O^-$) or *N*-cholestan-3α-ylpiperidine (II; R = $C_5H_{10}N{\cdot}$) (King and Bigelow, *J. Amer. Chem. Soc.*, 1952, **74**, 3338). Conversely cholestan-3α-yl toluene-*p*-sulphonate (III; *p*-$C_6H_4Me{\cdot}SO_2{\cdot}O$ axial) by methanolysis at 65° gives 3β-methoxycholestane (IV;

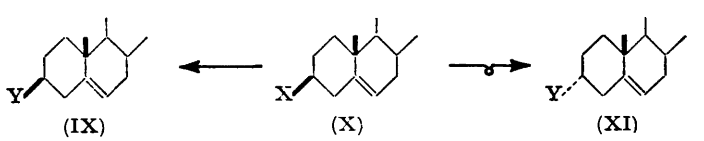


R = MeO) (23%), together with a mixture of cholest-2- and -3-ene (69%), but unaccompanied by the 3α-epimeride (Nace, *loc. cit.*), whilst use of pyridine or piperidine at 100° furnishes *N*-cholestan-3β-ylpyridinium toluene-*p*-sulphonate (IV; R = $C_5H_5N^+$}*p*-$C_6H_4Me{\cdot}SO_2{\cdot}O^-$) or *N*-cholestan-3β-ylpiperidine (IV; R = $C_5H_{10}N$) (King and Bigelow, *loc. cit.*). Similarly, coprostan-3α-yl toluene-*p*-sulphonate (V; *p*-$C_6H_4Me{\cdot}SO_2O$ equatorial) by methanolysis furnishes 3β-methoxycoprostane (VI) (82%), and coprost-2-ene (18%), unaccompanied by the 3α-epimeride (D. D. Evans and Shoppee, *J.*, 1953, 540),



whilst coprostan-3β-yl toluene-*p*-sulphonate (VII; *p*-$C_6H_4Me{\cdot}SO_2{\cdot}O$ axial) yields a little 3α-methoxycoprostane (VIII) (J. R. Lewis and Shoppee, *J.*, 1955, 1375) and much coprost-2-ene (~90%). The pattern of reaction is thus inversion accompanied by elimination with effectively complete absence of racemisation.

Until recently it was thought that nucleophilic replacement at $C_{(3)}$ in 3β-substituted Δ^5-steroids proceeds with complete retention of configuration by a unimolecular mechanism (S_Ni) involving participation of the π-electrons of the 5 : 6-double bond (Winstein and Adams, *J. Amer. Chem. Soc.*, 1948, **70**, 838; Hafez, Halsey, and Wallis, *Science*, 1949, **110**, 475; Davies, Meecham, and Shoppee, *J.*, 1955, 679). Thus, cholesteryl chloride and toluene-*p*-sulphonate (X; X = Cl or *p*-$C_6H_4Me{\cdot}SO_2{\cdot}O$ equatorial) by methanolysis give cholesteryl methyl ether (IX; Y = MeO) (~90%) unaccompanied by *epi*cholesteryl methyl ether (Diels and Blumberg, *Ber.*, 1911, **44**, 2874; Stoll, *loc. cit.*); the reaction at 34·8° has been shown to be of the first order with respect to the toluene-*p*-sulphonate with $k_1 = 0{\cdot}0046$ min.$^{-1}$ (Pearson, King, and Langer, *J. Amer. Chem. Soc.*, 1951, **73**, 4149) and so presumably proceeds by a unimolecular mechanism. Similar observations have been made for hydrolysis (Beynon, Heilbron, and Spring, *J.*, 1936, 907) and acetolysis (Wallis, Fernholz, and Gephart, *J. Amer. Chem. Soc.*, 1937, **59**, 137; Bergmann, *ibid.*, 1938, **60**,

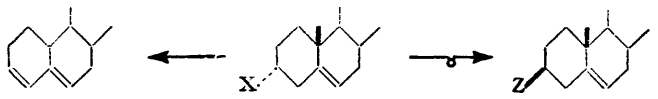


1996; Shoppee, *J.*, 1946, 1147; Shoppee and Summers, *J.*, 1952, 3361). Likewise, cholesteryl bromide, iodide, and toluene-*p*-sulphonate (X; X = Br, I, or *p*-$C_6H_4Me{\cdot}SO_2{\cdot}O$) react with pyridine at 120° to give the quaternary salt (IX; Y = $C_5H_5N^+$}*p*-$C_6H_4{\cdot}SO_2{\cdot}O^-$) (71%) with cholesta-3 : 5-diene (21%) (King and Regan, *J. Amer. Chem. Soc.*, 1952, **74**, 5617).

