Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.28; H, 9.97.

Alcohol 6.—Sodium borohydride (0.3 g.) was added slowly to an ice-cold solution of 0.4 g. of ketone **8** in 50 ml. of methanol and the mixture was kept at room temperature for 0.5 hr, then diluted with water and extracted with ether. The washed and dried extract on evaporation furnished 0.28 g. of a colorless solid which crystallized from aqueous methanol as colorless needles of alcohol **6**: m.p. 150–152°; infrared bands at 3600 (OH) and 1710 cm.$^{-1}$ (ester); n.m.r. signals at 3.67 (methoxyl), 2.9 (diffuse doublet, one proton, H-14, $J \sim 10$ c.p.s.), 1.18, 0.90, and 0.89 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{21}H_{36}O_3$: C, 74.95; H, 10.78. Found: C, 74.77; H, 10.52.

Acetylation of 70 mg. of **6** with acetic anhydride–pyridine at 80° for 3 hr gave acetate **7** as an oil: n.m.r. signals at 4.55 d (1 proton, H-14, J = 10 c.p.s.), 3.65 (methoxyl), 2.06 (acetate), 1.17, 0.89, 0.78 ppm (methyl singlets).

Methyl *trans-anti-trans*-Tetrahydropimarate (10).—A solution of 2.1 g. of ketone **8** in 6 ml. of ethanedithiol was treated with 4 ml. of boron trifluoride etherate for 16 hr at 25°. No reaction was apparent at first but a white precipitate slowly formed after several hours. Methanol was added and the thioketal **9** collected by filtration and crystallized from chloroform–methanol to give colorless needles: yield 2.16 g. (84%); m.p. 239–240°; infrared bands at 1725 and 1250 cm.$^{-1}$ (ester); n.m.r. signals at 3.62 (methoxyl), 3.09 s (four protons, thioketal), 1.17, 1.10, and 0.88 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{23}H_{38}O_2S_2$: C, 67.26; H, 9.33. Found: C, 67.48; H, 9.21.

A suspension of 1.60 g. of the above thioketal and 6 teaspoonsfull of Raney nickel in 500 ml. of absolute ethanol was refluxed for 50 hr., then filtered through celite, and the filtrate was evaporated to give an oil which rapidly solidified. Crystallization from methanol yielded 1.14 g. (91%) of methyl tetrahydropimarate **10** as colorless needles: m.p. 74.5–75.5°; $[\alpha]_D$ +10° (*c* 2.4) (lit.[3] m.p. 65–68°, $[\alpha]_D$ +6°); infrared bands at 1720 and 1250 cm.$^{-1}$ (ester); n.m.r. signals at 3.55 (methoxyl), 1.12, 0.85, and 0.75 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78.38; H, 11.37.

***trans-anti-trans*-Tetrahydropimaric Acid (12).**—A solution of 0.47 g. of ester **10** in 20 ml. of anhydrous ether was added to a suspension of 0.5 g. of lithium aluminum hydride in 100 ml. of anhydrous ether and the mixture was refluxed for 2 hr. The excess reagent was decomposed by careful addition of water, then dilute hydrochloric acid. The washed and dried ether layer was evaporated to give 0.41 g. of alcohol **11** which crystallized from pentane as colorless prisms: m.p. 93–94°; $[\alpha]_D$ +12° (*c* 2.17) (lit.[9] m.p. 90°, $[\alpha]_D$ +11°); infrared bands at 3350 and 1060 cm.$^{-1}$ (OH); n.m.r. signals at 3.41, 3.08 (AB quartet, two protons, CH_2OH, J_{AB} = 11 c.p.s.), 1.58 s (one proton, O*H*) (removed on exchange with D_2O), 0.89, 0.78, and 0.77 p.p.m. (methyl singlets).

A solution of 0.30 g. of alcohol **11** in 30 ml. of acetone was stirred at room temperature in the presence of 1 ml. of Jones reagent for 0.5 hr., then diluted and the precipitate was collected and washed well with water. Three recrystallizations of the crude product, m.p. 230–240°, yield 0.29 g., from methanol gave colorless needles of **12**: m.p. 246–247°; $[\alpha]_D$ +16° (*c* 1.84); infrared bands at 1695 cm.$^{-1}$ (acid); n.m.r. signals at 1.18, 0.87, and 0.77 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 77.98; H, 11.18.

