plex multiplets, 8 H), 2.33 (s, 3 H), 2.5–3.0 (broad, 3 H), 3.52 (s, 3 H), 4.05 (t, J = 6 Hz, 2 H), 7.1–7.9 (m, 8 H); uv λ_{max} 226 nm (ϵ 44,643), 283 (6420).

Anal. Calcd for $C_{28}H_{27}NSO_3$: C, 69.50; H, 6.85; N, 3.52; S, 8.05. Found: C, 69.61; H, 7.07; N, 3.39; S, 8.22.

The deuterated material, 3-(1,2,3,4-tetrahydro-9-methylcarbazol-1-yl)propyl tosylate-*1,1-d*$_2$, was prepared as just described using lithium aluminum deuteride for the reduction of ethyl 3-(1,2,3,4-tetrahydro-9-methylcarbazol-1-yl)propionate.

6*H*-1,2,3,3a,4,5-Hexahydropyrido[3,2,1-*jk*]carbazole (12).—A solution of **1** (0.192 g) in 10 ml of 0.5 *M* potassium *tert*-butoxide in *tert*-butyl alcohol was heated under reflux for 10 hr. The alcohol was evaporated under reduced pressure and the residue was treated with dilute hydrochloric acid and extracted with ether. Evaporation of the ether afforded 0.106 g (100%) of the carbazole derivative **12**: mp 82–84° after crystallization from hexane (lit.[5] mp 87–88°); pmr δ 0.8–4.5 (complex multiplets, 13 H), 7.0–7.65 (m, 4 H); mass spectrum molecular ion at m/e 211.

Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 3.11; N, 6.63. Found: C, 84.93; H, 8.25; N, 6.43.

A similar result obtained upon treatment of tosylate with ethylmagnesium iodide in ether solution.

Formolysis of 3-(1,2,3,4-Tetrahydro-9-methylcarbazol-1-yl)-prop-1-yl Tosylate (2).—Tosylate **2** (0.200 g, 0.005 mol), 88% formic acid (10 ml), and benzene (3 ml) were heated under reflux overnight. The cooled reaction mixture was diluted with 10 ml of 10% hydrochloric acid and washed with ether. The aqueous portion was basified with 20% sodium hydroxide solution and extracted with ether to give 0.090 g of a yellow oil which was subjected to preparative tlc on silica gel with benzene. The compounds were observed; the major product, with an intermediate R_f, was collected (0.046 g, 41%) as a colorless oil which quickly changed to cherry red on exposure to air; ir $\bar{\nu}_{max}$ 1670, 1600 cm^{-1}; pmr δ 0.8–3.4 (comlex multiplets, 11 H), 2.92 (s, 3 H), 4.75 (t, J = 5 Hz, 1 H), 6.3–7.30 (m, 4 H); uv λ_{max} 248 nm (ϵ 60,200), 287 (2350); mass spectrum molecular ion m/e 225.

A sample of the product **13** (0.217 g, 0.964 mmol) obtained as just described was hydrogenated in ethanol (100 ml) over 10% palladium on carbon at atmospheric pressure. After hydrogen uptake ceased, the catalyst was filtered and the solvent was evaporated to yield 0.195 g of oil which was crystallized from ethanol to give pure **14**: mp 27–29°; ir $\bar{\nu}_{max}$ 1600 cm^{-1}; pmr δ 1.15–2.5 (complex multiplets, 13 H), 2.68 (s, 3 H), 3.0 (t, J = 2.5 Hz, 1 H), 6.4–7.3 (m, 4 H); uv λ_{max} 255 nm (ϵ 7700), 262 (8880), 267 (7100); mass spectrum molecular ion at m/e 227.

Anal. Calcd for $C_{16}H_{19}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.76; H, 9.21; N, 6.12.

The methiodide of **14**, mp 203–204° dec, from ethanol, was obtained by treating **14** with methyl iodide in benzene solution.

Anal. Calcd for $C_{17}H_{24}NI$: C, 55.28; H, 6.50; N, 3.80; I, 34.42. Found: C, 54.97; H, 6.68; N, 3.54; I, 34.46.

Perhydro-4-indanone.—Commercially available 4-indanol (20 g, 0.149 mol) in ethanol (200 ml) was hydrogenated over 5% Rh/C (1.5 g) at 60 psi for 15 hr. The catalyst was filtered and the solvent was evaporated to give 19.5 g of crude perhydro-4-indanol: pmr (CCl_4) δ 1.8–2.4 (complex multiplets, 14 H), 3.3–4.2 (m, 2 H).

