of the eluants yielded 1.8 g. of **8,10-dimethyl-3,4-benzpyrene (XII)** as small yellow plates, m.p. 235–238° dec., m.p. 238–240° *in vacuo*. Recrystallization from benzene followed by sublimation at 200–210° and 0.5–1.0 mm. yielded 1.2 g. of hydrocarbon, m.p. 240.5–241.5° *in vacuo*. An additional 0.25 g., m.p. 240.5–241.5° *in vacuo*, was obtained by similar treatment of the mother liquors. The total yield of purified material was 1.45 g. (37% from X).

*Anal.* Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75. Found: C, 94.15; H, 5.67.

A **picrate** was prepared using a saturated solution of picric acid in benzene. Repeated recrystallization of the picrate from benzene yielded dark brown needles, m.p. 202.5–203.5°. Analysis did not give the expected values due to contamination of the picrate samples with the highly insoluble hydrocarbon.

**Ultraviolet Absorption Spectra.**—The ultraviolet absorption spectra of 10-methyl- and 8,10-dimethyl-3,4-benzpyrene in 95% ethanol were measured with a Model DU Beckman spectrophotometer (see Fig. 1). Maxima and (log $\epsilon$) values are: 10-methyl-3,4-benzpyrene (XI), 256 mμ (4.62), 266 mμ (4.69), 286 mμ (4.58), 297 mμ (4.64), 369 mμ (4.36), and 387 mμ (4.40); 8,10-dimethyl-3,4-benzpyrene (XII), 257 mμ (4.68), 268 mμ (4.70), 290 mμ (4.62), 304 mμ (4.69), 376 mμ (4.39) and 392 mμ (4.42).

ALBUQUERQUE, NEW MEXICO

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[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH]

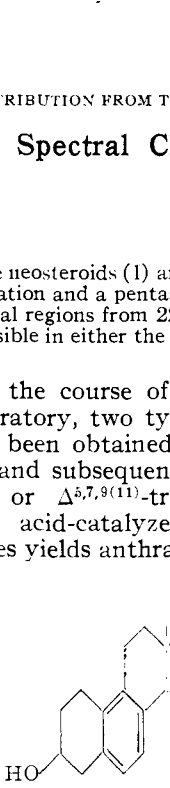
# The Spectral Characterization of Benzenoid Systems Derivable from $\Delta^{5,7}$-Steroids

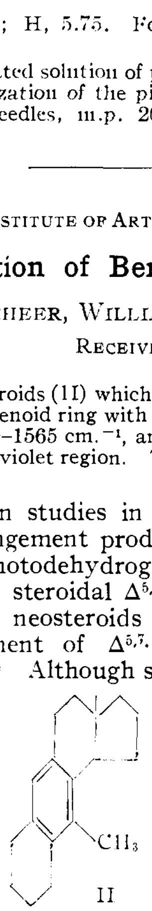
BY IRVING SCHEER, WILLIAM R. NES AND PHYLLIS B. SMELTZER

RECEIVED OCTOBER 27, 1954

The neosteroids (I) and the anthrasteroids (II) which possess, respectively, a tetrasubstituted benzenoid ring with angular annulation and a pentasubstituted benzenoid ring with linear annulation have been characterized by their absorption in the spectral regions from 220–400 mμ, 1630–1565 cm.$^{-1}$, and 900–720 cm.$^{-1}$. Differentiation of the two classes of compounds is possible in either the infrared or ultraviolet region. The spectra of some related aromatic compounds are discussed.

In the course of aromatization studies in this Laboratory, two types of rearrangement products have been obtained.[1,2] Thus, photodehydrogenation and subsequent pyrolysis of steroidal $\Delta^{5,7}$-dienes or $\Delta^{5,7,9(11)}$-trienes[3] yields neosteroids (I), while acid-catalyzed rearrangement of $\Delta^{5,7,9(11)}$-trienes yields anthrasteroids (II).[4] Although some spectral data for such systems are recorded in the literature,[5] we undertook a study of the spectral properties of a number of anthrasteroids, neosteroids and other benzenoid compounds in the infrared and ultraviolet regions in order to determine whether these compounds had definite and differential characteristics. This indeed has been found to be the case.