The pattern of reaction for substitution of 3β-substituted Δ^5-steroids thus appears to

be retention of configuration, absence of racemisation, and little or no elimination. It has, however, been shown that, for substitution of 3β-substituted Δ^5-steroids by sufficiently powerful nucleophiles [$Y = {}^-CH(CO_2R)_2, NH_2^-, NHR^-, NR_2^-$] under appropriate conditions, the unimolecular reaction (X ⟶ IX) can be accompanied, or even largely superseded, by the bimolecular reaction with inversion of configuration (X ⟶ XI), in which the π-electrons of the double bond do not participate (Pierce, Richards, Shoppee, Stephenson, and Summers, *J.*, 1955, 694).

In 3α-substituted Δ^5-steroids on account of the molecular geometry the π-electrons of the 5 : 6-double bond are unable effectively to participate in reactions at $C_{(3)}$, and unimolecular heterolysis generally leads to elimination (*E*1) with formation of 3 : 5-dienes rather than to substitution (S_N1). Thus the methanolysis (or ethanolysis) of *epi*cholesteryl toluene-*p*-sulphonate (XIII; X = *p*-$C_6H_4Me{\cdot}SO_2{\cdot}O$ axial) gives cholesta-3 : 5-diene (XII) (76%), and, by rearrangement involving hydrogen migration, 4β-methoxycholest-5-ene



(XII) (XIII) (XIV)

and 6β-methoxycholest-4-ene (7%) (Evans and Shoppee, *loc. cit.*), and takes place by a unimolecular mechanism (King and Bigelow, *J. Amer. Chem. Soc.*, 1952, **74**, 6238). Similarly, the acetolysis of *epi*cholesteryl chloride, bromide, and toluene-*p*-sulphonate (XIII; X = Cl, Br, or *p*-$C_6H_4Me{\cdot}SO_2{\cdot}O$) furnishes cholesta-3 : 5-diene (XII) (92—99%) Evans and Shoppee, *loc. cit.*) by a unimolecular mechanism (Shoppee and D. F. Williams, *J.*, 1955, 686). In none of these reactions has any detectable amount of a 3α- or a 3β-substitution product been reported. If, however, *epi*cholesteryl toluene-*p*-sulphonate is treated with pyridine or piperidine at 100°, then although much elimination occurs to give cholesta-3 : 5-diene (XII) (~75%), there is also bimolecular substitution at $C_{(3)}$ with inversion of configuration to give 3β-substituted Δ^5-derivatives [XIV; Z = $C_5H_5N^+$}*p*-$C_6H_4Me{\cdot}SO_2O^-$ (8%) or $C_5H_{10}N$ (11%)] (King and Bigelow, *loc. cit.*). The reversion of the reaction pattern to that characteristic of the saturated series (inversion + elimination) is consistent with the inability of the π-electrons in 3α-substituted Δ_5-steroids to intervene effectively in reactions at $C_{(3)}$, as suggested by Shoppee and Williams (*loc. cit.*).

King and Bigelow observed that the ethanolysis of *epi*cholesteryl toluene-*p*-sulphonate in the presence of ethoxide ions at 34·8° exhibited second-order kinetics (*loc. cit.*; Fig. 3); they concluded that the ethoxide ion can react directly with the toluene-*p*-sulphonate, although they did not attempt to isolate the product of such a reaction (XIV; Z = EtO). It seemed of interest to investigate the parallel but converse case of the solvolysis of cholesteryl toluene-*p*-sulphonate in methanol (dielectric constant 32) in the presence of methoxide ions at 35°. The product, on repeated chromatography, gave cholesteryl methyl ether (IX; Y = MeO) formed by unimolecular substitution with retention of configuration, 6β-methoxy-3 : 5-*cyclo*cholestane formed by rearrangement, and cholesta-3 : 5-diene (XII) formed by elimination. In methanol containing 75% of dioxan (dielectric constant 4·1) at 35°, and in methanol containing 75% of toluene (dielectric constant ~3) at 35° the same three products only were obtained; when similar experiments were carried out under reflux, *i.e.*, at ~100° and ~110°, mixtures of cholesteryl methyl ether and 6β-methoxy-3 : 5-*cyclo*cholestane but no cholesta-3 : 5-diene were obtained. In none of these experiments could *epi*cholesteryl methyl ether (XI; Y = MeO), which should result from bimolecular substitution, be isolated.

