XI afforded, after adsorption chromatography on a Florisil[19] magnesia–silica gel column with methylene chloride containing 5% acetone as eluent and crystallization from methanol, a 33% yield of 2,3-dihydro-9-formyl-5,7,8-triacetoxy-1H-pyrrolo[1,2-*a*]indole (X) as tan solid. Recrystallization of this solid from methanol gave nearly white needles: m.p. 234–238° dec.; λ_{max} 5.66, 6.02 μ; λ_{max} 219 mμ (ϵ 27,400), 247 (14,400), 304 (11,500).

Anal. Calcd. for $C_{18}H_{17}NO_7$ (359.32): C, 60.16; H, 4.77; N, 3.90. Found: C, 59.96; H, 4.60; N, 3.94.

7-Benzyloxy-2,3-dihydro-9-formyl-8-nitro-1H-pyrrolo[1,2-*a*]indole (IV).—A suspension of 1.02 g. (3.5 mmoles) of 7-benzyloxy-2,3-dihydro-9-formyl-1H-pyrrolo[1,2-*a*]indole (I) in 20 ml. of glacial acetic acid was treated with 1.4 ml. of yellow fuming nitric acid by dropwise addition. After 1 hr. at room temperature the mixture was poured into 50 ml. of ice–water and filtered. The solid that formed was washed with water and ether to give 1.115 g. (95%) of 7-benzyloxy-2,3-dihydro-9-formyl-8-nitro-1H-pyrrolo[1,2-*a*]indole (IV). Recrystallization from acetone afforded pale yellow crystals: m.p. 215–227°; λ_{max} 5.97, 6.52, 7.91 μ; λ_{max} 217 mμ (ϵ 36,300), 254 (18,200), 295 (10,800); n.m.r., 9.75 (CHO), 7.60 (doublet, $J_{5,6}$ = 9 c.p.s., C-5 proton), 7.42 (five protons, phenyl), 7.33 (doublet, $J_{5,6}$ = 9 c.p.s., C-6 proton), 5.30 (two protons, benzylic), 4.20 (apparent triplet, C-3 protons), 3.33 (peaks partially obscured by water, C-1 protons), 2.55 (peaks obscured by dimethyl sulfoxide, C-2 protons) p.p.m.

Anal. Calcd. for $C_{19}H_{16}N_2O_4$ (336.33): C, 67.85; H, 4.80; N, 8.33. Found: C, 67.75; H, 4.64; N, 8.42.

Ethyl 5-Benzyloxy-4-nitro-3-indoleglyoxylate (XIII) and Ethyl 5-Benzyloxy-6-nitro-3-indoleglyoxylate (XIV).[16]—A suspension of 2.46 g. of ethyl 5-benzyloxy-3-indoleglyoxylate (XII) in 61 ml. of acetic acid was treated with 2.03 ml. of yellow fuming nitric acid at room temperature. After 1 hr. the mixture was diluted with water, and the solid that formed was washed with water and ether and dried. A 1.3-g. sample of the resulting solid (2.64 g., m.p. 200–205°) was dissolved in 25 ml. of the lower phase of the system heptane–ethyl acetate–dimethylformamide–water, (100:100:40:5) mixed with 50 g. of Celite diatomaceous earth and packed atop a column prepared from 300 ml. of the lower phase and 600 g. of Celite diatomaceous earth. Elution with the upper phase produced two yellow bands on the column. Concentration of eluate from the first band (hold-back volumes 1–2.2, 830 ml./h.b.v.) afforded, after recrystallization from methanol, 92 mg. of ethyl 5-benzyloxy-6-nitro-3-indoleglyoxylate (XIV) as yellow crystals: m.p. 244–247°; λ_{max} 5.80, 6.15 (broad), 6.65, 7.55 μ; λ_{max} 260 mμ (ϵ 9200) (sh), 300 (13,300); n.m.r., 8.58 (C-2 proton), 8.10 (C-7 proton), 7.98 (C-4 proton), 6.92 (five protons, phenyl), 5.30 (two protons, benzylic), 4.35 (two-proton quartet, CH_2CH_3), 1.35 (three-proton triplet, CH_2CH_3) p.p.m.

Anal. Calcd. for $C_{19}H_{16}N_2O_6$ (368.33): C, 61.95; H, 4.38; N, 7.61. Found: C, 62.31; H, 4.36; N, 7.58.