The crude perhydro-4-indanol (19.5 g) was dissolved in acetone (200 ml) and stirred with 8 *N* chromic acid (50 ml) for 1 hr at 0°. The usual isolation and distillation afforded 14.0 g (68% based on 4-indanol) of perhydro-4-indanone, bp 100–104° (12 mm), ir $\nu_{max}^{CCl_4}$ 1710 cm^{-1}.

7*H*-2,3,3a,4,5,6,6a-Octahydrocyclopenta[*d*]carbazole (14).—A solution of perhydro-4-indanone (1.38 g, 0.01 mol) and α-methylphenylhydrazine (1.22 g, 0.01 mol) was heated at 120–125° for 2 hr. The crude phenylhydrazone was dissolved in acetic acid (3.0 g) and heated at 90° for 2 hr. The reaction mixture was diluted with water and washed with ether. The aqueous phase was then basified and extracted with ether to give 1.15 g (51%) of crude **13** as a red oil. The spectral properties of this material were virtually identical with those obtained from the solvolysis of **2**. The crude material was hydrogenated over Pd/C as previously described. The hydrogenation product was purified by preparative tlc on silica gel using benzene as eluent. The major product (0.596 g, 53%) was identical with the sample previously obtained.

Solvolysis of 3-(1,2,3,4-Tetrahydro-9-methylcarbazol-1-yl)propyl Tosylate-*1,1-d*$_2$.—Two samples of deuterated tosylate were solvolyzed in benzene–formic acid as previously described. In one experiment the crude product was hydrogenated over 10% Pd/C and separated by preparative tlc (silica gel–benzene). In the other experiment, the crude product was reduced with excess sodium borohydride in ethanol. The deuterated products were obtained in 40 and 65% yields, respectively, from the two experiments. The distributions of labeled material were computed from the 70 eV mass spectra. Under these conditions, the m − 1 peak for the parent compound was 9% of the parent peak. The calculations were carried out as described by Biemann.[10]

Registry No.—**1**, 32251-92-6; **2**, 32251-93-7; **7**, 32251-94-8; **8**, 32251-95-9; **9**, 32251-96-0; **10**, 32251-97-1; **11**, 32251-98-2; **12**, 32251-99-3; **13**, 32252-00-9; **14** methiodide, 32252-01-0; echitamine, 23106-72-1.

(10) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, p 204.

Reduction of 6β-Methoxy-3α,5-cyclo-5α Steroids with Mixed Hydrides

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The reduction of 6β-methoxy-3α,5-cyclo-5α steroids with lithium aluminum hydride–aluminum chloride mixtures gives 3α,5-cyclo-5α steroids as the major product. The mechanism of the reaction is discussed. The reduction of cholesteryl tosylate with lithium aluminum hydride and mixed lithium aluminum hydride–aluminum chloride is also considered.

In the past few years considerable attention has been paid to the use of lithium aluminum hydride–aluminum chloride[1] as a reagent capable of reducing a large number of functions insensitive to lithium aluminum hydride; a well-known example is the reduction with mixed hydride of allylic and benzylic alcohols.[2]

In view of the unique electronic structure and the unusual properties of the cyclopropane ring, we decided to investigate the reactivity of several cyclopropylcarbinyl derivatives toward lithium aluminum hydride–aluminum chloride.

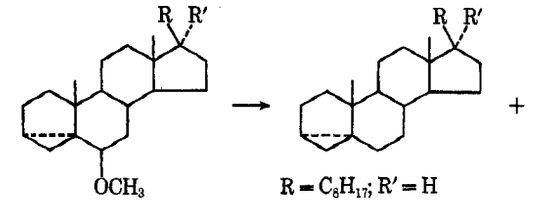
Preliminary work on 3α,5-cyclo-5α-cholestan-6β-ol showed that the reduction with mixed hydride gave 3α,5-cyclo-5α-cholestane, with a yield of 71%. This result seemed to support the similar behavior of the allylic alcohols and the 6β-hydroxy-3α,5-cyclo-5α

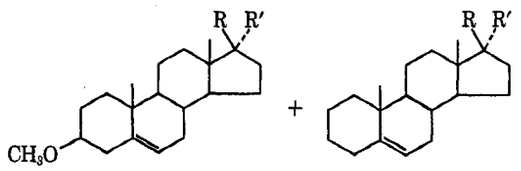
(1) E. L. Eliel, *Rec. Chem. Progr.*, **22** (3), 129 (1961); M. N. Rerick in Augustine's "Reduction," Vol. 2, Marcel Dekker, New York, N. Y., 1968.