The kinetic measurements were carried out at 35° in methanolic sodium methoxide, containing chloroform to give a homogeneous solution [$MeOH/CHCl_3$(10 : 1)], using a conductance method (Pearson, *J. Amer. Chem. Soc.*, 1947, **69**, 3100). For the reaction: $RX + Y^- \xrightarrow{k_1} RY + X^-$, the concentrations and conductances at zero time, time *t*, and infinite time are as tabulated. It follows that $a = (1/R_0 - 1/R_\infty)Z$, and $x = (1/R_0 - 1/R)Z$, where *Z* is a proportionality constant $A/[\lambda_{Y^-} - \lambda_{X^-}]$, and R_0, *R*, and R_∞ are the

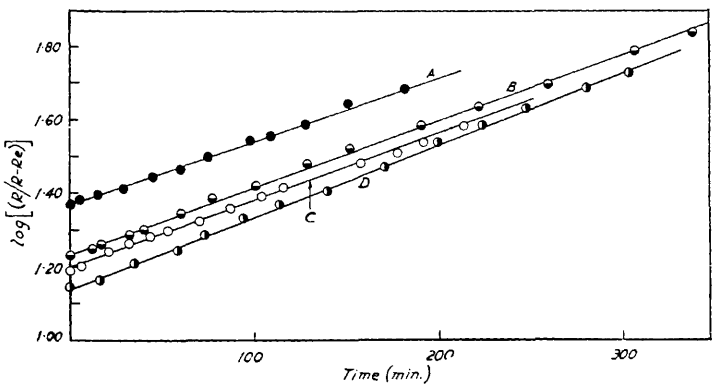
resistances at zero time, time t, and infinite time, whilst the usual first-order rate equation has the form

$$k_1 = \frac{2{\cdot}303}{t} \log \frac{R(R_0 - R_e)}{R_0(R - R_e)}$$

Since $(R_0 - R_e)/R_0$ is constant, the plot of log $[R/R - R_e)]$ against time gives the first-order rate constant; the results are shown in the Figure.

The reaction is clearly of the first order with respect to cholesteryl toluene-*p*-sulphonate with an average rate $k_1 = 0{\cdot}0043$ min.$^{-1}$. This value is close to that, $k_1 = 0{\cdot}0046$ min.$^{-1}$, found under identical conditions for the methanolysis of cholesteryl toluene-*p*-sulphonate in the absence of methoxide ions (Pearson, King, and Langer, *loc. cit.*); it is consistent with a unimolecular mechanism involving a rate-determining heterolysis and indicates that the methoxide ion does not react directly with cholesteryl toluene-*p*-sulphonate. This behaviour is in sharp contrast with the direct reaction of the methoxide ion with *epi*-cholesteryl toluene-*p*-sulphonate, and suggests that the methoxide ion is too weakly

Methanolysis of cholesteryl toluene-p-*sulphonate at* 35° ± 0·1°



Curve	*A*	*B*	*C*	*D*
Toluenesulphonate concn. (10^{-3}M)	1·11	1·48	1·50	1·24
NaOMe concn. (10^{-3}M)	6·60	5·73	5·20	3·21
$10^3 k_1$ (min.$^{-1}$)	4·03	4·34	4·05	4·56

	Concentrations				
Time	[RX]	[Y$^-$]	[RY]	[X$^-$]	Conductances
0	a	b	0	0	$1/R_0 = A[\lambda_{Y^-} . b]$
t	$a - x$	$b - x$	x	x	$1/R = A[\lambda_{Y^-}(b - x) + \lambda_{X^-} . x]$
∞	0	$b - a$	a	a	$1/R\infty = A[\lambda_{Y^-}(b - a) + \lambda_{X^-} . a]$

nucleophilic to compete with the π-electron-facilitated unimolecular heterolysis of a 3β-substituted Δ^5-steroid (Shoppee and Summers, *J.*, 1952, 3367). This conclusion is in agreement with the known low nucleophilic power of the methoxide ion as disclosed by the sequence of nucleophilic power: $SPh^- \gg$ piperidine $> OMe^- > OPh^- \gg OH^-$ found by Bunnett and Davis (*J. Amer. Chem. Soc.*, 1954, **76**, 3011).