Concentration of eluate from the second yellow band (hold-back volumes 3.5–4.4) afforded, after recrystallization from methanol, 786 mg. of ethyl 5-benzyloxy-4-nitro-3-indoleglyoxylate (XIII) as yellow crystals: m.p. 221–224°; λ_{max} 5.80, 6.10, 6.20, 6.53, 7.25 μ; λ_{max} 260 mμ (ϵ 12,500), 280 (12,000), 310 (10,000) (sh); n.m.r., 8.53 (C-2 proton), 7.70 (doublet, $J_{6,7}$ = 9 c.p.s., C-7 proton), 7.40 (doublet, $J_{6,7}$ = 9 c.p.s., C-6 proton), 7.37 (five protons, phenyl), 5.27 (two protons, benzylic), 4.33 (two-proton quartet, OCH_2CH_3), 1.33 (three-proton triplet, OCH_2CH_3) p.p.m.

Anal. Calcd. for $C_{19}H_{16}N_2O_6$ (368.33): C, 61.95; H, 4.38; N, 7.61. Found: C, 62.25; H, 4.75; N, 7.76.

Comparison of the relative areas of peaks in the n.m.r. spectrum of a sample of the mixture of XIII and XIV before partition chromatographic separation indicated that these two components were present in an approximate ratio of 4:1.

Acknowledgment.—We wish to thank Mr. J. F. Poletto for permission to publish the indicated experiment, Mr. C. Pidacks and staff for partition chromatographic separations, Mr. L. Brancone and staff for microanalyses, Mr. W. Fulmor and staff for spectral data, and Dr. G. R. Allen, Jr., for helpful discussions.

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[19] Florisil is the trademark of the Floridin Co. for a magnesia–silica gel adsorbent.

Some Transformation Products of 17-Keto Anthrasteroids

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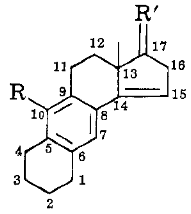
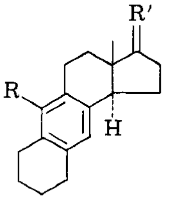
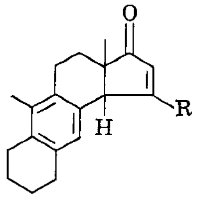
The formation of cyclopenteno-*s*-octahydroanthracenes of type I and VIa by acid-catalyzed elimination and rearrangement of steroidal 3β-hydroxy-5,7,9-(11)-trienes and their esters has been investigated extensively by Nes, Mosettig, and co-workers,[2] who have designated such products as anthrasteroids. In this paper, as an extension of the synthesis of 17-oxygenated anthrasteroids,[3] we report the preparation of several new anthrasteroids, along with the partial resolution of racemic 5,7,9,15-anthrastatetraene-15-carboxy-17-one (IIIb) and its conversion into *l*-5,7,9,14-anthrastatetraen-17β-ol (Id). We also record dehydrogenation studies leading to the dimethylcyclopentenoanthracene Va synthesized recently in a different manner by Nakazaki and co-workers.[4]



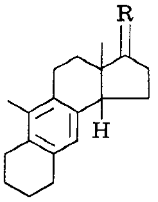
Ia, R = H; R′ = O
b, R = CH_3; R′ = O
c, R = H; R′ = $\langle^{OH}_{H}$
d, R = CH_3; R′ = $\langle^{OH}_{H}$



IIa, R = CH_3; R′ = O
b, R = H; R′ = $\langle^{OH}_{H}$
c, R = CH_3; R′ = $\langle^{OH}_{H}$
d, R = CH_3; R′ = CH_2
e, R = CH_3; R′ = $\langle^{CH_3}_{H}$



IIIa, R = H
b, R = COOH



IVa, R = O
b, R = $\langle^{H}_{OH}$

The three racemic 17-keto anthrasteroids Ia, Ib, and IIIa, prepared essentially as described previously,[3] but with certain improvements, were used as starting

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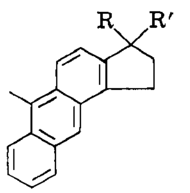
[1] (a) Alfred P. Sloan Research Fellow, 1961–1964. (b) U. S. Public Health Service Predoctoral Fellow, 1961–1962. This work comprises part I of the Ph.D. Thesis of C. P. K., The University of Kansas, Aug. 1962, and was supported in part by Research Grant CY-4413 from the National Cancer Institute.

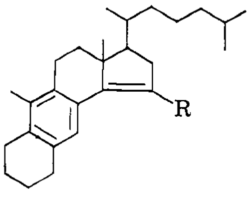
[2] W. R. Nes and D. L. Ford, *J. Am. Chem. Soc.*, **85**, 2137 (1963); J. A. Steele, L. A. Cohen, and E. Mosettig, *ibid.*, **85**, 1134 (1963), and earlier papers cited therein.