I



II

## Results and Discussion

**A. Infrared Absorption Spectra. The 900–720 Cm.$^{-1}$ Region.**—It is known[6,7] that the out-of-plane deformation vibrations of the C–H bands of an aromatic nucleus absorb with moderate to strong intensity in the 900–650 cm.$^{-1}$ region. Orr and Thompson[6] reported that the strong band at 810–800 cm.$^{-1}$ exhibited by polycyclic aromatic compounds such as phenanthrene can be attributed to the 1,2,3,4-tetrasubstituted ring, and they have predicted that simple (*i.e.*, with only one aromatic ring) 1,2,3,4-tetrasubstituted benzene derivatives also would exhibit a strong band close to this value. We have found that the neosteroids (steroids with an aromatic B-ring) in fact do exhibit a single sharp band of moderate to strong intensity at 812–803 cm.$^{-1}$ (Fig. 1), thus confirming this prediction.[8] Compounds of this type without the D-ring, such as *sym*-octahydrophenanthrene, also exhibit a strong band in this region, although it is shifted to 795 cm.$^{-1}$. However, the results, as shown in Table I, reveal that this absorption is *not* exclusively characteristic of the 1,2,3,4-tetrasubstituted benzene derivatives, for the anthrasteroids (II) which have a double bond conjugated with the aromatic ring show a strong band in this region at 813–812 cm.$^{-1}$ (Fig. 2). Steroids with an aromatic A-ring or with aromatic A/B-rings also exhibit a sharp band of moderate to strong intensity at 819–803 cm.$^{-1}$.[9] The band near 810 cm.$^{-1}$ for the neosteroids, for the anthrasteroids with a double bond in conjugation with the aromatic ring, and for compounds like *sym*-octahydrophenanthrene is by far the strongest one (*ca.* 60% absorption for 15 mg./ml. in a 1-mm. cell) in the 900–720 cm.$^{-1}$ region (Figs. 1, 2), while the band near 810 cm.$^{-1}$ for the aromatic A-ring and aromatic A/B ring compounds is not always the strongest in this region (Fig. 3).

The compounds which contain a pentasubstituted aromatic ring, *e.g.*, the anthrasteroids, exhibit a band of weak to moderate intensity at 869–859 cm.$^{-1}$.[10] The strong absorption near 810 cm.$^{-1}$ is not exhibited, however, by those compounds, such

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[1] E. Mosettig and I. Scheer, *J. Org. Chem.*, **17**, 764 (1952).

[2] (a) W. R. Nes and E. Mosettig, THIS JOURNAL, **76**, 3182 (1954); (b) **76**, 3186 (1954).

[3] A. Windaus and C. Roosen-Runge, *Ber.*, **73**, 321 (1940).

[4] An alternate formula for the anthrasteroids is equally possible but it does not alter the substitution on the aromatic ring (ref. 2a.)

[5] See ensuing discussion for references.

[6] S. F. D. Orr and H. W. Thompson, *J. Chem. Soc.*, 218 (1950), and references cited therein.

[7] C. G. Cannon and G. B. B. M. Sutherland, *Spectrochimica Acta*, **4**, 373 (1951), and references cited therein.

[8] Recently P. J. Launer and D. A. McCaulay (*Anal. Chem.*, **23**, 1875 (1951)) have shown that 1,2,3,4-tetramethylbenzene likewise exhibits a band in this region as predicted.

[9] The acetates of the aromatic A-ring compounds exhibit a doublet of weak to moderate intensity at 822–813 cm.$^{-1}$.

[10] C. G. Cannon and G. B. B. M. Sutherland (ref. 7) have attributed this band to a pentasubstituted aromatic ring.

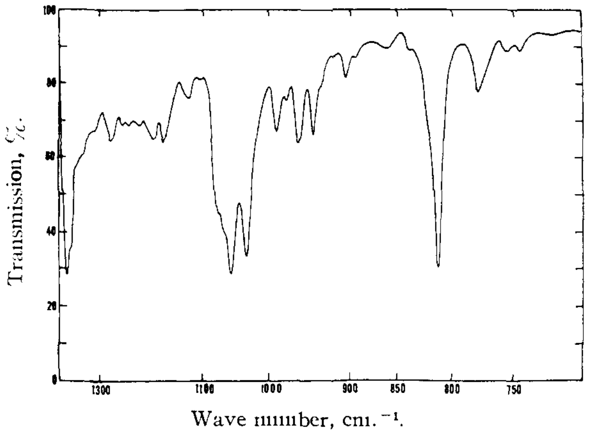

Fig. 1.—Infrared spectrum of dihydroneoergosterol (solvent carbon disulfide).

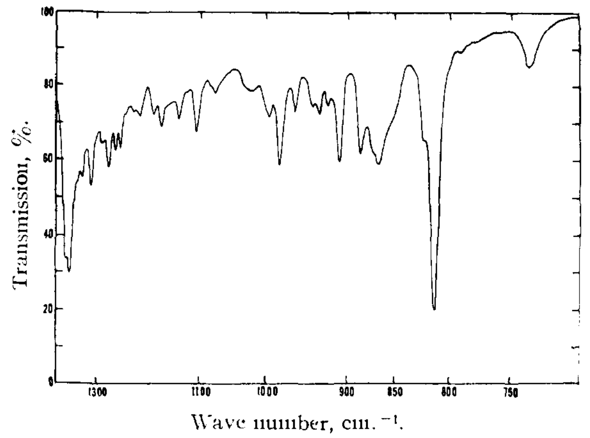

Fig. 2.—Infrared spectrum of anthracholestatetraene (solvent carbon disulfide).

