Anal. Calcd for $C_{22}H_{30}N_2O_2$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.23; H, 8.36; N, 8.07.

3-Oxo-17β-acetamidoandrost-4-ene-18-nitrile (19.)—A solution of 0.5 g of **18** in 2.0 ml of pyridine was cooled in an ice bath and 1 ml of cold phosphorus oxychloride was added dropwise, while maintaining the temperature below 15°. After 3 hr, the mixture was poured into cold dilute HCl. This solution was extracted with methylene chloride and the combined extracts were washed with water and dried (Na_2SO_4). When the gummy residue from evaporation of the dried solvent was chromatographed on alumina, 0.20 g of 3,20-dioxopregn-4-ene-18-nitrile was recovered together with 0.06 g of **19**: mp 294–296°; $[\alpha]^{20}D$ +15° (*c* 1, $CHCl_3$); ν_{max}^{KBr} 3340, 2225, 1685, 1663, 1610, 1535 cm^{-1}; nmr 74 (19-H_3), 123 (CH_3CO–), 257 (17α-H, two broad peaks), 368 Hz (17β-NH, two broad peaks).

Anal. Calcd for $C_{21}H_{28}N_2O_2$: C, 74.08; H, 8.29; N, 8.23. Found: C, 73.84; H, 8.09; N, 8.45.

17β-Aminoandrost-4-en-3-one-18-nitrile Hydrochloride (20).—To a solution of 0.27 g of **18** in 2 ml of ethanol and a small amount of tetrahydrofuran, there was added 2 ml of concentrated HCl. The solution was refluxed for 24 hr and poured into ice–water. The precipitate which formed (0.1 g) was filtered and shown to be starting material. The filtrate was evaporated to dryness under vacuum giving 0.15 g of almost pure **20**. Recrystallization from methylene chloride gave a hygroscopic sample: mp 240°; $[\alpha]^{20}D$ +90° (*c* 0.082, $CHCl_3$).

Anal. Calcd for $C_{19}H_{29}N_2OCl$: N, 8.37; Found: N, 8.60.

Androst-4,16-dien-3-one-18-nitrile (21) and 17α-Hydroxyandrost-4-en-3-one-18-nitrile (22).—To a stirred, ice-cold solution of 0.15 g of **20** in 2 ml of 50% acetic acid, there was added, dropwise, a solution of 0.5 g of $NaNO_2$ in 2 ml of 50% acetic acid. After 18 hr at 27° the solution was made alkaline and extracted with ether. The ethereal extract was mixed with 2 ml of 5% methanolic KOH solution and stirred for 0–5 hr. After addition of water and back extraction with ether, the combined ethereal extracts were evaporated to dryness giving solid material. Purification by preparative tlc resulted in two products. The major product (0.04 g) was shown to be **21**: mp 128–130° after recrystallization from hexane–benzene; $[\alpha]^{20}D$ +224° (*c* 0.19, $CHCl_3$).

Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 80.82; H, 8.16; N, 5.19.

The minor product (25 mg) was **22** as indicated by the doublet of the 17β proton. Recrystallization from hexane–benzene gave the analytical sample: mp 183–185°.

Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42; N, 4.68. Found: C, 76.33; H, 7.67; N, 5.89.

3,20-Bismethylenedioxypregn-5-ene-18-nitrile (23).—3,20-Dioxopregn-4-ene-18-nitrile[16] (0.80 g) was dissolved in 15 ml of hot ethylene glycol. The solution was acidified with 0.10 g of *p*-toluenesulfonic acid and very slowly distilled at 1.5 mm at 70° for 3 hr. The resulting suspension was made alkaline with a small amount of methanolic KOH and poured into an excess of ice-water. Recrystallization of the preciptated product from methylene chloride–hexane gave the analytical sample: mp 195–197°; $[\alpha]^{20}D$ −32° (*c* 1, $CHCl_3$); nmr 64 (19-H_3), 79 (21-H_3), 235 (20-ketal-H_4, slightly broad), 241 Hz (3-ketal-H_4).