[3] A. W. Burgstahler and E. Mosettig, *ibid.*, **81**, 3697 (1959).

[4] M. Nakazaki and S. Isoe, *Bull. Chem. Soc. Japan*, **32**, 1202 (1959); M. Nakazaki, K. Yamagami, and S. Isoe, *ibid.*, **34**, 1189 (1961).



Va, $R = CH_3$; $R' = H$
b, $R = R' = CH_3$



VIa, R = H
b, R = Br

materials in the present study. Reduction of Ia and Ib[3] with sodium borohydride gave the products Ic and Id, respectively, in which the β configuration is assigned to the hydroxyl group by analogy with the stereochemistry of the similar reduction of the related Δ^{14}-17-keto steroid system.[5] Catalytic hydrogenation of the double bond in the ketone Ib and in the borohydride reduction products Ic and Id then gave the C/D-*trans*-dihydro anthrasteroids IIa, IIb, and IIc, respectively. Hydrogenation of the Δ^{15}-17-ketone IIIa obtained as a by-product in the production of the Δ^{14}-ketone Ia afforded the C/D-*cis*-dihydro anthrasteroid IVa. By analogy with the reduction of 14β-17-keto steroids,[5] the product from the borohydride reduction of IVa is assigned the 17α-ol structure IVb.

Through the Wittig reaction,[6] the ketone IIa was converted into the 17-methylene derivative IId. Catalytic hydrogenation of IId then furnished the desired 17-methyl compound IIe, presumably having the 17β-alkyl configuration.[5] Surprisingly, this reduction required considerably more vigorous conditions (platinum–acetic acid) than did hydrogenation of the double bond in either the Δ^{14}- or the Δ^{15}-anthrasteroids (palladium–ethanol).

Partial optical resolution of the unsaturated keto acid IIIb[3] was achieved by means of the cinchonidine salt. From the less soluble diastereomer of this salt the pure dextrorotatory enantiomer of IIIb, $[\alpha]_D$ +429°, was obtained. However, the keto acid recovered from the more soluble fraction was not fully resolved, since its $[\alpha]_D$ was only −286°. Efforts to complete the resolution with salts of other bases were unsuccessful.

Decarboxylation of the dextrorotatory keto acid IIIb in refluxing pyridine–hydrochloric acid[7] furnished the levorotatory 17-keto anthrasteroid Ib, $[\alpha]_D$ −12°. Reduction of this compound with sodium borohydride[3] then gave the levorotatory 17β-hydroxy derivative Id, $[\alpha]_D$ −57°, which was spectrally identical with the product obtained by Nes, Steele, and Mosettig[8] from acid treatment of *d*-5,7-9(11)-androstatriene-3β,17β-diol 17-benzoate. However, since the optical rotation of their product was not recorded, and since a sample is no longer available, a direct rotational comparison of their material with ours could not be made. Nevertheless, in view of the fact that all known 17β-alkyl anthrasteroids are levorotatory,[9] and since there is usually only a very small difference in rotation between a 17β-alkyl steroid and its 17β-hydroxy counterpart,[10] it is reasonable to propose that our levorotatory anthrasteroid Id is the same enantiomer as that obtained by Nes, *et al.*,[8] from the elimination–rearrangement reaction. Strong support for this view was later found in the presence of the same negative Cotton effect (trough at 312 mμ) in the optical rotatory dispersion curves of our resolved levorotatory anthrasteroids Ib and Id as was measured for the "naturally" derived anthrasteroids 5,7,9,14-anthracholestatetraene (VIa)[9] and 5,7,9,14,22-anthraergostapentaene.[11,12]

In view of the possible carcinogenicity of aromatized derivatives of anthrasteroids,[2] the conversion of several of our synthetic products into 3,6-dimethyl-2,3-dihydro-1H-cyclopent[*a*]anthracene (Va) was undertaken. As already mentioned, the synthesis of this hydrocarbon (in racemic form) has been reported previously.[4] Our initial attempts to prepare it by dehydrogenation of the carbinol formed by the addition of methyllithium to the ketone IIa appeared to give mainly the trimethylcyclopentenoanthracene Vb. Later we found that the boric acid dehydration method of Johns,[13] as applied to the alcohol IIc, yielded a conjugated olefin which on dehydrogenation over palladium on carbon did give the hydrocarbon Va. In addition, Va was also obtained by dehydrogenation of the 17β-methyl anthrasteroid IIe.