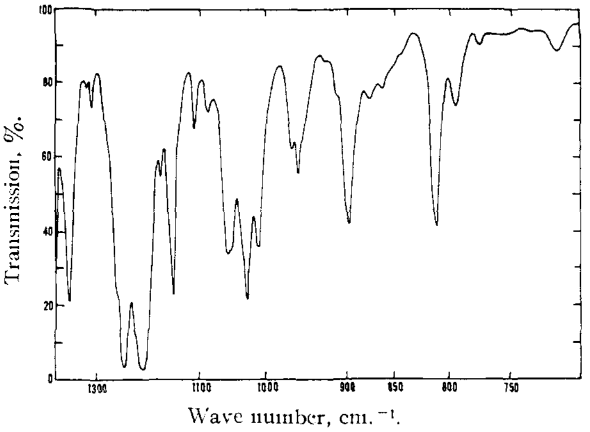

Fig. 3.—Infrared spectrum of $\alpha$-dihydroequilenin diacetate (solvent carbon disulfide).

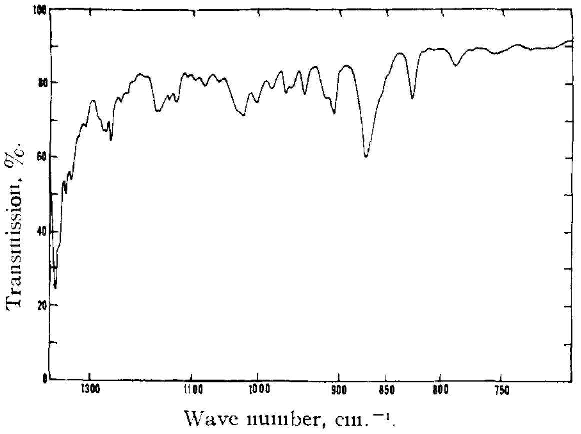

Fig. 4.—Infrared spectrum of anthraergostatriene (solvent carbon disulfide).

as anthraergostatriene, which do not have an ethylenic bond in conjugation with the aromatic ring (Fig. 4).

**The 1630–1565 Cm.$^{-1}$ Region.**—Differentiation between the types of compounds which have similar absorption near 810 cm.$^{-1}$ can be made by reference to their absorption in the C=C stretching region. Jones, *et al.*,[11] have shown that the steroids with aromatic A/B-rings exhibit three absorption maxima in this region at 1625, 1605 and 1573 cm.$^{-1}$. We found that the neosteroids (I) absorb at the same frequencies (1629–1621, 1603–1600 and 1577–1572 cm.$^{-1}$),[12] but the intensity of the absorption is only about 10% of that exhibited by the steroids with aromatic A/B-rings (Fig. 5). In the

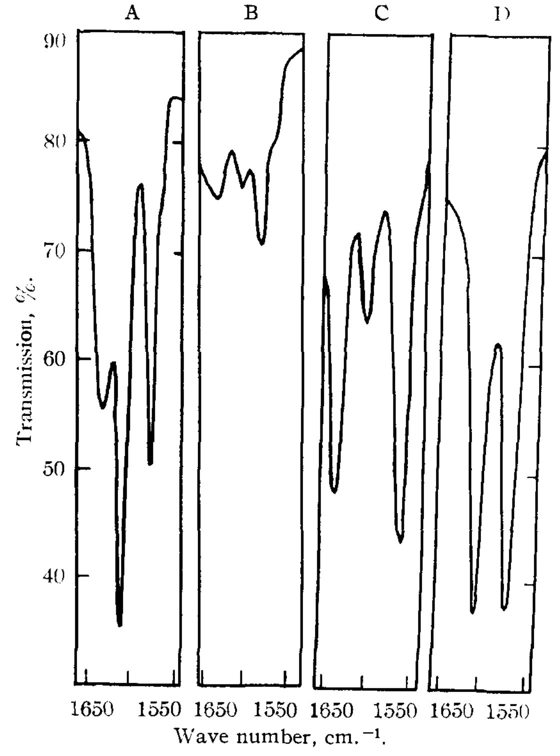

Fig. 5.—Infrared spectra in the C=C stretching region (solvent chloroform, 0.5-mm. micro-cell): A, equilenin acetate (*c* 50 mg./ml.); B, dihydroneoergosterol (*c* 200 mg./ml.); C, anthraergostapentaene (*c* 200 mg./ml.); D, anthracholestatriene (*c* 200 mg./ml.).

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[11] R. N. Jones, P. Humphries, E. Packard and K. Dobriner, This Journal, **72**, 86 (1950).

[12] Neoergostatriene is exceptional in that the bands occur at 1645, 1600 and 1572 cm.$^{-1}$. Also, 5,7,9-estratrien-17-ol does not show a band near 1625 cm.$^{-1}$ but a very broad band is present at 1610 cm.$^{-1}$ and a band of moderate intensity appears at 1572 cm.$^{-1}$.