Anal. Calcd for $C_{25}H_{35}NO_4$: C, 72.61; H, 8.53; N, 3.39. Found: C, 72.86; H, 8.26; N, 3.68.

Registry No.—**1**, 14418-17-8; 20α-hydroxy-5α-pregnane nitrite, 16797-50-5; **4**, 16778-28-2; **5**, 16778-29-3; **7**, 16778-30-6; **8**, 16778-31-7; **9**, 13583-64-7; **10**, 13583-63-6; **11**, 16778-34-0; **12**, 16797-45-8; **13**, 16797-46-9; **14**, 16797-49-2; **15**, 16777-99-4; **16**, 16778-00-0; **17**, 16778-01-1; **18**, 16778-02-2; **19**, 16778-03-3; **20**, 16778-04-4; **21**, 16797-47-0; **22**, 16778-05-5; **23**, 16778-06-6.

The Action of Bromine on a Chol-7-enic Acid Derivative

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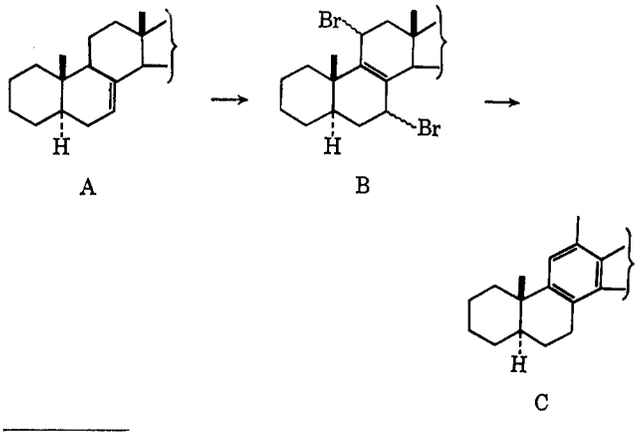
The behavior of a ring A/B *cis*-fused steroid unsaturated at C-7 toward bromine differs from that of the corresponding unsaturated ring A/B *trans*-fused steroids. On treatment with bromine, methyl 3α-ethoxycarbonyloxychol-7-enate yields methyl 14ξ-bromo-3α-ethoxycarbonyloxychol-7-enate. This allylic halide on dehydrobromination with silver acetate or alumina gives methyl 3α-ethoxycarbonyloxychola-7,14-dienate, and on debromination with zinc gives a mixture of methyl 3α-ethoxycarbonyloxychol-7-enate and methyl 3α-ethoxycarbonyloxychol-8-enate.

It has been shown[1] that bromine reacts with Δ^7-unsaturated steroids having rings A/B *trans*-fused (general part structure A) to yield, as major products, the 7,11-dibromo-Δ^8-unsaturated derivatives (part structure B) which are readily transformed into ring C benzenoid steroids (part structure C).[2,3] To ascertain if this route is feasible for the preparation of ring C benzenoid steroids in which rings A/B are *cis*-fused, we have examined the action of bromine on a Δ^7-unsaturated steroid derived from cholic acid.



A B C

Methyl cholate was selectively and quantitatively converted into the 3-ethoxycarbonyl derivative (**1**)[4] which was then dehydrated by the action of phosphorus oxychloride in pyridine to yield the known $\Delta^{7,11}$-diene (**2**)[5,6] (Scheme I). It has been reported[6] that the diene (**2**) undergoes selective hydrogenation of the Δ^{11}-ethylenic bond with platinum catalyst in acetic acid solution to yield the desired ester, methyl 3α-ethoxycarbonyloxychol-7-enate (**4**). In our hands, however, these condi-

(1) C. F. Hammer and R. Stevenson, *Steroids*, **5**, 637 (1965).

(2) C. F. Hammer, D. S. Savage, J. B. Thomson, and R. Stevenson, *Tetrahedron*, **20**, 929 (1964).