In another experiment, an attempt to add bromine to the 14,15 double bond of 5,7,9,14-anthracholestatetraene (VIa)[9] resulted in the formation of a monobromo substitution product instead of the desired dibromide addition product. Treatment of this monobromide with hot ethanolic sodium hydroxide or with zinc in refluxing acetic acid gave only recovered bromide. The ultraviolet and n.m.r. spectra of this compound are also strikingly similar to those recorded for 15-bromo-5,7,9,14,22-anthraergostapentaene.[14] Hence, the compound is assigned structure VIb.

Finally, 1,10-dimethylanthracene, previously unknown, was prepared in the course of this work by addition of methyllithium to the synthetic intermediate 1-oxo-10-methyl-*s*-octahydroanthracene,[3] followed by dehydration and dehydrogenation of the resulting 1,10-dimethyl-*s*-octahydro-1-anthrol.

Experimental Section

General Information.—Melting points were determined on a microscope hot stage or in open capillary tubes on a Hershberg apparatus, both calibrated against standard substances. Optical rotations were measured at 25–28° in chloroform at a concentration of 1 to 2% on a Zeiss polarimeter. Ultraviolet spectra were taken in ethanol on either a Beckman DK-1 recording spectrophotometer or a Bausch and Lomb Model 505 recording spectrophotometer. Infrared spectra were determined in chloroform or carbon disulfide solution, as indicated, on a Perkin-Elmer Infracord or Model 21 double-beam spectrophotometer. Petroleum ether refers to the fraction with b.p. 37–40°. Analytical samples were dried *in vacuo* at 80° or 30° below their melting point, whichever was lower. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.,

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[5] *Cf.* A. F. St. Andre, H. B. MacPhillamy, J. A. Nelson, A. C. Shabica, and C. R. Scholz, *J. Am. Chem. Soc.*, **74**, 5506 (1952); also, D. K. Banerjee, S. Chatterjee, C. H. Pillai, and M. V. Bhatt, *ibid.*, **78**, 3769 (1956).

[6] *Cf.* F. Sondheimer and R. Mechoulam, *ibid.*, **79**, 5029 (1957).

[7] W. S. Johnson, J. W. Peterson, and C. D. Gutsche, *ibid.*, **69**, 2942 (1947).

[8] W. R. Nes, J. A. Steele, and E. Mosettig, *ibid.*, **80**, 5233 (1958).

[9] W. R. Nes, R. B. Kostic, and E. Mosettig, *ibid.*, **78**, 436 (1956); see also ref. 8.

[10] For example, 5α-pregnane has $[\alpha]_D$ +18°, while 5α-androstan-17β-ol has $[\alpha]_D$ +13°: F. Radt, Ed. "Elsevier's Encyclopedia of Organic Chemistry," Vol. 14S, Elsevier Publishing Co., Amsterdam, 1954, pp. 1403S, 1512S.

[11] W. R. Nes and E. Mosettig, *J. Am. Chem. Soc.*, **76**, 3182 (1954).

[12] We thank Mr. H. K. Miller and Dr. Ulrich Weiss, National Institutes of Health, Bethesda, Md., for making these determinations.

[13] W. F. Johns, *J. Org. Chem.*, **26**, 4583 (1961).

[14] W. R. Nes and D. L. Ford, *J. Am. Chem. Soc.*, **83**, 4811 (1961).

the Spang Microanalytical Laboratory, Ann Arbor, Mich., or the Huffman Microanalytical Laboratory, Wheatridge, Colo.

1-Oxo-10-methyl-*s*-octahydroanthracene.—A number of improvements were made in the previously described[3,15] route to 9-methyl-*s*-octahydroanthracene, from which this ketone was prepared. Thus, a total of 91 g. (80% yield) of recrystallized *s*-octahydroanthracene was obtained from 120 g. of technical grade (90% pure) anthracene when freshly prepared W-5 Raney nickel catalyst and 1 ml. of concentrated hydrochloric acid were used in the hydrogenation. By addition of acetic anhydride (10 ml./mole) to the chloromethylation reaction, the yield of recrystallized 9-chloromethyl-*s*-octahydroanthracene was increased to 85–90%. Hydrogenolysis of the chloromethyl derivative with lithium aluminum hydride in ether furnished pure 9-methyl-*s*-octahydroanthracene, b.p. 104–106° (0.06 mm.), as colorless plates from methanol, m.p. 51-51.5°, in yields of 95–97%. Oxidation of this hydrocarbon at 3–5°, instead of 15–20° as reported previously,[3] gave a 1.5-fold increase in the yield of 1-oxo-10-methyl-*s*-octahydroanthracene after purification through the semicarbazone.

dl-**19-Nor-5,7,9,14-anthrastatetraen-17β-ol** (**Ic**).—Reduction of 340 mg. (1.35 mmoles) of the ketone Ia[3] with excess sodium borohydride at 0° in the manner described for the reduction of Ib[3] furnished 274 mg. (80% yield) of colorless needles of the alcohol Ic, m.p. 125–129°, after one crystallization from benzene–petroleum ether. Recrystallized from the same solvent pair, these melted at 132–134° (softening at 127°): $\lambda_{\max}^{\mathrm{CS_2}}$ 12.30 μ.