Experimental

For general experimental directions see *J.*, 1955, 1375. $[\alpha]_D$ are in $CHCl_3$, with $c \sim 1{\cdot}0$.

Anhydrous Methanol.—Methanol was distilled over potassium hydroxide pellets, and then refluxed over lime for 24 hr.; finally, it was dried by treatment with magnesium (Lund and Bjerrum, *Ber.*, 1931, **64**, 210). For preparation of sodium methoxide solutions, dry nitrogen was bubbled for 0·5 hr. through methanol, which thereafter was allowed to drip on to sodium, at a speed sufficient to maintain refluxing, in an atmosphere of nitrogen.

Reaction of Cholesteryl Toluene-p-*sulphonate with Sodium Methoxide in Methanol.*—Cholesteryl toluene-*p*-sulphonate (1·238 g.) was dissolved in chloroform (5 c.c.), methanolic 0·039N-sodium methoxide (100 c.c.) was added under nitrogen, and further chloroform (5 c.c.) was

added to give a homogeneous solution 0·021M with respect to toluenesulphonate; the ampoule was sealed and left at 35° for 20 hr. The product was isolated in the usual way, and chromatographed on aluminium oxide (45 g.) in pentane. Elution with pentane (4 × 100 c.c.) gave fractions: A1, trace of oil; A2 (95 mg.), crude cholesta-3 : 5-diene giving a positive Rosenheim test; A3 (32 mg.), m. p. 72°, after recrystallisation from acetone; A4 (78 mg.), m. p. 82°, $[\alpha]_D$ −41°, after recrystallisation from acetone. Elution with benzene–pentane (1 : 19; 5 × 100 c.c.) gave fractions: B1, B2, B3, B4 (159 mg.; 244 mg.; 122 mg.; 69 mg.), consisting of 3β-methoxycholest-5-ene, which had m. p. 83—84°, $[\alpha]_D$ −45°, after recrystallisation from acetone; B5 contained only traces of material. Elution with benzene–pentane (1 : 9; 2 × 100 c.c.) gave fractions: C1, C2 (34 mg., 25 mg.), consisting of 3β-methoxycholest-5-ene, m. p. 82—84°, $[\alpha]_D$ −46°; further elution with benzene gave insignificant amounts of material.

The recrystallised fractions A2, A3, and A4 were combined (188 mg.) and rechromatographed on aluminium oxide (20 g.) in pentane. Elution with pentane (5 × 20 c.c.) gave fractions: D1 (9 mg., positive Rosenheim test); D2 and D3 (33 mg., 30 mg.), cholesta-3 : 5-diene, m. p. 80°, $[\alpha]_D$ −114°, giving positive Rosenheim tests, after recrystallisation from acetone: D4 and D5 (13 mg., 17 mg.), 6β-methoxy-3 : 5-*cyclo*cholestane, m. p. 79°, $[\alpha]_D$ +54°, after recrystallisation from acetone; D6, traces. Elution with benzene–pentane (1 : 1) gave 3β-methoxycholest 5-ene, m. p. 82°, $[\alpha]_D$ −46° (82 mg.), after recrystallisation from acetone. A second experiment furnished only the same three products.

Kinetic measurements. The rate of methanolysis was measured conductometrically at 35·0° ± 0·1° with a conventional bridge assembly which incorporated a 1000-cycle oscillator. Resistance measurements were made to ±1 ohm. The cell employed was after the design of Jones and Bollinger (*J. Amer. Chem. Soc.*, 1931, **53**, 441). The electrodes were lightly platinised and the cell constant was approx. 5 cm.$^{-1}$.