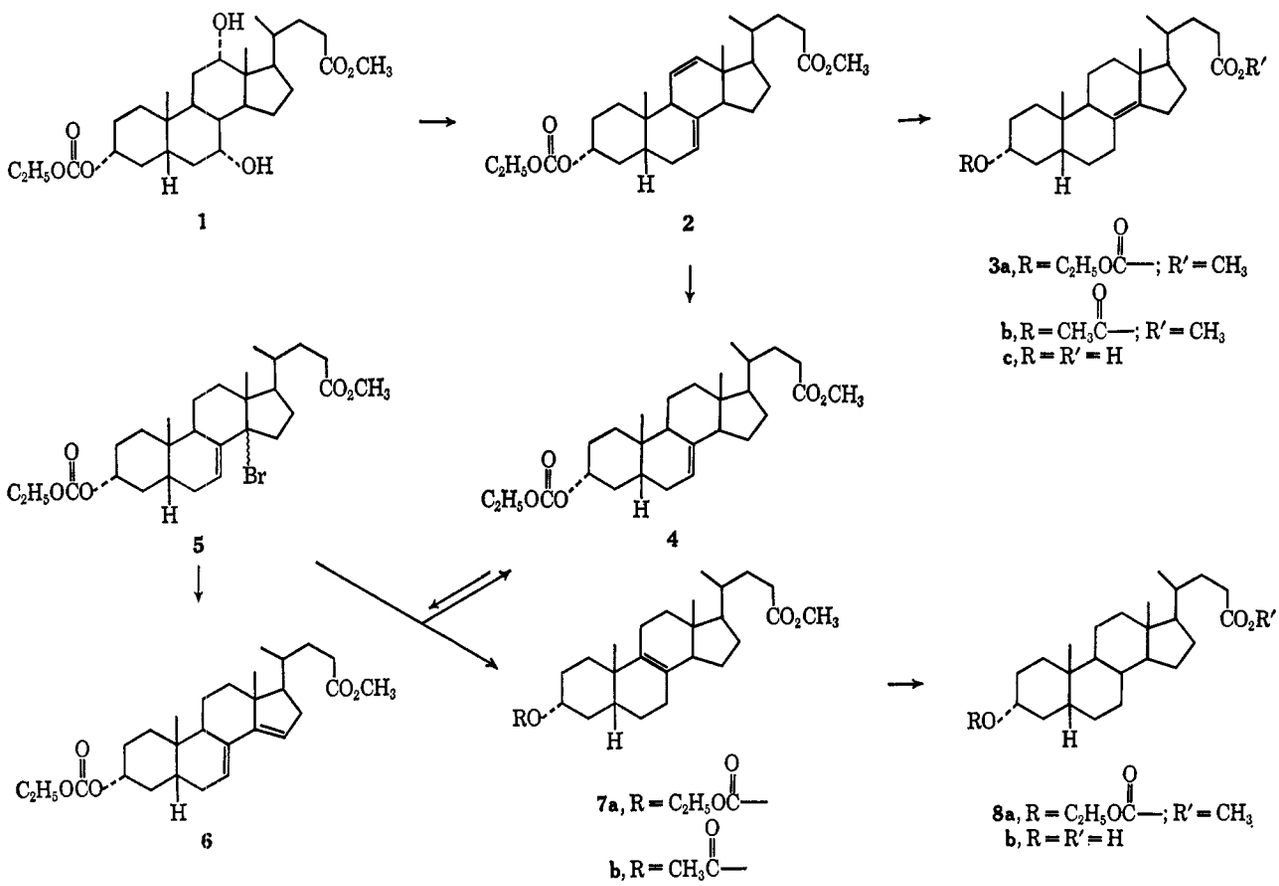
(3) T. N. Margulis, C. F. Hammer, and R. Stevenson, *J. Chem. Soc.*, 4396 (1964).

(4) L. F. Fieser and S. Rajagopalan, *J. Amer. Chem. Soc.*, **71**, 3935 (1949).

(5) K. Yamasaki and I. Ushizawa, *Proc. Jap. Acad.*, **28**, 546 (1952).