(2) J. Broome, B. R. Brown, A. Roberts, and A. M. S. Whithe, *J. Chem. Soc.*, 1406 (1960); R. F. Nystrom and C. R. A. Berger, *J. Amer. Chem. Soc.*, **80**, 2896 (1958).

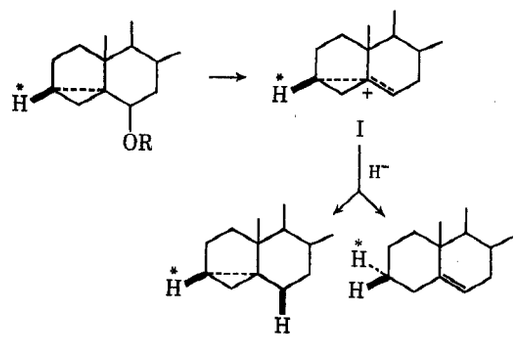
steroids with respect to the reduction with mixed hydride, and encouraged us to extend the investigation to other 3α,5-cyclo-5α steroids, containing a methoxyl group on C-6.

The formation of 3α,5-cyclo-5α steroids with yields ranging from 70 to 75% was observed in the androstane and pregnane series, as illustrated in the following scheme.





The most likely mechanism for this process seems to involve an intermediate mesomeric carbonium ion, usually represented by the nonclassical structure I, the intervention of which would account for the formation of both the 3α,5-cyclo-5α steroids and Δ⁵ steroids.



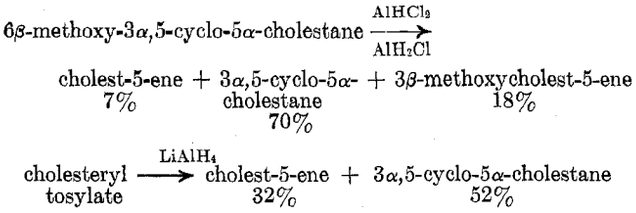
The formation of I was also suggested by Corey,[3] in order to account for the formation of 3α,5-cyclo-5α steroids and Δ⁵ steroids in the reduction of the tosylates of 3β-hydroxy-Δ⁵ steroids with $LiAlH_4$. Using ir spectroscopy, Corey observed the formation of 3β-deuteriocholest-5-ene and 6β-deuterio-3α,5-cyclo-5α-cholestane from the reduction of cholesteryl tosylate with lithium aluminum deuteride.

However, the ratio of the yields of 3α,5-cyclo-5α-cholestane and cholest-5-ene from the reduction of 6β-methoxy-3α,5-cyclo-5α-cholestane with mixed hydrides is considerably different, showing a noticeable discrepancy between two reactions which should involve the same intermediate (Scheme I).

The formation of 3β-methoxycholest-5-ene cannot clearly justify the large differences encountered using the two reagents. In our opinion, the most likely

(3) E. J. Corey, M. G. Howell, A. Boston, R. L. Young, and R. A. Sneen, *J. Amer. Chem. Soc.*, **78**, 5036 (1956).

Scheme I

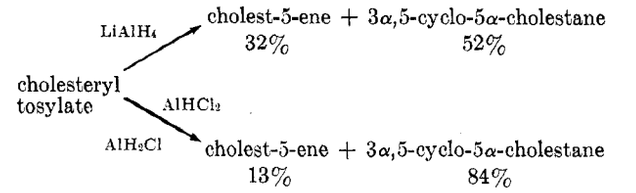


hypothesis is based on the assumption that the reaction of tosylate with $LiAlH_4$ does not involve exclusively the formation of the mesomeric ion I (the precursor of both cholest-5-ene and 3α,5-cyclo-5α-cholestane), but also a normal reduction of the tosylate, which leads exclusively to cholest-5-ene. Such a hypothesis would easily explain the observed increase in the yield of 3α,5-cyclo-5α-cholestane in the reduction of 6β-methoxy-3α,5-cyclo-5α-cholestane with the mixed hydrides.