### TABLE I

### POSITIONS OF ABSORPTION BANDS USED FOR CHARACTERIZING AROMATIC STEROIDS AND THEIR ANALOGS

| Compound[a] | Wave number, cm.$^{-1}$ | | | | | Wave length, mμ λmax.[c] (ε) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 900–720 cm.$^{-1}$ region[b] | | 1630–1565 cm.$^{-1}$ region | | | | | | | |
| | $CS_2$ | Nujol | $CHCl_3$ | | | | | | | |
| Class A: Tetrasubstituted benzenoid compounds with angular annulation | | | | | | | | | | |
| Neoergosterol[1] | 809 | 808 | 1629 | 1603 | 1575 | 269(600) | 278(440) | | | |
| Neoergosterol acetate[d] | 809 | 807 | 1629 | 1603 | 1575 | 269(550) | 278(420) | | | |
| Epineoergosterol[e] | 809 | 807 | 1629 | 1603 | 1577 | | | | | |
| Epineoergosterol acetate[e] | 809 | 812 | 1621 | 1603 | 1572 | | | | | |
| Dihydroneoergosterol[f] | 810 | 809 | 1629 | 1603 | 1577 | 269(400) | 278(310) | | | |
| Dihydroneoergosterol acetate[f] | 811 | 810 | 1623 | 1603 | 1577 | 269(380) | 278(280) | | | |
| Dihydroepineoergosterol[1] | 810 | 808 | 1626 | 1603 | 1575 | 270(410) | 279(310) | | | |
| Dihydroepineoergosterol acetate[e] | 810 | 810 | 1626 | 1603 | 1575 | | | | | |
| 3β-Hydroxy-$\Delta^{5,7,9(10)}$-22-iso-19-norspirostatriene[1] | 811 | | 1623 | 1603 | 1577 | 270(440) | 279(350) | | | |
| 3β-Acetoxy-$\Delta^{5,7,9(10)}$-22-iso-19-norspirostatriene[1] | 811 | | 1629 | 1603 | 1577 | 270(430) | 279(320) | | | |
| *dl*-5,7,9-Estratrien-17β-ol[g] | | 806 | | | | 270(430) | 279(360) | | | |
| *dl*-5,7,9-Estratrien-3β,17β-diol[g] | | 812 | | | | | | | | |
| *dl*-5,7,9-Estratrien-3β,17β-diol diacetate[g] | 808 | 812 | 1626 | 1603 | 1572 | 269(510)* | 278(340)* | | | |
| α-(3β-Acetoxy-5,7,9-estratrien-17-yl)-propionic acid[1] | 810 | | 1629 | 1603 | 1577 | 269(430)* | 278(310)* | | | |
| Methyl α-(3β-hydroxy-5,7,9-extratrien-17-yl)-propionate[1] | 810 | | 1626 | 1603 | 1572 | 269(450)* | 278(340)* | | | |
| Methyl α-(3β-acetoxy-5,7,9-estratrien-17-yl)-propionate[1] | 812 | | 1629 | 1603 | 1575 | 269(450)* | 278(340)* | | | |
| 3β-Hydroxy-17-acetyl-5,7,9-estratriene[h] | 808 | | 1629 | 1603 | 1575 | 269(540)* | 278(400)* | | | |
| 3β-Acetoxy-17-acetyl-5,7,9-estratriene[h] | 809 | | | | | 269(500)[i]* | 278(340)[i]* | | | |
| Neoergosterone[1] | 810 | 810 | 1629 | 1603 | 1577 | 269(604)[i]* | | | | |
| Neoergostatriene[j] | 805 | 803 | 1645 | 1600 | 1572 | 270(380)[i]* | 279(280)[i]* | | | |
| *sym*-Octahydrophenanthrene[i] | 795 | 794[m] | | | | 270(440)[i]* | 279(350)[i]* | | | |
| 2-Hydroxy-*sym*-octahydrophenanthrene[l] | 796 | | | | | 269(360)[i]* | 279(280)[i]* | | | |
| Class B: Pentasubstituted benzenoid compounds with angular annulation | | | | | | | | | | |
| 9-Methyl-*sym*-octahydrophenanthrene[2b] | 859 | 863[k] | | 1600 | 1572 | 271(399) | 277(331) | 281(355) | | |
| Class C: Tetrasubstituted benzenoid compounds with linear annulation | | | | | | | | | | |
| *sym*-Octahydroanthracene[2b] | | | | | | 270(980) | 275(1550) | 280(1360) | 285(1960) | |
| Class D: Pentasubstituted benzenoid compounds with linear annulation | | | | | | | | | | |
| Anthracholestatriene[h] | 866 | | | 1605 | 1570 | 273(650) | 277(546) | 283(690) | | |
| Anthraergostatriene[2a] | 869 | | | 1608 | 1567 | 273(670) | 278(550) | 282(695) | | |
| Methyl bisnoranthracholatriene[h] | 870 | | | 1600 | 1567 | 273(705) | 277(584) | 282(744) | | |
| 9-Methyl-*sym*-octahydroanthracene[2b] | 860 | | | 1608 | 1575 | 274(664) | 279(548) | 283(720) | | |
| Class E: Pentasubstituted benzenoid compounds with linear annulation and a conjugated double bond | | | | | | | | | | |
| Anthracholestatetraene[2a] | 812 | | 1631 | 1600 | 1563 | 222(23,900) | 227(25,400) | 266(17,000) | 296(2590) | 308(2040) |
| Anthraergostapentaene[2a] | 813 | | 1629 | 1600 | 1560 | 222(26,100) | 227(27,100) | 266(18,600) | 296(2760) | 308(2220) |
| Methyl bisnoranthracholatetraenate[h] | 813 | | 1631 | 1600 | 1558 | 221(24,800) | 227(26,300) | 266(17,000) | 296(2380) | 308(1970) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Class F: Naphthalenic compounds with angular annulation | | | | | | | | |
| 7-Acetoxy-1,2,3,4-tetrahydrophenanthrene[n] | 794 | 801 | | | | | | |
| *d*-Equilenin[o] | | 816 | | | | | | |
| Estrone[p] | | 819 | | | | | | |
| α-Estradiol[q] | | 819 | | | | | | |
| Estriol[o] | | 817 | | | | | | |
| Equilin[p] | | 807 | | | | | | |
| α-Dihydroequilenin[p] | | 809 | | | | | | |
| Estrone acetate | 820<br>814 | | | 1610 | 1585 | | | |
| Estradiol diacetate | 819<br>813 | | | 1611 | 1589 | | | |
| Estriol triacetate | 822<br>816 | | | | | | | |
| α-Dihydroequilenin acetate | 811 | | 1626 | 1603 | 1570 | | | |
| β-Dihydroequilenin acetate | 804 | | 1626 | 1603 | 1570 | | | |
| *dl*-Equilenin methyl ether[r] | 813 | | 1626 | 1600 | 1572 | | | |
| *d*-Equilenin acetate | 811 | | 1626 | 1603 | 1572 | | | |
| Class G: Benzenoid compounds with a hydroxymethyl or chloromethyl group | | | | | | | | |
| 9-Chloromethyl-*sym*-octahydroanthracene[h,b] | 868 | | | 1600 | 1570 | ...... | ...... | 292(1780) |
| 9-Hydroxymethyl-*sym*-octahydrophenanthrene[h,b] | 868 | | 1629sh | 1608 | 1575 | 272(379) | | |
| 9-Chloromethyl-*sym*-octahydrophenanthrene[h,b] | 868 | | | 1608 | 1575 | 272(560) | 278(570) | |