Anal. Calcd. for $C_{18}H_{22}O$ (254.4): C, 84.99; H, 8.72. Found: C, 84.72; H, 8.90.

dl-**19-Nor-14α-5,7,9-anthrastatrien-17β-ol** (**IIb**).—Hydrogenation of 217 mg. (0.885 mmole) of the unsaturated alcohol Ic over 10% palladium on charcoal in ethanol proceeded rapidly with absorption of the theoretical quantity of hydrogen. Crystallization of the product IIb from benzene–petroleum ether gave 185 mg. (85% yield) of colorless microspores. Recrystallized from the same solvent pair these melted at 128–129° (softening at 125°): $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.75 and 2.9 μ.

Anal. Calcd. for $C_{18}H_{24}O$ (256.4): C, 84.32; H, 9.44. Found: C, 84.63; H, 9.67.

dl-**14α-5,7,9-Anthrastatrien-17-one** (**IIa**).—Hydrogenation of 2.0 g. (7.5 mmoles) of the ketone Ib[3] over 10% Pd–C in ethyl acetate afforded 1.8 g. (90% yield) of the dihydro product IIa, which crystallized from benzene–petroleum ether in fine clusters, m.p. 92–94° (softening at 91°), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.75 μ.

Anal. Calcd. for $C_{19}H_{24}O$ (268.4): C, 85.01; H, 9.01. Found: C, 84.98; H, 9.12.

dl-**14α,5,7,9-Anthrastatrien-17β-ol** (**IIc**).—Similar hydrogenation of 86 mg. (0.32 mmole) of the alcohol Id[3] over 10% Pd–C in ethyl acetate furnished 70 mg. (88% yield) of the dihydro product IIc, which crystallized from benzene–petroleum ether in colorless plates, m.p. 169–170°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.73 and 2.91 μ.

Anal. Calcd. for $C_{19}H_{26}O$ (270.4): C, 84.39; H, 9.69. Found: C, 84.16; H, 9.96.

dl-**14β-5,7,9-Anthrastatrien-17-one** (**IVa**).—Hydrogenation of 5.6 g. (21 mmoles) of the neutral oily residue (mainly IIIa) from the decarboxylation of the keto acid IIIb[3] was conducted over 10% Pd–C in ethyl acetate. Crystallization of the product from benzene–petroleum ether yielded 5.1 g. (91%) of the ketone IVa as colorless clusters, m.p. 105–107°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.74 μ.

Anal. Calcd. for $C_{19}H_{24}O$ (268.4): C, 85.04; H, 9.01. Found: C, 85.14; H, 8.83.

dl-**14β,5,7,9-Anthrastatrien-17α-ol** (**IVb**).—Reduction of 3.0 g. (11.2 mmoles) of the ketone IVa with excess sodium borohydride at 0° in ether–methanol[3] furnished, after recrystallization from benzene–petroleum ether, 2.9 g. (96% yield) of colorless microprisms of the alcohol IVb, m.p. 102–104°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.75 and 2.9 μ.

Anal. Calcd. for $C_{19}H_{26}O$ (270.4): C, 84.39; H, 9.69. Found: C, 85.54; H, 9.75.

dl-**17-Methylene-14α,5,7,9-anthrastatriene** (**IId**).—A solution of 296 mg. (1.1 mmoles) of the ketone IIa in 50 ml. of dry ether was added over 5 min. to 50 ml. of an ether solution of triphenylmethylenephosphorane prepared from 6.0 mmoles of methyltriphenylphosphonium iodide and *ca.* 7.0 mmoles of phenyllithium. Succeeding operations were conducted according to the tetrahydrofuran procedure of Sondheimer and Mechoulam.[6] After chromatography, the hydrocarbon IId crystallized from acetone as colorless prisms, m.p. 92–93°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.10 and 11.32 (s) μ, yield 160 mg. (55%).