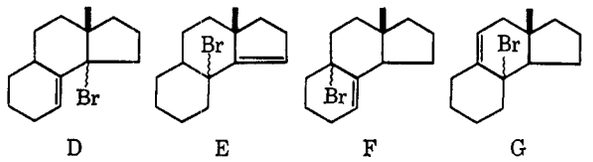
(6) F. Nakada, *Steroids*, **2**, 45 (1963).

SCHEME I



tions resulted in isolation of the $\Delta^{8(14)}$ isomer (**3a**).[7] In contrast, when the reduction was performed in ethyl acetate solution with palladium–carbon catalyst, the Δ^7 isomer (**4**) was readily obtained. (See Scheme I.)

Treatment of this methyl chol-7-enate derivative (**4**) with bromine, using the procedures developed for ergostene and cholestene analogs,[1,8] yielded a rather unstable product (solutions in the common solvents rapidly darkened) which gave a positive Beilstein test and a positive unsaturation test with tetranitromethane. Elemental analysis indicated an empirical formula $C_{28}H_{43}BrO_5$, which is in marked contrast to the behavior of Δ^7-A/B *trans* systems, in which two bromine atoms are introduced into the ring system. The similarity of the ultraviolet spectrum (λ 254 mμ, ϵ 6900) to that reported[1] for 7,8,22,23-tetrabromoergost-14-en-3β-yl acetate (λ 253 mμ, ϵ 7600) suggested that the halogen atom was situated in an allylic position. This conclusion, coupled with evidence from the integrated nmr spectrum that the bromination product had *one* vinyl proton, led us to regard one of the compounds represented by part structure (D, E, F, G) as most probable.



D E F G

A distinction among these was sought by identification of the products of dehydrobromination and of debromination.

The allyl bromide underwent dehydrobromination on treatment with silver acetate to yield a product whose ultraviolet spectrum (λ 248 mμ, ϵ 11,500) indicated the presence of a cisoid heteroannular diene chromophore and which was accordingly formulated as methyl 3α-ethoxycarbonyloxychola-7,14-dienate (**6**). Evidence in support of this structure was obtained by catalytic hydrogenation to yield the known methyl 3α-ethoxycarbonyloxychol-8(14)-enate (**3a**), further characterized by hydrolysis to 3α-hydroxychol-8(14)-enic acid (**3c**). The diene (**6**) could also be simply obtained by filtration of the allyl bromide through chromatographic alumina. The identification of the dehydrobromination product (**3a**) established that no molecular rearrangement had occurred during the bromination or dehydrobromination steps, and also rendered part structures F and G unlikely representations of the allyl bromide.

Debromination of the allyl bromide in acetic acid by zinc dust yielded a sharp-melting product, $C_{28}H_{44}O_5$. The complexity of the nmr spectrum, particularly in the methyl group resonance region, indicated however that the product was a mixture. Catalytic hydrogenation of the mixture in a solution of acetic acid and hydrochloric acid, conditions devised to isomerize Δ^7, Δ^8, and $\Delta^{8(14)}$ double bonds to the Δ^{14} position where reduction is known to occur,[9] yielded methyl 3α-ethoxycarbonyloxycholanate (**8a**), characterized by hydrolysis to cholanic acid (**8b**). This finding suggested that the debromination mixture consisted of ethoxycarbonyloxy esters of isomeric methyl cholenates. Since the inte-

(7) F. Nakada, *Steroids.*, **2**, 403 (1963).

(8) R. C. Anderson, R. Stevenson, and F. S. Spring, *J. Chem. Soc.*, 2901 (1952).