Pimarane (14).—A solution of 0.41 g. of alcohol **11** in 50 ml. of acetone was treated dropwise at 0° with deaerated Jones reagent under nitrogen until a brown color persisted. The mixture was then diluted with water and extracted with ether, and the washed and dried extract was evaporated to furnish the oily aldehyde **13**, infrared bands (CCl_4) at 2700 and 1730 cm.$^{-1}$. The crude aldehyde, 20 ml. of diethylene glycol, 3 ml. of hydrazine hydrate, and 3 g. of potassium hydroxide were heated under reflux for 4 hr. then cooled, diluted, and extracted thrice with hexane. The combined extracts were washed successively with water, 1 *N* hydrochloric acid, and water, dried, and evaporated to yield a yellow oil. Chromatography of this residue on 50 g. of alumina and elution with hexane furnished 0.27 g. (70% from **11**) of pimarane **14** as a colorless oil which slowly solidified and was collected with the aid of methanol: m.p. 33–34° (lit.[9] m.p. 32–34°), infrared bands (film) at 1385 and 1370 cm.$^{-1}$ (*gem*-dimethyl), n.m.r. signals at 0.80 (nine protons, three methyl singlets) and 0.73 p.p.m. (three protons, methyl singlet).

Hydrogenation of Dihydropimaric Acid.—A mixture of 0.21 g. of dihydropimaric acid and 0.45 g. of platinum oxide in 50 ml. of acetic acid was shaken under hydrogen at 14 lb. for 26 hr. at room temperature. The catalyst was removed by filtration through celite and the filtrate was evaporated to give a solid residue which crystallized from methanol as colorless needles, m.p. 239–241°, m.m.p. 239–242°, infrared and n.m.r. spectra identical with that of acid **12** described above.

Steroids. CCLXXXI.[1a] Spectra and Stereochemistry. XXI.[1b] Nuclear Magnetic Resonance Spectra of Methylated Phenanthrenes

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Newman, Meutzer, and Slomp recently reported that benzo[*c*]phenanthrenes bearing methyl groups at the 1- or 1,12-positions (Ia and Ib) show smaller downfield shifts, or even upfield shifts, of methyl proton resonances (relative to toluene) than would be expected if the methyl protons lay in or near the plane of the aromatic system.[2] Interactions leading to displacement of the methyl group away from the plane of the rings with consequent increased shielding were postulated to account for the observed shifts. We recently reported on the n.m.r. spectra of several phenanthrenes noting the paramagnetic shifts of resonances for the "inside" protons (at C-1 and C-11 on the steroid numbering system) relative to those for other aromatic protons due to extra deshielding by the proximate rings A and C.[3] We have since examined several methylated phenanthrenes, some derived by dehydrogenation of steroids. Collected n.m.r. data are presented in Table I together with relevant comparative data gleaned from the literature.[4] Comparison of the methyl proton shift values for toluene and 1-methylestra-1,3,5(10)-trien-17-one (IIa) with values for the 6-methylphenanthrene derivatives IIIa and IIIb shows that the more extensive aromatic system of phenanthrene shifts the 6-methyl proton resonance downfield by approximately 0.2 p.p.m. For the "inside" 5-methyl group R_3 in the phenanthrene IIIc a pronounced paramagnetic shift of 0.68 p.p.m. relative to toluene is observed, consistent with deshielding of the methyl protons by all three proximate aromatic

(1) (a) Steroids. CCLXXX: A. D. Cross and I. T. Harrison, manuscript in preparation. (b) Spectra and Stereochemistry. XX: A. D. Cross, C. Djerassi, A. El-Hamidi, L. Pijewska, and F. Santavý, *Collection Czech. Chem. Comm.*, in press.

(2) M. S. Newman, R. G. Meutzer, and G. Slomp, *J. Am. Chem. Soc.*, **85**, 4018 (1963).

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(4) N.m.r. spectra were recorded at 60 or 100 Mc. using 8–10% solutions in deuteriochloroform containing tetramethylsilane as an internal reference. Chemical shifts are expressed in parts per million downfield from the reference standard. One of us (A. D. C.) thanks the Universidad Nacional de México for time on a Varian A-60 spectrometer.

rings.[5] This result contrasts sharply with the minute shift found by Slomp[2] for the homologous 1-methylbenzo[*c*]phenanthrene (Ia) and suggests that structural deformation of the aromatic ring system or the aromatic methyl from planarity due to steric interactions[2] is small or nonexistent in the phenanthrene IIIc, where only *one* "inside" methyl is present. However, from the n.m.r. evidence it is now concluded that the presence of *two* "inside" methyls leads to distortion in the phenanthrene case also.

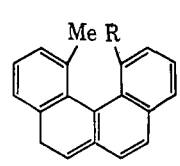
TABLE I
CHEMICAL SHIFTS OF METHYL PROTONS IN SOME AROMATIC SYSTEMS[a]

Compd.	Methyl proton resonances, p.p.m.
Toluene	2.32[b]
1-Methylbenzo[*c*]phenanthrene (Ia)	2.36[b]
1,12-Dimethylbenzo[*c*]phenanthrene (Ib)	1.92[b]
1-Methylestra-1,3,5(10)-trien-17-one (IIa)	2.34[c]
3-Hydroxy-1-methylestra-1,3,5(10)-trien-17-one (IIb)	2.29[c]
6-Methyl-1,2-cyclopentenophenanthrene (IIIa)[d]	2.57
3,6-Dimethyl-1,2-cyclopentenophenanthrene (IIIb)[d]	2.53 (6-Me) 2.43 (3-Me)
7-Hydroxy-3′,3′,5-trimethyl-1,2-cyclopentenophenanthrene (IIIc)[e]	1.33 (*gem*-diMe) 3.00 (5-Me)
9,10-Dihydro-4,5-dimethylphenanthrene (IVa)	2.25[f]
4,5-Dimethylphenanthrene (IVb)	2.57[f]