[a] References given are for the source or mode of preparation of these compounds. The spectroscopic data reported were determined in this Laboratory. [b] Only the significant band in this region is listed. [c] Determined on a Cary recording spectrophotometer unless otherwise noted. Solvent isoöctane unless marked with an asterisk indicating absolute alcohol as solvent. [d] A. Windaus and P. Borgeaud, *Ann.*, **460**, 235 (1928). [e] A. Windaus and M. Deppe, *Ber.*, **70**, 76 (1937). [f] R. E. Marker, *et al.*, THIS JOURNAL, **64**, 720 (1942). [g] W. E. Bachmann, A. S. Dreiding and E. F. M. Stephenson, *ibid.*, **73**, 2765 (1951). [h] The preparation and properties of this compound will be described in forthcoming publications from this Laboratory. [i] Beckman model DU spectrophotometer. [j] K. Bonstedt, *Z. physiol. Chem.*, **185**, 165 (1929). [k] Liquid smear spectrum. This is a doublet band. [l] See Experimental. [m] Liquid smear spectrum. [n] Dr. R. C. Elderfield. [o] Dr. L. A. Sweet, Parke, Davis & Co. [p] Mr. J. Carol, Food and Drug Administration, D. H. E. W. [q] Dr. G. Rosenkranz, Syntex S.A. [r] Dr. Wm. S. Johnson. [s] J. R. Durland and H. Adkins, THIS JOURNAL, **59**, 135 (1937).

spectra of the neosteroids (I) taken for routine qualitative survey (30 mg./ml. in a 0.5-mm. cell, solvent chloroform) there is no indication of the C=C stretching absorption whereas the absorption in the spectra of the steroids with aromatic A/B-rings is clearly apparent at this concentration. The anthrasteroids (II) with a double bond in conjugation with the aromatic ring exhibit characteristic absorption near 1630, 1600 and 1562 cm.$^{-1}$ with an intensity of the same order of magnitude as that of the neosteroids (I) (Fig. 5), thereby affording a means of differentiation of these compounds from the neosteroids and the steroids with aromatic A/B-rings. On the other hand, only two bands of equal intensity at 1608–1600 and 1575–1567 cm.$^{-1}$ are exhibited by the anthrasteroids which do not have a double bond conjugated with the aromatic ring (Fig. 5). Likewise, the aromatic A-ring steroids exhibit only two maxima at 1612 and 1590 cm.$^{-1}$ (Table I) as previously reported by Jones, *et al.*[11,13]

It is of interest that the spectra of the epimers in the neosteroid pairs, neoergosterol and epineoergosterol, dihydroneoergosterol and dihydroepineoergosterol, and their respective pairs of acetates, are identical when determined in carbon disulfide solutions of these compounds. The epimers exhibit different spectra, however, when determined as Nujol mulls.