This hypothesis does not agree with the observation of Corey, that in the reduction of cholesteryl tosylate with lithium aluminum deuteride the isolated cholest-5-ene contained only one 3β-deuterio atom. According to our hypothesis, the product must be a mixture of 3β-deuteriocholest-5-ene and 3α-deuteriocholest-5-ene; the former derives from the hybrid ion, while the normal reduction of the tosylate, in agreement with the usual steric course of such reductions, must lead to an inverted configuration, with the formation of 3α-deuteriocholest-5-ene.

Eliel[4] stated that β-phenylethyl tosylate is not easily reduced by the mixed reagent, which probably involves a normal reduction mechanism. We therefore studied the reductions of cholesteryl tosylate with lithium aluminum hydride–aluminum chloride. The results are given in Scheme II. It should be noted

Scheme II



that in Scheme II the product ratio for $AlHCl_2 \cdot AlH_2Cl$ reduction is very similar to that found with 6β-methoxy-3α,5-cyclo-5α-cholestane (first scheme) assuming that only two compounds are formed in this case.

These results agree with our hypothesis that, in the reduction of cholesteryl tosylate with $LiAlH_4$, the cholest-5-ene must be formed from both the mesomeric ion and a normal reduction mechanism of the tosylates.

To confirm this we prepared the 3α-deuteriocholestane and the 3β-deuteriocholestane following the method of Corey[3] and then studied their ir spectra and those of mixtures of various composition. This preliminary survey showed that mixtures of the two compounds may be distinguished by studying the relative intensity of the two bands in the region between 2190 and 2110 cm^{-1}.

(4) E. L. Eliel, personal communication.