In different runs the concentration of cholesteryl toluene-*p*-sulphontae was maintained approx. 1·5 × 10^{-3}M, whilst that of the sodium methoxide was varied in the range 3—7 × 10^{-3}M; the latter solutions were standardised immediately before use against 0·01N-hydrochloric acid. The methanolic sodium methoxide was introduced into the cell and allowed to attain 35°, and a weighed amount of the ester, dissolved in the volume of purified chloroform required to give the ratio MeOH : $CHCl_3$ = 10 : 1, was added. Resistances were determined at appropriate intervals. The results are given in the Figure and its legend.

Reaction of Cholesteryl Toluene-p-*sulphonate with Sodium Methoxide in Dioxan and Toluene.*—(*a*) The ester (1·95 g.), dissolved in dioxan (75 c.c.), was treated with methanolic 0·041N-sodium methoxide (25 c.c.) at 35° for 37 hr.; the concentration of the ester was 0·036N. The product was isolated in the usual way, and chromatographed on aluminium oxide in pentane. Elution with pentane gave fractions A1—5 (12, 393, 209, 79, and 44 mg.) all giving the Rosenheim test; use of benzene–pentane (1 : 19) gave fractions B1 and B2 (83, 10 mg.) as oils; use of benzene–pentane (1 : 9) gave no material, but use of benzene–pentane (1 : 3) yielded fractions C1 (37 mg.) and C2 (30 mg.) consisting of slightly impure 3β-methoxycholest-5-ene which had m. p. 70—72°, $[\alpha]_D$ −39°, and m. p. 74—76°, $[\alpha]_D$ −40°, after recrystallisation from acetone. Elution with benzene gave no material, but use of acetone gave some cholesteryl toluene-*p*-sulphonate, m. p. and mixed m. p. 132°. Fractions A2—5 were united and rechromatographed: exhaustive elution with pentane gave fractions E1, E2, consisting of cholesta-3 : 5-diene (257, 166 mg.), m. p. 80°, $[\alpha]_D$ −114°, after recrystallisation from acetone, E3, E4, and E5 consisting essentially of 6β-methoxy-3 : 5-*cyclo*cholestane (99, 31, 17 mg.), m. p. 72°, $[\alpha]_D$ +30°, m. p. 69°, $[\alpha]_D$ +37°, and m. p. 74° respectively, after recrystallisation from acetone. Fractions B1 and B2, and the mother-liquors from the crystallisation of fractions C1 and C2 were combined and rechromatographed; elution with pentane gave fractions F1 and F2 consisting of 6β-methoxy-3 : 5-*cyclo*cholestane (24 mg., —), m. p. 74°, $[\alpha]_D$ +50°, and m. p. 76°, $[\alpha]_D$ +51° respectively, after recrystallisation from acetone. Further elution with pentane and benzene–pentane (1 : 19, 1 : 9) yielded no material, but use of benzene–pentane (1 : 4) gave fractions G1, G2, and G3 (8, 10, and 6 mg.) which were united and recrystallised from acetone to give 3β-methoxycholest-5-ene, m. p. and mixed m. p. 81—84°, $[\alpha]_D$ −46°.

(*b*) The ester (2·43 g.), dissolved in dioxan (75 c.c.), was heated at 100° with methanolic 0·06N-sodium methoxide (25 c.c.) under nitrogen for 6 hr. Chromatography of the product on aluminium oxide gave by elution with pentane (3 × 200 c.c.) fractions: A1 (346 mg.), 6β-methoxy-3 : 5-*cyclo*cholestane, m. p. 76—78°, $[\alpha]_D$ +53° after crystallisation from acetone; A2 (1·17 g.), m. p. 66°, $[\alpha]_D$ +32°, after crystallisation from acetone; A3 (40 mg.). Use of benzene gave fraction B1 (40 mg.), an oil. Fraction A2 was rechromatographed; elution with pentane (3 × 100 c.c.; 2 × 50 c.c.) gave fractions: C1 (493 mg.), m. p. 76°; C2 (417 mg.), m. p. 76—79°;

C3 (170 mg.), m. p. 79—80°; C4 and C5, m. p. 81°; these fractions were crystallised from acetone and gave no m. p. depressions on admixture with 3β-methoxycholest-5-ene although giving depressions of ~15° on admixture with 3α-methoxycholest-5-ene. Fractions A3 and B1 were united and rechromatographed; elution with pentane gave no material, but use of benzene–pentane (1 : 19) gave fractions D1, D2, and D3, which after examination were combined and recrystallised from acetone to yield 3β-methoxycholest-5-ene, m. p. and mixed m. p. 80°, $[\alpha]_D$ −45°; fraction D4 (25 mg.) also consisted of this substance, m. p. 78—80°, mixed m. p. 80°. No cholesta-3 : 5-diene was detected, nor could 3α-methoxycholest-5-ene be isolated.