(9) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, pp 425–427.

grated nmr spectrum of the debromination product revealed only a fraction of one vinyl proton, this could best be interpreted as the mixture being constituted of two alkenes, one of which had a trisubstituted and the other a tetrasubstituted double bond. A mixture of Δ^7 or Δ^{14} and Δ^8 or $\Delta^{8(14)}$ isomers would most reasonably satisfy this requirement. The expected C-18 and C-19 methyl group resonances of these four isomers (Δ^7, Δ^8, $\Delta^{8(14)}$, and Δ^{14}) were calculated using the characteristic substituent frequency shift data compiled by Zürcher[10] and are tabulated as τ values (Table I). Since the

TABLE I

	RESONANCE, τ			
	Δ^7	Δ^8	$\Delta^{8(14)}$	Δ^{14}
C-18	9.47	9.43	9.17	9.10
C-19	9.07	8.93	9.17	9.05

methyl group region of the nmr spectrum of the debromination product had signals at τ 9.46, 9.37, 9.13 and 8.97, this implied that the mixture consisted of the Δ^7 and Δ^8 isomers and, from the intensities, in a ratio of approximately 1:2, respectively. This was firmly established by crystallization of a mixture of authentic methyl 3α-ethoxycarbonyloxychol-7-enate (**4**) and methyl 3α-ethoxycarbonyloxychol-8-enate (**7a**) in a ratio of 1:2 to give the sharp melting product, identical with that obtained by zinc debromination of the allylic bromide which is consequently formulated as methyl 14-bromo-3α-ethoxycarbonyloxychol-7-enate (**5**).

The failure of the chol-7-enic acid derivative to yield on bromination the corresponding 7,11-dibromochol-8-enic acid, the precursor necessary for aromatization of ring C led us to seek successfully alternative pathways to achieve this objective.[11] Further interest in the development of routes to ring C aromatic steroids, related particularly to steroid hormones, is evident in two recent communications,[12,13] in both of which the ring C aromatic hormone analog products lack asymmetry at C-5 and hence complement the series.

Experimental Section

Melting points were determined using a Gallenkamp melting point apparatus. Rotations were measured in chloroform solution and ultraviolet absorption spectra in ethanol solution unless otherwise stated. Nuclear magnetic resonance spectra were determined in deuteriochloroform solution with tetramethylsilane as an internal standard, using a Varian 4300 B spectrometer at 60 Mc.

Methyl 3α-Ethoxycarbonyloxy-7α,12α-dihydroxycholanate (**1**).—Ethyl chloroformate (30 ml) was added to a solution of methyl cholate (20 g) in pyridine (50 ml) and the mixture was allowed to stand at room temperature for 1 hr, then worked up in the usual way *via* ether. Crystallization from ether yielded **1** (21.8 g), mp 176–178° (lit.[4,5] mp 176–178°).

Methyl 3α-Ethoxycarbonyloxychola-7,11-dienate (**2**).—Phosphorus oxychloride (53 g) was added to a solution of methyl 3α-ethoxycarbonyloxy-7α,12α-dihydroxycholanate (10 g) in pyridine (80 ml) and the mixture was kept at 50° for 24 hr, then cooled, diluted with ice water (100 ml), and extracted with ether. Evaporation of the washed and dried extract yielded an oil that crystallized from ether–methanol to yield the diene as plates (5.1 g), mp 105–107° (lit.[6] mp 105–108°).

Methyl 3α-Ethoxycarbonyloxychol-8(14)-enate (**3a**).—Platinum dioxide (20 mg) was added to a solution of the diene **2**, (100 mg) in acetic acid (10 ml). The mixture was stirred for 4 hr under a hydrogen atmosphere, filtered, and evaporated under reduced pressure to yield a colorless oil, which crystallized on standing. Recrystallization from methanol gave methyl 3α-ethoxycarbonyloxychol-8(14)-enate as plates (80 mg): mp 113–115°; $[\alpha]_D$ +57° (*c* 1.0) (lit.[7] mp 115–117°; $[\alpha]_D$ +60°).

Methyl 3α-Ethoxycarbonyloxychol-7-enate (**4**).—Palladium-on-carbon catalyst (10%, 1.9 g) was added to a solution of the diene **2** (2.0 g) in ethyl acetate (40 ml). This mixture was stirred for 4 hr under a hydrogen atmosphere, filtered and evaporated. Recrystallization of the solid residue from methanol gave methyl 3α-ethoxycarbonyloxychol-7-enate as plates (1.85 g): mp 135–136°; $[\alpha]_D$ +69° (*c* 1.0) (lit.[6] mp 135–136°; $[\alpha]_D$ +70°).