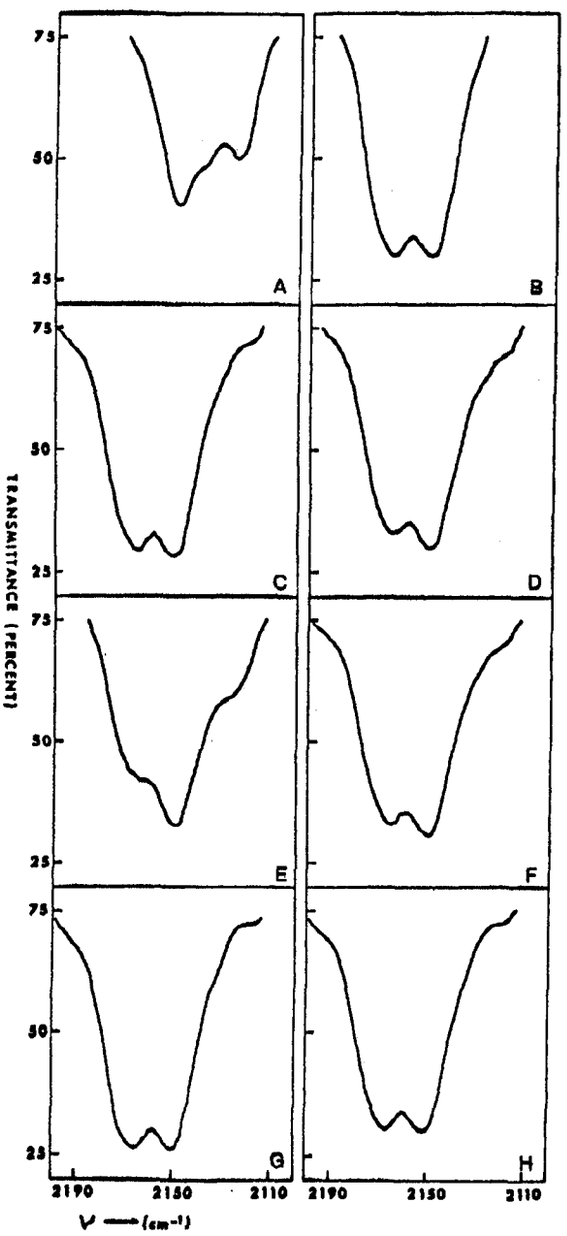


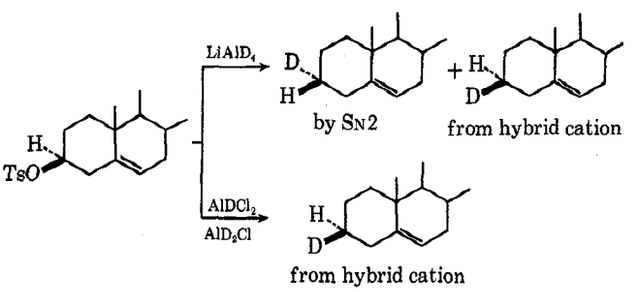
Figure 1.—C–D stretching bands of cholestanes-3-*d*, CCl_4 solution (10%) at 25°: A, cholestane-3α-*d*; B, cholestane-3β-*d*; C, 10% 3α, 90% 3β; D, 20% 3α, 80% 3β; E, 50% 3α, 50% 3β; F, G, H, cholestanes-3-*d* obtained by catalytic hydrogenation of Δ⁵-cholestanes-3-*d* (synthesized from F, cholesteryl tosylate–$LiAlD_4$; G, 6β-methoxy-3α,5-cyclocholestane–$LiAlD_4$ and $AlCl_3$; H, cholesteryl tosylate–$LiAlD_4$ and $AlCl_3$).

Lithium aluminum deuteride–aluminum chloride reduction of 6β-methoxy-3α,5-cyclo-5α-cholestane gave 6β-deuterio-3α,5-cyclo-5α-cholestane, together with 3-deuteriocholest-5-ene which, when catalytically hydrogenated,[3] gave a deuteriocholestane (see Figure 1, spectrum G) which proved to correspond to the 3β-deuterio derivative.

Cholesteryl tosylate was then treated with lithium aluminum deuteride;[3] cholest-5-ene, deuterated at C-3, was isolated and catalytically hydrogenated to form the C-3 deuterated cholestane. We followed a similar scheme using lithium aluminum deuteride–aluminum chloride.

The ir spectra in the previously observed region (see Figure 1, spectra F, H) suggest that reduction of cholesteryl tosylate with lithium aluminum deuteride gives a mixture of 3α- and 3β-deuteriocholest-5-ene, while in the case of lithium aluminum deuteride–aluminum chloride only 3β-deuteriocholest-5-ene is formed.

These results confirm our hypothesis of the mechanism of the reduction.



Experimental Section

Melting points were taken on a Culatti capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 521 infrared spectrophotometer; all measurements were made in carbon tetrachloride. Optical rotations were measured with a Schmidt Haensch polarimeter and were obtained on 1% solutions in a 1-dm cell. Vpc analyses were taken on a Perkin-Elmer F 20 gas chromatograph. Analyses of the reaction mixture were made by vpc using a 6-ft column packed with nitrile silicone gum X E 60 on Anacrom "As" 90–100 mesh; separation conditions: column temperature 200°, injection port temperature 200–250°; N_2 flow rate 40 cc/min. Woelm alumina was used for column chromatography.

General Procedure for Mixed Hydride Reductions.—The mixed hydride reagents were prepared by slowly adding measured amounts of an ethereal solution of $AlCl_3$ to a stirred solution of known amounts of $LiAlH_4$ in dry diethyl ether. A solution of the steroid compound in diethyl ether was added dropwise to this reagent. The resulting mixture was allowed to stand and then carefully hydrolyzed with a small amount of water.

The ethereal solutions were separated by filtration and the solid residues were washed with ether. The ethereal solution was washed with water, dried, and evaporated.

Reduction of 6β-Methoxy-3α,5-cyclo-5α-cholestane.—To 0.54 g of $LiAlH_4$ in 20 ml of ether was added 1.9 g of $AlCl_3$ in 20 ml of ether, at room temperature. 6β-Methoxy-3α,5-cyclo-5α-cholestane (2.7 g) in 20 ml of ether was added.

The reaction was carried out as described above. The resulting residue (2.6 g) was chromatographed on a column packed with 78 g of basic alumina (Brockmann I). The eluents used were 60 ml of hexane and 210 ml of benzene, and 30-ml fractions were collected. Fractions 1 and 2 gave 2.1 g of a mixture of 3α,5-cyclo-5α-cholestane (90.5%) and cholest-5-ene (9.5%) (analyzed by vpc); fractions 5–9 gave 0.49 g of a solid which was recrystallized from acetone, mp 82°, $[\alpha]D$ −42° ($CHCl_3$), and was identified as 3β-methoxycholest-5-ene [lit.[5] mp 82–83°, $[\alpha]D$ −45.6° ($CHCl_3$)].