Anal. Calcd. for $C_{20}H_{26}$ (266.4): C, 90.16; H, 9.84. Found: C, 89.87; H, 10.11.

dl-**17β-Methyl-14α-5,7,9-anthrastatriene** (**IIe**).—Attempted hydrogenation of 253 mg. (0.95 mmole) of the methylene derivative IId in ethyl acetate over a 10% Pd–C or a platinum (Adams) catalyst resulted in the absorption of only 10% of the required amount of hydrogen. With platinum in acetic acid, however, the reduction was completed rapidly. Crystallization of the product from acetone yielded 215 mg. (85%) of the hydrocarbon IIe as colorless spores, m.p. 82–85°.

Anal. Calcd. for $C_{20}H_{28}$ (268.4): C, 89.49; H, 10.51. Found: C, 89.37; H, 10.40.

d-**5,7,9,15-Anthrastatetraene-15-carboxy-17-one** (**IIIb**).—The *dl*-unsaturated keto acid IIIb[3] (931 mg., 3 mmoles) and cinchonidine (883 mg., 3 mmoles) were dissolved separately in the minimum amount of hot ethyl acetate containing enough ethanol to hasten the dissolving process. The two solutions were combined, excess solvent was removed, and ethyl acetate was added until most of the ethanol was replaced. Concentration was continued until crystallization commenced, at which point the minimum amount of hot ethyl acetate was added to redissolve the precipitate. When allowed to cool slowly, the solution deposited flocculent crystals contaminated by a small amount of granular material. Seven similar recrystallizations of these crystals afforded a homogeneous product, m.p. 194–196°. Recovery of the free acid IIIb by acidification of the salt with 6 *N* hydrochloric acid, extraction with ether, and crystallization from benzene–ethanol furnished 150 mg. (33% yield) of light yellow diamond-shaped crystals, m.p. 198–201°, $[\alpha]_D$ +429°.

Anal. Calcd. for $C_{20}H_{22}O_3$ (310.4): C, 77.39, H, 7.14. Found: C, 77.12; H, 7.21.

The keto acid regenerated from the more soluble granular salt had $[\alpha]_D$ −286°, which was not improved by further efforts at resolution.

l-**5,7,9,14-Anthrastatetraen-17-one** (**Ib**).—Decarboxylation[3] of 104 mg. (0.33 mmole) of the dextrorotatory keto acid IIIb, $[\alpha]_D$ +429°, was conducted at reflux (bath temperature 160°) for 1 hr. in 4.35 ml. of concentrated hydrochloric acid containing 2.1 ml. of pyridine. Recovery of the neutral fraction by ether extraction[3] and crystallization from benzene–petroleum ether furnished 37 mg. (42% yield) of colorless needles of the resolved ketone Ib. After sublimation at 0.05 mm. (bath temperature to 130°) and recrystallization from the same solvent pair, this substance melted at 177–178° (softening at 174°), $[\alpha]_D$ −12°.

l-**5,7,9,14-Anthrastatetraen-17β-ol** (**Id**).—Reduction of 16 mg. (0.060 mmole) of the foregoing levorotatory ketone with sodium borohydride in the manner described previously[3] afforded a nearly quantitative yield of the resolved alcohol Id as colorless needles, m.p. 130–132°, after one crystallization from benzene–petroleum ether. Sublimation of this product at 0.06 mm. (bath temperature 140–160°), followed by one additional recrystallization from the same solvent pair, gave product with m.p. 133–134°, $[\alpha]_D$ −57°. A melting point of 136–138° was reported by Nes, Steele, and Mosettig[8] for the optically active alcohol Id obtained by them from *d*-5,7,9(11)-anhydrostatriene-3β,17β-diol 17-benzoate. The detailed infrared and ultraviolet spectra of our product were identical with those found by these workers (and kindly made available to us by the late Dr. Erich Mosettig): $\lambda_{\max}^{\mathrm{CS_2}}$ 12.31 μ; $\lambda_{\max}^{\mathrm{EtOH}}$, mμ (ε), 221 (24,300), 227 (25,500), 266 (17,100), 298 (2450), 309 (2050), and 233 (16,500) (infl.).

dl-**3,3,6-Trimethyl-2,3-dihydro-1H-cyclopent[*a*]anthracene** (**Vb**).—5,7,9-Anthrastatrien-17-one (IIa, 100 mg., 0.37 mmole) was treated with an excess of methyllithium, and the resulting carbinol was mixed with an equal weight of 30% Pd–C and heated for 3 hr. in a sealed tube at 320°. The product was taken up in petroleum ether–benzene (9:1) and purified by elution from basic alumina. A nearly colorless fraction which exhibited strong blue fluorescence in ultraviolet light was eluted with petroleum ether–benzene (6:1). This crystallized readily from ethanol to give 25 mg. of Vb as pale yellow crystals, m.p. 118–120°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.25 and 7.33 μ. The **picrate** crystallized from ethanol in deep purple needles, m.p. 144–145°.