**B. Ultraviolet Absorption Spectra.**—It has been well established[14] that the ultraviolet absorption of benzenoid compounds is influenced by the number and position of alkyl substituents. While not as much attention has been paid to the effect of changing the type of alkyl substituent, recent work[15] has

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(13) It should be noted that chloroform with very small amounts of water has a band at 1603–1600 cm.$^{-1}$ (H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 52, have assigned a strong band at 1615–1595 cm.$^{-1}$ to the bending frequency of the OH group in compounds such as water.) For this reason the intensities of absorption at this wave number were not reproducible despite precautions to keep the solvent and system either anhydrous or uniformly wet. However, the difference in intensity of the band near 1600 cm.$^{-1}$ for the steroids with aromatic A/B-rings compared to that for the neosteroids is too large to be accounted for on this basis and must be a real effect.

(14) For example, see M. S. Norris and N. D. Coggeshall, *Anal. Chem.*, **25**, 183 (1953).

(15) D. A. McCaulay, A. P. Lien and P. J. Launer (THIS JOURNAL, **76**, 2354 (1954)), for example, have demonstrated that the length of a substituent carbon chain and the degree of branching affect the posi-

shown that this too can have a definite influence on the absorption. We have found that the combination of these effects, *i.e.*, of the position, number and kind of substitution, produces changes in the fine structure of the so-called B-[16] or $\alpha$-[17] band of the absorption spectra which are significant enough to allow various types of benzenoid compounds to be differentiated.

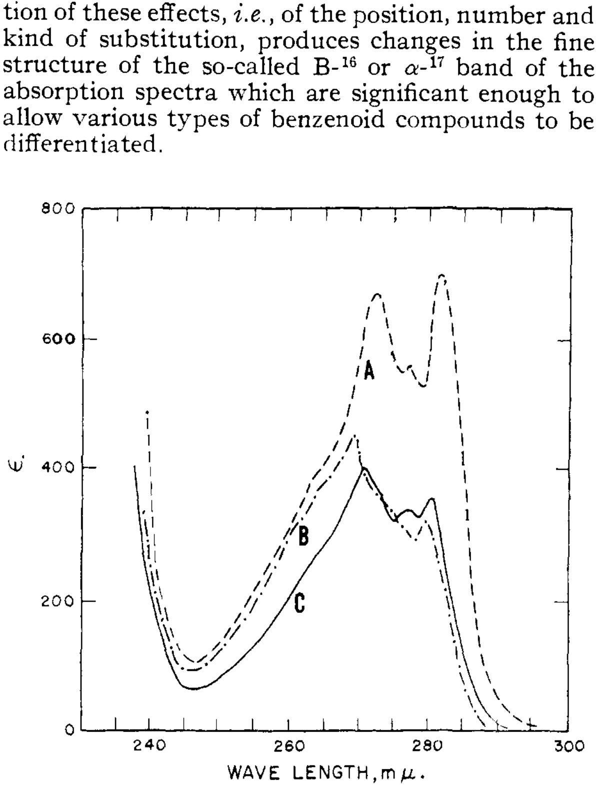

Fig. 6.—Ultraviolet spectra: A, anthraergostatriene (solvent isoöctane); B, typical neosteroid absorption (solvent abs. alcohol); C, 9-methyl-*sym*-octahydrophenanthrene (solvent isoöctane).

The neosteroids (angular annulation) possess *two* distinct maxima at 269–270 and 278–279 mμ,[18] the former having the larger extinction coefficient. The spectra of *sym*-octahydrophenanthrene,[19] 2-hydroxy-*sym*-octahydrophenanthrene and 1,2,3,4,7,8,9,10,11,12,12a,12b-dodecahydrochrysene[19] are, as expected, substantially the same as those of the neosteroids (I). The introduction of a methyl group on the benzenoid nucleus, as in 9-methyl-*sym*-octahydrophenanthrene, produces a marked change in the fine structure of the spectrum and *three* maxima are now evident at 271, 277 and 281 mμ, the first of these having the largest extinction coefficient. When the annulation is changed from angular to linear for the pentasubstituted compounds, *i.e.*, the change to the anthrasteroids and 9-methyl-*sym*-octahydroanthracene, the three maxima appear at 273–274, 278–279 and 282–283 mμ and the third or long wave length maximum now has the largest extinction coefficient. The spectrum[20] of *sym*-octahydroanthracene, which was the only compound available to us with linear annulation and no methyl substituent on the aromatic ring, showed the same fine structure as the corresponding pentasubstituted compound, but the inflection at *ca.* 265 mμ was resolved, the whole system was shifted to the red, and the intensity of absorption was increased considerably.