Methyl 14ξ-Bromo-3α-ethoxycarbonyloxychol-7-enate (**5**).—A solution of bromine (360 mg) in acetic acid (1.1 ml) was added to a solution of methyl 3α-ethoxycarbonyloxychol-7-enate (420 mg) in ether (35 ml) at 0°, the mixture rapidly cooled to −60°, then allowed to regain room temperature over 2 hr with frequent shaking. The resultant crystalline precipitate was collected and washed with cold ether to give **methyl 14ξ-bromo-3α-ethoxycarbonyloxychol-7-enate**: mp 134–135° dec; $[\alpha]_D$ −103° (*c*, 1.1); λ (isooctane) 254 mμ (ϵ 6900). The nmr spectrum gives a multiplet signal at τ 4.93 (vinyl proton) with integrated intensity equivalent to one proton. The compound gives positive tetranitromethane and Beilstein tests. Warming solutions in the common recrystallizing solvents caused rapid decomposition (considerable darkening of solutions after 1–2 hr at room temperature).

Anal. Calcd for $C_{28}H_{43}BrO_5$: C, 62.27; H, 8.03; Br, 14.83. Found: C, 61.97; H, 8.31; Br, 15.01.

Methyl 3α-Ethoxycarbonyloxychola-7,14-dienate (**6**). **A.**—Silver acetate (80 mg) was added to a solution of methyl 14ξ-bromo-3α-ethoxycarbonyloxychol-7-enate (75 mg) in isooctane (20 ml) and the suspension vigorously stirred at room temperature for 20 hr. It was then filtered, the filtrate evaporated to dryness and the residue crystallized from methanol to give **methyl 3α-ethoxycarbonyloxychola-7,14-dienate** as needles (52 mg): mp 97–99°; $[\alpha]_D$ +115° (*c* 0.7); λ 248 mμ (ϵ 11,500). The nmr spectrum gives multiplet signals at τ 4.97 and 4.33, each of integrated intensity equivalent to one proton.

Anal. Calcd for $C_{28}H_{42}O_5$: C, 73.31; H, 9.24. Found: C, 72.95; H, 9.15.

B.—The monobromide (**5**) was chromatographed on alumina (Spence, Type H) and the column eluted with chloroform. Evaporation of the eluate (50 ml) yielded an oil (56 mg) which crystallized from methanol to give the diene (**6**) as needles: mp and mmp 97–99°; $[\alpha]_D$ +111° (*c* 0.6); λ 248 mμ (ϵ 11,700); and infrared spectrum identical with that obtained by method A.

Catalytic Hydrogenation of Methyl 3α-Ethoxycarbonyloxychola-7,14-dienate (**6**).—To a solution of the diene (50 mg) in acetic acid (10 ml) was added platinum dioxide (20 mg), the mixture stirred for 2 hr under a hydrogen atmosphere, filtered, concentrated to small volume (*ca.* 3 ml) and diluted with water. The crystalline precipitate was recrystallized from methanol to give methyl 3α-ethoxycarbonyloxychol-8(14)-enate (**3a**) as needles (35 mg): mp 114–116°; $[\alpha]_D$ +55° (*c* 1.0).

3α-Hydroxychol-8(14)-enic Acid (**3c**).—Methyl 3α-ethoxycarbonyloxychol-8(14)-enate (30 mg) was dissolved in 5% methanolic potassium hydroxide solution (5 ml), left at room temperature overnight, then worked up in the usual way. Crystallization of the product from methanol gave 3α-hydroxychol-8(14)-enic acid (15 mg) as prisms: mp 165–166°; $[\alpha]_D$ +57° (*c* 0.8) (lit.[7] mp 165–166°; $[\alpha]_D$ +54°).