(*c*) The ester (1·024 g.), dissolved in toluene (75 c.c.), was treated with methanolic 0·022N-sodium methoxide (25 c.c.) under nitrogen at 35° for 37 hr. The product was isolated in the usual way, and chromatographed on aluminium oxide in pentane. Elution with pentane (4 × 100 c.c.) gave fractions A1 and A2 (262 mg., 239 mg.) consisting mainly of cholesta-3 : 5-diene, m. p. 66° after recrystallisation from acetone, giving an immediate positive Rosenheim reaction, then A3 (38 mg.), and A4 (28 mg.), whilst use of benzene–pentane (1 : 19) gave fraction B1 (58 mg.), consisting of nearly pure 3β-methoxycholest-5-ene, m. p. and mixed m. p. 81°, $[\alpha]_D$ −44°; no further material was eluted except by acetone which furnished a small quantity of cholesteryl toluene-*p*-sulphonate, m. p. 131°. The considerable mother-liquors from fractions A1 and A2 were united and rechromatographed, to give by elution with pentane fractions as follows: C1 and C2 (184 mg.; 115 mg.), m. p. 66—70° and 69—71°, $[\alpha]_D$ +34°, after recrystallisation from acetone, giving the Rosenheim test after a long induction period and consisting of 6β-methoxy-3 : 5-*cyclo*cholestane contaminated by cholesta-3 : 5-diene; C3 (69 mg.) and C4 (43 mg.) consisting of nearly pure 6β-methoxy-3 : 5-*cyclo*cholestane, m. p. 74—76°, mixed m. p. 76—79°, after recrystallisation from acetone. Elution with benzene–pentane (1 : 9) gave only 23 mg. of material, m. p. 72°. Fractions C1 and C2 were united and rechromatographed, to give by elution with pentane fractions: E1 (10 mg.), oil; E2 (34 mg.), giving a positive Rosenheim test; E3 (66 mg.); E4 and E5 (47 mg.; 27 mg.) consisting of 6β-methoxy-3 : 5-*cyclo*cholestane, m. p. 74°, m. p. 76—79°; all material was then removed from the column by elution with acetone, and the material obtained (70 mg.) chromatographed anew. Elution with pentane gave fractions: F1 and F2 (8 mg.; 23 mg.), m. p. 80°, m. p. 82°, which after examination were combined and recrystallised from acetone to give 3β-methoxycholest-5-ene, m. p. and mixed m. p. 82°; F3 (16 mg.), m p. 70—74°, and F4 (8 mg.), m. p. 64°, too small for further purification.

(*d*) The ester (0·88 g.), dissolved in toluene (75 c.c.), was heated under reflux in an atmosphere of dry nitrogen with methanolic 0·022N-sodium methoxide (25 c.c.) for 5 hr. Isolation of the product in the usual way and chromatography on aluminium oxide gave by elution with pentane (5 × 100 c.c.) fractions: A1 (192 mg.), m. p. 79°, $[\alpha]_D$ +54°; A2 (185 mg.), m. p. 79°; A3 (64 mg.), m. p. 77°; A4 (78 mg.), m. p. 77°, $[\alpha]_D$ +53°; all these fractions were crystallised from acetone and consisted of 6β-methoxy-3 : 5-*cyclo*cholestane. Elution with benzene–pentane (1 : 4; 3 × 100 c.c.) gave fractions: B1 (58 mg.), a mixture, m. p. 74°, not further examined; B2 (48 mg.), m. p. 82—84°; B3 (20 mg.), m. p. 81°; the last two fractions were recrystallised from acetone and consisted of 3β-methoxycholest-5-ene. Neither cholesta-3 : 5-diene nor 3α-methoxycholest-5-ene could be isolated.

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