Thus, compounds with angular annulation such as the neosteroids (I) possess spectra as in Fig. 6B, while compounds with linear annulation and a methyl group substituted on the benzenoid ring such as the anthrasteroids (II) possess spectra as in Fig. 6A. Although neosteroids with a methyl group on the benzenoid ring were not available for this study, it is to be expected that their absorption would be similar to that of 9-methyl-*sym*-octahydrophenanthrene (Fig. 6C).

If an atom with lone electron pairs is introduced on the alkyl substituent of the benzenoid ring of these compounds (as in the hydroxymethyl and chloromethyl derivatives in Table I), then the spectra do not conform to these generalizations. Spectral differentiation in the ultraviolet region has been possible, however, between the three compounds at our disposal. This has been discussed in an earlier publication[2a] in which a generalization was found that can include these compounds. The chloro compounds, in addition, can be distinguished from the others by the position of the minimum of absorption which is displaced *ca.* 18 mμ to the longer wave lengths, *i.e.*, from *ca.* 245 to *ca.* 263 mμ.

## Experimental

A Perkin–Elmer model 21 double beam spectrophotometer with sodium chloride optics was used with the settings as follows: resolution 4, response 1, gain 6.5, suppression 0, scanning speed 3 min./μ. Atmospheric water vapor and carbon dioxide as well as ammonia gas were used for calibration. The estimated errors in the frequencies reported are ±5 cm.$^{-1}$ in the 1700–1500 cm.$^{-1}$ region and ±2 cm.$^{-1}$ in the 1200–650 cm.$^{-1}$ region.

The spectra from 5000–650 cm.$^{-1}$ were determined in carbon disulfide solutions and/or as Nujol mulls. The carbon disulfide solutions (15 mg./ml.) were examined in a sealed sodium chloride cell approximately 1 mm. in thickness. A matched cell filled with solvent was used for compensation. The mulls were prepared by grinding approximately 5 mg. of material in one drop of Nujol for five minutes. A salt plate was used as compensation. The spectra from 2000–1500 cm.$^{-1}$ were examined in chloroform solution using a 0.5-mm. sealed sodium chloride cell at concentrations of 100–200 mg./ml.

The carbon disulfide was purified by distillation over phosphorus pentoxide. The chloroform was prepared by shaking reagent grade chloroform with 0.1 its volume of concentrated sulfuric acid; the organic layer was washed with water, 3 *N* sodium hydroxide solution, and again with water, dried over calcium chloride, and distilled. The distillate was stabilized by adding 0.1 to 0.5% of absolute ethyl alcohol.

The ultraviolet spectra were determined in "Spectro Grade" isoöctane or absolute ethanol (as indicated in Table I) on a Cary recording spectrophotometer, model 11.

**2-Hydroxy-*sym*-octahydrophenanthrene.**—A mixture of 2.0 g. of twice-distilled 7-hydroxy-1,2,3,4-tetrahydrophen-

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tion of absorption, and L. Lang and M. Vizesy (*Acta Chim.* (*Hungary*), **4**, 1 (1954)) demonstrated that the benzenoid absorption is affected when an asymmetric center in the side chain of a substituted benzene is inverted.

(16) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1954, p. 125.

(17) E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin/Göttingen/Heidelberg, 1952, pages 27–28.

(18) The existence of this second maximum was not recognized in most of the earlier papers. For references see L. Dorfman, *Chem. Revs.*, **53**, 47 (1953).

(19) See also F. A. Askew, *J. Chem. Soc.*, 512 (1935).

(20) See also R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Fig. 14.

anthrene,[21] 0.4 g. of sodium hydroxide, 10 ml. of ethanol and 2.0 g. of Raney nickel was shaken in a hydrogen atmosphere at 3000 p.s.i. and 100° for 24 hr. The mixture was filtered through a Celite mat and the solution concentrated to dryness. The residue was dissolved in 20 ml. of benzene and chromatographed on ethyl acetate-washed alumina. Elution with benzene yielded 1.1 g. of **2-hydroxy-*sym*-octahydrophenanthrene** with a low melting point. Distillation of this material at a bath temperature of 180° and 0.5 mm. and crystallization from ether afforded 0.9 g. of white needles, m.p. 128–129.5° (capillary m.p., corrected).

*Anal.*[22] Calcd. for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 83.1; H, 9.1.

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[21] We are grateful to Dr. R. C. Elderfield for a generous supply of this material.

[22] The microanalysis is by the Analytical Service Laboratory of this Institute under the direction of Dr. William C. Alford.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# Bromination of 5α,6β-Dibromocholestane-3-one

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Reinvestigation of the bromination of 5α,6β-dibromocholestane-3-one has shown that the initial products, depending upon the conditions, are the 2α- and 2β-bromo derivatives II and III and that further bromination affords the 2α,2β,5α,6β-derivative IV. The structures were established largely by dehydrohalogenations conducted with collidine under non-rearrangement conditions; the configurations of the bromine substituents were established by synthetic operations. Transformations of the bromo ketones are accounted for, and the structures and configurations assigned accord with established ultraviolet and infrared absorption data.