Action of Zinc on Methyl 14ξ-Bromo-3α-ethoxycarbonyloxychol-7-enate.—Zinc dust (500 mg) was added to a solution of the bromo ester (**5**, 100 mg) in acetic acid (30 ml), the mixture stirred at 50° for 3 hr, then cooled, filtered and the filtrate concentrated under reduced pressure (to *ca.* 3 ml). The concentrate was diluted with water, extracted with ether and the extract washed with sodium bicarbonate solution and water. Evaporation of the dried ($MgSO_4$) extract gave a colorless oil which crystallized from methanol to yield a mixed crystal of **methyl 3α-ethoxycarbonyloxychol-7-enate** (**4**) and **methyl 3α-ethoxycarbonyloxychol-8-enate** (**7a**) as needles (70 mg): mp 139–140°;

(10) R. F. Zürcher, *Helv. Chim. Acta*, **44**, 1380 (1961); **46**, 2054 (1963). For the 3α-ethoxycarbonyloxy group, the values 0.5 and 1.5 cps are used for the C-18 and C-19 protons, respectively.

(11) D. Levy and R. Stevenson, *Tetrahedron Lett.*, 3063 (1966).

(12) A. J. Birch and G. S. R. Subba Rao, *ibid.*, 857 (1967).

(13) T. B. Windholz, B. Arison, R. D. Brown, and A. A. Patchett, *ibid.*, 3331 (1967).

$[\alpha]_D$ + 40° (*c* 0.8); ultraviolet end absorption (ε 3650 at 210 mμ).

Anal. Calcd for $C_{28}H_{44}O_5$: C, 72.99; H, 9.63. Found: C, 72.95; H, 9.41.

The nmr spectrum included signals at τ 4.95 (multiplet, less than one proton), 8.97 and 9.13 (singlets, three proton total), 9.37 and 9.45 (singlets, three proton total).

Catalytic Hydrogenation of Methyl Cholenate Mixture (4 + 7a).—The mixture (25 mg) was dissolved in acetic acid (3 ml), concentrated hydrochloric acid (0.3 ml), and platinum dioxide (15 mg) added, and the mixture stirred vigorously for 2 hr under a hydrogen atmosphere. Filtration and dilution with water yielded methyl 3α-ethoxycarbonyloxycholanate (**8a**, 11 mg) as needles, mp 130–137° (lit.[14] mp 120–135°).

Hydrolysis of Methyl 3α-Ethoxycarbonyloxycholanate.—The ester (10 mg) was dissolved in 5% methanolic potassium hydroxide solution (3 ml), left at room temperature overnight, and worked up in the usual way. Crystallization of the product from aqueous methanol gave 3α-hydroxycholanic acid (**8b**) as prisms (6 mg): mp 181–182°; $[\alpha]_D$ +36° (*c* 0.5) (lit.[14] mp 182–183°; $[\alpha]_D$ + 32°).

Catalytic Hydrogenation of Methyl 3α-Acetoxychola-7,9(11)-dienate.—A solution of methyl 3α-acetoxychola-7,9(11)-dienate[15] (100 mg, mp 148–150°) in acetic acid (4 ml) was shaken with platinum dioxide (20 mg) for 1 hr under a hydrogen atmosphere. Filtration, concentration of the filtrate, and dilution with methanol yielded crystals which on recrystallization from methanol gave methyl 3α-acetoxychol-8-enate (**7b**) as plates: mp 143–145°; $[\alpha]_D$ + 55° (*c* 1.0); ultraviolet end absorption (ε 4200 at 210 mμ) (lit.[12] mp 144.5–146°; $[\alpha]_D$ +60°). Water was added to the mother liquor and, after cooling for several hours, methyl 3α-acetoxychol-8(14)-enate (**3b**) was collected as fine needles: mp 79–81°; $[\alpha]_D$ +50° (*c* 1.0); ultraviolet end absorption (ε 5900 at 210 mμ) (lit.[16] mp 81–82°; $[\alpha]_D$ +56°).