Anal. Calcd. for $C_{26}H_{23}N_3O_7$ (489.5): C, 63.80; H, 4.74; N, 8.31. Found: C, 63.62; H, 4.65; N, 8.19.

dl-**3,6-Dimethyl-2,3-dihydro-1H-cyclopent[*a*]anthracene** (**Va**). **A.**—An intimate mixture of 69 mg. (0.26 mmole) of *dl*-14α-5,7,9-anthrastatrien-17β-ol (IIc) and 18 mg. (0.29 mmole) of boric acid was heated for 20 min. at 140° under nitrogen at atmospheric

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[15] G. M. Badger, W. Carruthers, J. W. Cook, and R. Schoental, *J. Chem. Soc.*, 169 (1949); J. R. Durland and H. Adkins, *J. Am. Chem. Soc.*, **59**, 135 (1937).

pressure.[13] The pressure was reduced to 20–25 mm., and the temperature was raised rapidly to 350° and maintained there for 0.5 hr. Extraction of the neutral fraction with ether and chromatography over basic alumina (elution with 9:1 petroleum ether–benzene) gave a colorless oil whose infrared and ultraviolet spectra very closely resembled those of anthrasteroids: $\lambda_{max}^{CS_2}$ 12.3 μ; λ_{max}^{EtOH} 222, 228, 268, and 308 mμ (absorption in the ratio 12:12: 8:1, as for anthrasteroids[1]).

For dehydrogenation, 35 mg. of this oil was mixed with an equal weight of 10% Pd–C and heated in a sealed tube at 320° for 3 hr. Elution of the product from basic alumina with petroleum ether–benzene (8:1) furnished *ca.* 5 mg. of a nearly colorless fraction of Va which exhibited strong blue fluorescence in ultraviolet light: λ_{max}^{EtOH} 261, 333, 355, 374, and 394 mμ. Owing to lack of material, further work was deferred on this product.

B.—Similar dehydrogenation of 40 mg. (0.15 mmole) of the hydrocarbon IIe afforded *ca.* 10 mg. of Va as a colorless fraction by elution from basic alumina with petroleum ether–benzene (8:1). This also exhibited strong blue fluorescence in ultraviolet light: λ_{max}^{EtOH} 261, 336, 354, 374, and 394 mμ.[4] The picrate crystallized as reddish brown needles, m.p. 126–128° (lit.[4] for the picrate of *dl*-Va m.p. 128–128.5°). Chromatography of this derivative on alumina, elution with petroleum ether–benzene (3:1), and crystallization from methanol furnished the free hydrocarbon Va, m.p. 79–81°.[4]

15-Bromo-5,7,8,14-anthracholestatetraene (VIb).—To a stirred solution of 1.0 g. (2.82 mmoles) of 5,7,9,14-anthracholestatetraene (VIa)[9] in 20 ml. of carbon tetrachloride, a solution of 0.45 g. (2.82 mmoles) of bromine in 20 ml. of carbon tetrachloride was added dropwise over the course of 4 min. During the addition, hydrogen bromide was evolved, and after 20 min. water was added, and the organic product was recovered by extraction with carbon tetrachloride. The organic layer was washed with water, 5% sodium bisulfite solution, and again with water. It was then dried over anhydrous magnesium sulfate and evaporated *in vacuo*. Crystallization of the residue from ethyl acetate–ethanol gave 0.8 g. (64% yield) of colorless needles of VIb, m.p. 93–97°. Twice recrystallized from this same solvent pair, these melted at 99–100°, gave a positive Beilstein halogen test, and had $\lambda_{max}^{CS_2}$ 12.33 μ; $\lambda_{max}^{isooctane}$, mμ (ε), 222 (21,500), 227 (21,700), 270 (19,900), and 306 (1640). The n.m.r. spectrum had a single sharp benzenoid proton peak at τ 2.12 (determined in CCl_4 on a Varian Associates A-60 spectrometer with tetramethylsilane as an internal reference).

Anal. Calcd. for $C_{27}H_{39}Br$ (443.5): C, 73.12; H, 8.86; Br, 18.02. Found: C, 73.25; H, 8.98; Br, 18.12.