The mixture (2.1 g) of 3α,5-cyclo-5α-cholestane and cholest-5-ene was chromatographed on a column packed with 250 g of basic alumina (Brockmann I). The eluent used was petroleum ether (bp 30–50°). The first fractions gave 3α,5-cyclo-5α-cholestane, mp 76–78° from ether–ethanol mixture, $[\alpha]D$ +78° ($CHCl_3$) [lit.[6] mp 77–78°, $[\alpha]D$ +80° ($CHCl_3$)]; the later fractions gave cholest-5-ene, mp 90–91° (from acetone), $[\alpha]D$ −50° ($CHCl_3$) [lit.[7] mp 92–93°, $[\alpha]D$ −53° ($CHCl_3$)]. $LiAlD_4$–$AlCl_3$ was used to prepare the 3-deuteriocholestene following the previously described scheme.

Reduction of 6β-Hydroxy-3α,5-cyclo-5α-cholestane.—To 0.20 g of $LiAlH_4$ in 10 ml of ether was added 0.70 g of $AlCl_3$ in 10 ml of ether, at room temperature. 6β-Hydroxy-3α,5-cyclo-5α-cholestane (0.68 g) in 10 ml of ether was added.

(5) A. Romeo and R. Villotti, *Ann. Chim. (Rome)*, **47**, 618 (1957).
(6) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 3361 (1952).
(7) R. E. Ireland, T. I. Wrigley, and W. G. Young, *J. Amer. Chem. Soc.* **80**, 4604 (1958).

The reaction was carried out as described before. The resulting residue (0.660 g) was chromatographed on a column packed with 66 g of basic alumina (Brockmann II).

The eluent used was 225 ml of petroleum ether, and 25-ml fractions were collected. Fractions 1–5 gave 0.54 g of a mixture of 3α,5-cyclo-5α-cholestane (88.5%) and cholest-5-ene (11.5%) (analyzed by vpc).

The mixture (0.53 g) of 3α,5-cyclo-5α-cholestane and cholest-5-ene was chromatographed as described previously (reduction of 6β-methoxy-3α,5-cyclo-5α-cholestane) to give 3α,5-cyclo-5α-cholestane and cholest-5-ene.

Reduction of 6β-Methoxy-3α,5-cyclo-5α-androstan-17-one.—The reaction was carried out as described for 6β-methoxy-3α,5-cyclo-5α-cholestane, using 1.14 g of $LiAlH_4$, 4 g of $AlCl_3$, and 3.04 g of 6β-methoxy-3α,5-cyclo-5α-androstan-17-one.

The resulting residue (2.84 g) was chromatographed on a column packed with 85 g of alumina (Brockmann III). The eluents used were 420 ml of petroleum ether–benzene (1:1), 180 ml of benzene, and 90 ml of ether; 30-ml fractions were collected. After crystallization (from methanol–water mixture), fractions 1–15 gave 2.0 g of 17β-hydroxy-3α,5-cyclo-5α-androstan, mp 120–121°, $[\alpha]_D$ +76° ($CHCl_3$) [lit.[8] mp 122–124°, $[\alpha]_D$ +77° ($CHCl_3$)]; fractions 20–23 gave 0.3 g of 3β-methoxy-17β-hydroxyandrostan-5-ene, mp 139–141°, $[\alpha]_D$ −53° (ethanol 95%) [lit.[9] mp 142.5–143°, $[\alpha]_D$ −51° (ethanol 95%)].

Reduction of 6β-Methoxy-3α,5-cyclo-5α-pregnan-20-one.—The reaction was carried out as described for 6β-methoxy-3α,5-cyclo-5α-cholestane using 1.14 g of $LiAlH_4$, 4 g of $AlCl_3$, and 3.4 g of 6β-methoxy-3α,5-cyclopregnan-20-one. The resulting residue (3.11 g), containing a mixture of epimeric 20-ols, was oxidized in acetic acid (46 ml) by chromium trioxide (0.92 g) in water (5 ml). After 12 hr ice was added and the mixture was made alkaline with ammonia, the precipitated product was extracted with ether, and the ethereal solution was washed with water, dried, and evaporated. The resulting residue (3.06 g) was chromatographed on a column packed with 95 g of alumina (Brockmann III). The eluents used were 600 ml of petroleum ether and 300 ml of benzene; 100-ml fractions were collected. Fractions 1–6 gave after crystallization (from methanol) 2.19 g of 3α,5-cyclo-5α-pregnan-20-one, mp 107–109°, $[\alpha]_D$ +173° ($CHCl_3$) [lit.[8] mp 109–111°, $[\alpha]_D$ +179° ($CHCl_3$)].