Authentic Mixture of 4 and 7a.—Methyl 3α-acetoxychol-8-enate was hydrolyzed with methanolic potassium hydroxide solution and converted into methyl 3α-ethoxycarbonyloxychol-8-enate by successive treatment with diazomethane and ethyl chloroformate in the standard manner. The methyl ester (**7a**) so obtained (10 mg) was mixed with the methyl ester (**4**, 5 mg) and the mixture dissolved in methanol. Concentration yielded the mixed crystals as needles, mp 139–140°, identical with that (**4** + **7a**) obtained by the action of zinc on **5**.

Registry No.—**3a**, 16797-63-0; **4**, 16797-64-1; **5**, 16797-65-2; **6**, 16797-66-3; **7a**, 16797-67-4; **7b**, 16797-68-5; bromine, 7726-95-6; **3b**, 16797-69-6.

Acknowledgment.—The award of Research Grant AM-03439 from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, to R. S. is gratefully acknowledged.

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(15) L. F. Fieser, W.-Y. Huang, and J. C. Babcock, *J. Amer. Chem. Soc.*, **75**, 116 (1953).

(16) F. Nakada, R. Osawa, and K. Yamasaki, *Bull. Chem. Soc. Jap.*, **34**, 538 (1961).

The Dehydration of Coronopilin

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The dehydration of coronopilin (**1**) in sulfuric acid–acetic acid was known to yield coronophilic acid (**4**), but it also yields the isomer **10** in formic or trifluoroacetic acid. $\Delta^{1,2}$-Anhydrocoronopilin (**6**), the product of thionyl chloride–pyridine dehydration of **1**, has been shown not to undergo the rearrangement. A proposed mechanism for the rearrangement is supported by nmr and CD data, and the absolute configuration of isocoronophilic acid is shown to be that expressed in **10a**.

Sesquiterpene dilactones have been isolated from some collections of *Ambrosia psilostachya*,[1-3] and we we were interested in the chemical correlation of psilostachyin B (**5**)[3] with coronopilin (**1**) through the unknown $\Delta^{1,10}$-anhydrocoronopilin (**2**). The stereochemistry of **1**, a major sesquiterpene lactone in this species, has been completely elucidated through X-ray analysis and chemical correlations,[4] but it had also been correctly postulated earlier by Geissman and Turley[5] as a result of their study of the unusual rearrangement of **1** to coronopilic acid (**4**).

When this work was initiated, the dehydration of **1** without rearrangement had not been achieved and our first goal was therefore to complete such a reaction.

Discussion

It is now known[4] that thionyl chloride–pyridine treatment of **1** yields $\Delta^{1,2}$-anhydrocoronopilin (**6**) rather than the desired $\Delta^{1,10}$ isomer. We expected that acid treatment of **6** would shift the 1,2 double bond to the more substituted 1,10 position, but we were also concerned with the possibility that this latter compound would further rearrange to **4**, as described by Geissman and Turley in their study of the acid-catalyzed dehydration of **1**.[5] These authors postulated that **2** was the first intermediate formed in the treatment of **1** with acetic acid–sulfuric acid and that it efficiently yielded the cyclopropane derivative **3**, which further reacted with acid to yield their observed product **4**.

We therefore anticipated that acid treatment of **6** would yield **4** readily and that the difficulty in the work would lie in defining the conditions required for stopping the reaction after double-bond migration to **2**. Actually, a double-bond migration into conjugation within the five-membered ring was the only reaction which was observed when **6** was submitted to the conditions of the coronopilic acid rearrangement. The conjugated ketone which was isolated after treatment was identified as epiambrosin (**7**) by direct comparison. It is therefore probable that **6** is also one intermediate in the acid-catalyzed isomerization of ambrosin (**8**) to **7**.[4]

Our failure to achieve the conversion of **6** into **2** led us to reinvestigate the acid-catalyzed reaction of corono-

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(3) T. J. Mabry, H. B. Kagan, and H. E. Miller, *Tetrahedron*, **22**, 1943 (1966).

(4) A. Romo de Vivar, L. Rodriguez, J. Romo, M. V. Lakshmikantham, R. N. Mirrington, J. Kagan, and W. Herz, *ibid.*, **22**, 3279 (1966).

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