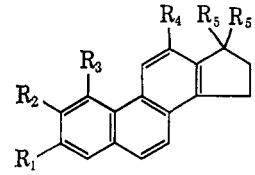
[a] Footnote 4. [b] See ref. 2. [c] See ref. 6. [d] Gift sample kindly supplied by Professor H. Dannenberg, Max Planck Institute for Biochemistry, Munich, Germany. [e] Made available by Dr. S. Kaufmann, Syntex. [f] Spectral data of H. Joshua, Ph.D. Dissertation, New York University, 1964. This information was generously provided, together with a sample of IVa, by Professor K. Mislow, Princeton University. N.m.r. data for IVa has also been published elsewhere.[6]

Mislow and his colleagues recently made a comprehensive comparative study of the ultraviolet and n.m.r. spectra of numerous bridged biphenyls related to, and including, 9,10-dihydro-4,5-dimethylphenanthrene (IVa).[7] They concluded that nonbonded molecular strain in the latter (IVa) is very likely relieved by in-plane and out-of-plane deformations of the methyl groups.

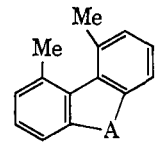
Introduction of a second "inside" methyl group on the fully aromatic phenanthrene nucleus leads to a strong diamagnetic shift of *ca.* 0.4 p.p.m. (*cf.* IIIc and IVb), a value similar to that recorded earlier for introduction of an extra "inside" methyl into benzo[*c*]-phenanthrenes (*cf.* Ia and Ib).[2] A severe methyl–methyl nonbonded interaction leading to reduced deshielding of the methyl groups by the ring currents of the phenanthrene system is indicated. That the integrity of the aromatic system in IVb remains largely



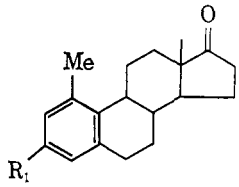
Ia, R = H
b, R = Me



IIIa, $R_1 = R_3 = R_4 = R_5 = H$; R_2 = Me
b, $R_1 = R_3 = R_5 = H$; $R_2 = R_4$ = Me
c, R_1 = OH; $R_2 = R_4 = H$; $R_3 = R_5$ = Me



IVa, A = CH_2—CH_2
b, A = CH=CH



IIa, R_1 = H
b, R_1 = OH

undisturbed has already been deduced from ultraviolet spectral data.[8] Molecular distortion appears to be achieved, therefore, principally by a bending of the C–Me σ bonds out of the plane of the ring system.

No firm evidence for long-range coupling between protons of ring A and C-methyl substituents was derived from these studies.

(5) The additional saturated cyclopentane ring of the phenanthrenes derived from steroids does not affect the aromatic 1- and 2-methyl proton resonances significantly (*cf.* toluene and IIa, Table I). Caspi and coworkers[6] have already shown that for 1-methylestra-1,3,5(10)-trienes a 3-hydroxyl causes a small *diamagnetic* shift of the 1-methyl proton resonance (*cf.* IIa and IIb). The effect of a similar substituent in the phenanthrene IIIc would be expected, therefore, to diminish slightly the paramagnetic shift induced by the aromatic rings B and C.

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3,5-Cyclo-6-norcholestan-7-one[1]

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With the view of preparing steroid hormone analogs with a contracted ring B, we turned to a consideration of 3,5-cyclo steroids as intermediates in which the functional integrity of C-3 could be preserved during the rigorous conditions of pyrolysis necessary to bring about the contraction of the ring as envisaged in our synthesis. Because of the low cost of cholesterol and the fact that functional groups are not present elsewhere in the molecule, we chose to carry out model studies in the cholestane series.

For the starting material in our proposed synthesis we employed the previously reported[3] 3,5-cyclo-6,7-secocholestane-6,7-dioic acid (1), which may be pre-

(1) The initial preparation of 3,5-cyclo-6-norcholestan-7-one is described in a thesis presented by W. W. Zorbach to the Faculty of Graduate Studies and Research, McGill University, Montreal, Canada, in partial fulfillment of the requirements for Degree of Doctor of Philosophy in Biochemistry, May 1951.

2) (a) To whom correspondence should be sent: Department of Chemistry, Georgetown University, Washington, D. C. (b) The present study is taken from a thesis submitted by J. Al-Kassir to the Graduate School of Georgetown University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry, Dec. 1963. A scholarship for the graduate education of J. Al-Kassir by the Government of Iraq is gratefully acknowledged. (c) Deceased.

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