1,10-Dimethyl-*s*-octahydro-1-anthrol.—To a refluxing solution of excess methyllithium in diethyl ether [prepared from 555 mg. (80 mg.-atoms) of lithium shot and 5.68 g. (40 mmoles) of methyl iodide], 1.61 g. (7.5 mmoles) of 1-oxo-10-methyl-*s*-octahydroanthracene[8] in diethyl ether was added, with stirring, under nitrogen. The reaction was allowed to proceed for 10 hr. before ice-cold water was cautiously added and the organic product was recovered by ether extraction. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated *in vacuo*. Crystallization of the residue from methanol gave 1.07 g. (62% yield) of colorless needles of 1,10-dimethyl-*s*-octahydro-1-anthrol, m.p. 116–118°. Recrystallized from the same solvent, these melted at 117–119° and had $\lambda_{max}^{CHCl_3}$ 2.7 and 2.9 μ.

Anal. Calcd. for $C_{16}H_{22}O$ (230.4): C, 83.43; H, 9.63. Found: C, 83.73, H, 9.66.

1,10-Dimethylanthracene.—A portion of the above alcohol (575 mg., 2.5 mmoles) was mixed with an equal weight of 30% Pd–C and heated in a sealed tube at 320° for 3 hr. The product was taken up in petroleum ether and purified by elution from basic alumina. A nearly colorless fraction, which exhibited a strong blue fluorescence in ultraviolet light, was eluted slowly with petroleum ether and crystallized readily from ethanol to give 150 mg. (29% yield) of very pale green needles of 1,10-dimethylanthracene, m.p. 86–89°. Crystallized from the same solvent, these melted at 88–89° and showed λ_{max}^{EtOH}, mμ (log ε), 257 (3.4) (shoulder), 350 (3.7), 268 (3.9), and 389 (3.8).

Anal. Calcd. for $C_{16}H_{14}$ (206.3): C, 93.16; H, 6.84. Found: C, 93.03; H, 6.95.

The picrate crystallized from ethanol as deep purple needles, m.p. 127.5–128°.

Anal. Calcd. for $C_{22}H_{17}N_3O_7$ (435.4): C, 60.70; H, 3.94; N, 9.65. Found: C, 60.67; H, 4.01; N, 9.78.

5-Isodehydroabietic Lactones[1]

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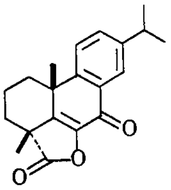
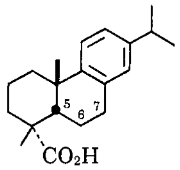
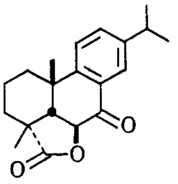
In a recent study of the chemistry of dehydroabietic acid, formation of the enol lactone I was reported.[2] Its several reduction products were assumed to possess A–B *trans* stereochemistry. However, since the product of its catalytic hydrogenation has recently been shown to be 5-isodehydroabietic acid (II),[3] an investigation of the structure of the hydroxylactone obtained on sodium borohydride reduction of I and its oxidation product, a 7-ketolactone, was undertaken. Two facts showed rapidly that the reduced lactones also belonged to the 5-iso series. Clemmensen reduction of the 7-ketolactone yielded 5-isodehydroabietic acid (II).[4] Analysis of the p.m.r. spectrum of the lactone revealed its 5β-H (doublet at 2.32 p.p.m.) strongly coupled (*J* = 13.0 c.p.s.) with its C-6 hydrogen (doublet at 5.04 p.p.m.) indicating a *trans*, diaxial relationship between them.[5] Hence the compound possessed structure III.



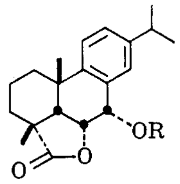
I



II



III



IVa, R = H
b, R = Ac

Despite attempts to repeat the preparation of the hydroxylactone and thereupon ketolactone III,[2] sodium borohydride reduction of I has led recently consistently to a new hydroxylactone. Jones oxidation of this compound yielded a new ketolactone whose sodium borohydride reduction reyielded the hydroxylactone while calcium–ammonia reduction, followed by hydrogenation, gave 5-isodehydroabietic acid (II). The p.m.r. spectrum of the ketolactone showed its 5β-hydrogen (doublet at 2.70 p.p.m.) coupled (*J* = 8.0 c.p.s.) with the C-6 hydrogen (doublet at 5.05 p.p.m.). These data are consistent only with struc-

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(1) This research was supported by the National Science Foundation.

(2) E. Wenkert, R. W. J. Carney, and C. Kaneko, *J. Am. Chem. Soc.*, **83**, 4440 (1961).

(3) E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30**, 713 (1965).

(4) This experiment was performed by R. W. J. Carney.

(5) Both 4- and 10-methyl signals appeared at 1.50 p.p.m.