In 1936, Inhoffen[1] and Butenandt and Schramm[2] investigated the monobromination of 5α,6β-dibromocholestane-3-one[3] (I) under slightly different conditions and obtained different tribromo ketones. Inhoffen's product, m.p. 138°, resulted from bromination in ether–acetic acid; Butenandt and Schramm's product, 106°, was obtained by bromination in acetic acid alone. Since both tribromo ketones on further bromination yielded the same tetrabromo ketone they were regarded as stereoisomers, an inference confirmed by Corey's observation[4] that the lower-melting tribromo ketone is converted by ethereal hydrogen chloride into the higher-melting isomer.

Both Inhoffen and Butenandt and Schramm regarded the two epimeric tribromo ketones as 4,5,6-derivatives and the tetrabromo ketone as the 4,4,-5,6-derivative mainly on the apparent evidence of three transformations. One was conversion of both tribromo ketones by the action of boiling ethanol into 6-ethoxy-$\Delta^{4,6}$-cholestadiene-3-one, the enol ethyl ether of $\Delta^4$-cholestene-3,6-dione.[1,2] A second was formation of cholestane-3,6-dione in 60% yield from the lower-melting tribromo ketone on treatment with sodium iodide followed by reaction with potassium acetate (200°, five hours).[2] The third transformation considered to support the postulated structures was conversion of Inhoffen's tribromo ketone and of the tetrabromo ketone on drastic treatment with potassium acetate into the enol acetate of diosterol-II, at the time formulated as 4-acetoxy-$\Delta^{4,6}$-cholestadiene-3-one, but now considered to be 3-acetoxy-$\Delta^{2,5}$-cholestadiene-4-one.[5] The second and third transformations involve reaction with potassium acetate at a high temperature, which is now known to be accompanied rather frequently by rearrangement.[6] The only reaction with potassium acetate at room temperature reported was that of Inhoffen's tribromo ketone. The product, originally formulated as 4,6-dibromo-$\Delta^4$-cholestene-3-one, has since been shown to be a 2,6-dibromo-$\Delta^4$-cholestene-3-one,[7] and hence this evidence favors location of the bromine introduced by substitution at position 2 rather than 4.

Another reason for questioning the original formulations is that bromination of A/B *trans* 3-ketones ordinarily gives rise to 2-bromo derivatives, even when the 5α-hydrogen is replaced by a substituent, such as a hydroxyl group.[8] Moreover the ultraviolet absorption characteristics of the transformation products are such as to throw some doubt on the assigned structures.[9]

Since dehydrohalogenation with collidine is seldom attended with rearrangements,[10] we have studied the reaction of the polysubstituted ketones with this reagent. The results show that the tribromo ketones are 2,5,6-derivatives. Brief treatment of either isomer II or III with collidine results in elimination of two equivalents of hydrogen bromide with formation of a bromodienone, which has

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[1] H. H. Inhoffen, *Ber.*, **69**, 1134, 1702 (1936).

[2] A. Butenandt and G. Schramm, *ibid.*, **69**, 2289 (1936).

[3] The configuration of the bromine atoms since has been established by D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 1066 (1950).

[4] E. J. Corey, *ibid.*, **76**, 175 (1954).

[5] L. F. Fieser, M. Fieser and S. Rajagopalan, *J. Org. Chem.*, **13**, 800 (1948).

[6] Examples: 2α-bromocholestane-3-one → $\Delta^5$-cholestene-4-one, A. Butenandt and G. Ruhenstroth-Bauer, *Ber.*, **77**, 397 (1944); 2α,4α-dibromocholestane-3-one → cholestane-3,4-dione; 2-bromo-5-chlorocholestane-3-one → cholestane-3,6-dione and cholestane-3,4-dione, A. Butenandt, G. Schramm, A. Wolff and H. Kudszus, *ibid.*, **69**, 2779 (1936); 6β-bromo-$\Delta^4$-cholestene-3-one → 2α-acetoxy-$\Delta^4$-cholestene-3-one, L. F. Fieser and M. A. Romero, THIS JOURNAL, **75**, 4716 (1953).

[7] C. Djerassi, G. Rosenkranz, J. Romo, St. Kaufmann and J. Pataki, *ibid.*, **72**, 4534 (1950).

[8] B. Ellis and V. Petrow, *J. Chem. Soc.*, 1078 (1939); 2194 (1950).

[9] L. Dorfman, *Chem. Revs.*, **53**, 47 (1953).

[10] Dehydrohalogenation of 2α-bromochloestane-3-one with collidine affords $\Delta^4$-cholestene-3-one as a minor product (12–23% yield), but the major product is the expected $\Delta^1$-cholestene-3-one; C. Djerassi and C. Schultz, THIS JOURNAL, **69**, 2404 (1947).