Reduction of 3β-Tosyloxycholest-5-ene.—To 0.35 g of $LiAlH_4$ in 16 ml of ether was added 1.25 g of $AlCl_3$ in 16 ml of ether, at room temperature. 3β-Tosyloxycholest-5-ene (4 g) in 20 ml of benzene was added.

The reaction was carried out as described before. The resulting residue (2.9 g) was chromatographed on a column packed with 580 g of basic alumina (Brockmann II). The eluent used was 350 ml of petroleum ether, 50-ml fractions being collected. Fractions 1–5 gave 2.7 g of a mixture of 3α,5-cyclo-5α-cholestane (86%) and cholest-5-ene (14%) (analyzed by vpc).

The mixture (2.7 g) of 3α,5-cyclo-5α-cholestane and cholest-5-ene was chromatographed as described previously (reduction of 6β-methoxy-3α,5-cyclo-5α-cholestane) to give 3α,5-cyclo-5α-cholestane and cholest-5-ene.

$LiAlD_4$–$AlCl_3$ was used to isolate the 3-deuteriocholest-5-ene following the preparation scheme previously described.

Registry No.—6β-Methoxy-3α,5-cyclo-5α-cholestane, 2867-93-8; 6β-hydroxy-3α,5-cyclo-5α-cholestane, 465-54-3; 6β-methoxy-3α,5-cyclo-5α-androstan-17-one, 14425-92-4; 6β-methoxy-3α,5-cyclo-5α-pregnan-20-one, 32249-55-1; 3β-tosyloxycholest-5-ene, 1182-65-6; lithium aluminum hydride, 16853-85-3; aluminum chloride, 7446-70-0.

(8) A. Kasal, V. Cerny, and F. F. Sorm, *Collect. Czech. Chem. Commun.*, **30** (2), 472 (1965).

(9) M. N. Huffmann and J. W. Sadler, *J. Org. Chem.*, **18**, 919 (1953).

The Structure of Lycorenine and the 7-Hydroxy Alkaloids Derived from the [2]Benzopyrano[3,4-*g*]indole Nucleus[1]

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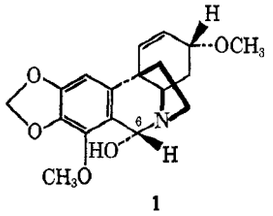
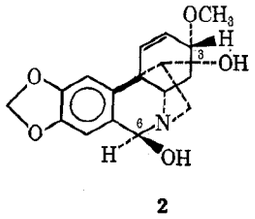
Received June 25, 1971

An X-ray crystallographic study of lycorenine methiodide has established the configuration of the C_7 hydroxyl group in the alkaloid to be that shown in **3**. A comparison of specific and molecular rotations of analogous alkaloids and their 7-oxo derivatives indicates that all alkaloids with the general structure **4** have an α-C_7 hydroxyl group. These data provide complete structures for oduline, nerinine, krigeine, unsevine, and krigenamine.

Amaryllidaceae alkaloids containing a benzylic hydroxyl group (as in **1**, **2**, and **4**) provide a number of

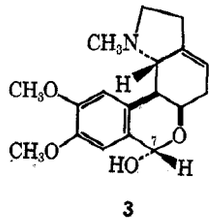


1



2

reactive compounds of chemical, biosynthetic, and spectroscopic interest.[2] Although the structures for many of these bases frequently have been assigned to the extent of the absolute configuration, the configuration of the benzylic hydroxyl group has been ignored in most representations. The structures of 6-hydroxybuphanidrine (**1**)[3] and 6-hydroxycrinamine (**2**)[4] have been determined by X-ray crystallographic techniques. No chemical methods exist for the assignment of con-



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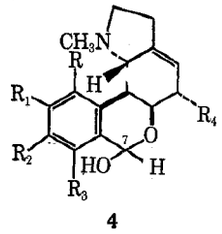

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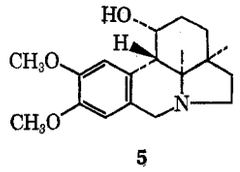

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(2) For a summary of the chemistry of these alkaloids see W. C. Wildman, *Alkaloids*, **11**, 307 (1968).

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(4) J. Karle, J. A. Estlin, and I. L. Karle, *ibid.*, **89**, 6510 (1967).