# SYNTHESIS AND INFRARED SPECTRA OF SOME 3α-HYDROXY $\Delta_5$-STEROIDS

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## ABSTRACT

A generally applicable method for the preparation of 3α-hydroxy $\Delta_5$-steroids is used to obtain 3α-hydroxyandrost-5-ene, 3α-hydroxypregn-5-ene, 3α-hydroxypregn-5-ene-20-one and their corresponding acetates. The infrared spectra of these compounds and of 3α-hydroxycholest-5-ene and 3α-hydroxyandrost-5-ene-17-one, known steroids, are measured in the range of 3700-900 $cm^{-1}$ and the characteristic group frequencies reported.

The characteristic group frequencies of 3-hydroxysteroids [1-4] and 3-acetoxysteroids [3, 5, 6] have already been reported. The spectra of 3α-hydroxy $\Delta_5$-steroids, however, have not yet been determined. In the present work, the infrared spectra of these compounds were measured and surveyed. For this purpose, a suitable general method for the preparation of 3α-hydroxy $\Delta_5$-steroids was sought and a number of such compounds was prepared : 3α-hydroxyandrost-5-ene and 3α-hydroxypregn-5-ene, not until now described, 3α-hydroxypregn-5-ene-20-one already prepared by another method [7] and the known 3α-hydroxycholest-5-ene [8, 9, 10, 11] and 3α-hydroxyandrost-5-ene-17-one [12, 13]

## I. - SYNTHESIS

Ruzicka et al. [12] prepared 3α-hydroxyandrost-5-ene-17-one from androst-5-ene-3, 17-dione on partial hydrogenation in alcohol in the presence of Raney nickel. Butenandt et al. [7] applied the same reaction to the preparation of 3α-hydroxypregn-5-ene-20-one from pregn-5-ene-3, 20-dione. Several methods relating to the isomerisation of 3β-hydroxy $\Delta_5$-steroids

into 3α-hydroxy $\Delta_5$-steroids have also been studied. Barnett et al. [8] obtained epicholesterol by refluxing cholesterol in xylene in the presence of aluminium isopropoxide. Fieser [9] prepared epicholesterol by reaction of sodium dichromate with cholesterol in a benzene-acetic acid solution and subsequent chromatography on alumina of the resulting complex. These methods generally give pure substances in a low yield. The five-step synthesis by which Plattner et al. [10,11] converted cholesterol to epicholesterol and by which Williams et al. [13] prepared 3α-hydroxyandrost-5-ene-17-one was found to be more efficient. In the present study, this method has been applied with minor modifications.

To begin with , 3β-hydroxy $\Delta_5$-steroids, the starting material, were submitted to p. nitroperbenzoic acid oxidation[14] and gave the corresponding α-epoxide as principal product ; p. nitroperbenzoic acid was chosen because of its stability and reactivity. The crude epoxides, about 80 % yield, melted within 5 to 10 degrees, range which indicated the presence of a small amount of β-epoxide ; as earlier studies had shown, peracid oxidation of $\Delta_5$-steroids gives α and β isomers in yields varying according to steroid structure and experimental procedure [10,15]. Chromatography on alumina column of crude 3β-hydroxy-5,6-epoxyandrostane failed to separate the pure β-epoxide although it is less polar[10] than the corresponding α-isomer. However, fractionnal crystallization from methanol or acetone allowed pure α-epoxide to be obtained. When crude epoxide samples and analytical samples of α-epoxide were compared, the infrared spectra appeared to be identical ; in view of this fact, it was assumed that the β-epoxide yield was low enough to perform the following steps of the synthesis on the crude epoxide.

3β-hydroxy-5,6-epoxysteroids were reduced with LAH in tetrahydrofuran according to the procedure of Plattner et al. [16]. After destroying the excess of LAH, quick filtration of the alumina sludge (in order to avoid steroid adsorption) and subsequent extraction, yielded about 80 % of 3β,5α-dihydroxyandrostane while the same procedure gave only about 60 % of the two dihydroxypregnanes.

According to the original technique, treatment of 3β,5α-dihydroxy-

steroids with methanesulfonyl chloride in pyridine afforded the corresponding 3β-methanesulfonyloxy derivatives in about 90 % yield.

The epimerization was performed by refluxing the mesylates with acetyl chloride and diethylaniline in chloroform. Saponification by refluxing the epimerized products with 10 % potassium hydroxide in aqueous methanol gave the corresponding 3α-hydroxy derivatives mixed with some secondary reaction products.

Chromatography on a short column packed with neutral alumina deactivated with 6 % water, allowed the elimination of hydrocarbons, small amounts of incompletely saponified acetates and polar impurities. The overall average of epimerization was about 33 %.

A final chromatography was performed according to Reichstein's procedure [17] in order to obtain pure steroids for physical measurements.

The synthesis of 3α-hydroxyandrost-5-ene (Va) and 3α-hydroxypregn-5-ene (Vb) required initial reduction of the carbonyl groups of DHA and pregnenolone respectively. The Wolff-Kishner reduction technique, modified by Huang-Minlon [18] and applied to DHA, furnished 3β-hydroxyandrost-5-ene (Ia) in 86 % yield ; hydrazone was formed with gentle reflux of the oxo-steroid with hydrazine hydrate in diethylene glycol in the presence of sodium hydroxide ; then, without isolation, hydrazone was reduced by raising temperature to 195° and refluxing for 5 hours more. Surprisingly enough, the same technique applied to 3β-hydroxypregn-5-ene-20-one yielded the corresponding reduced derivative (Ib) in about 40 % only. In view of this fact, the two-step procedure described by A. Cavé [19], which allows reduction of the carbonyl group at $C_{(20)}$ with a good yield, was substituted for the previous process with advantage. The hydrazone prepared in the usual way was isolated in the first step ; the second step involved its reduction by refluxing with sodium in diethylene glycol for 24 hours. This procedure gave Ib in 79 % yield.

The synthesis of 3α-hydroxypregn-5-ene-20-one (Vc) involved the conversion of the $C_{(20)}$ carbonyl group into the corresponding ethylene ketal in order to prevent the effect of subsequent LAH reduction. The starting ma-

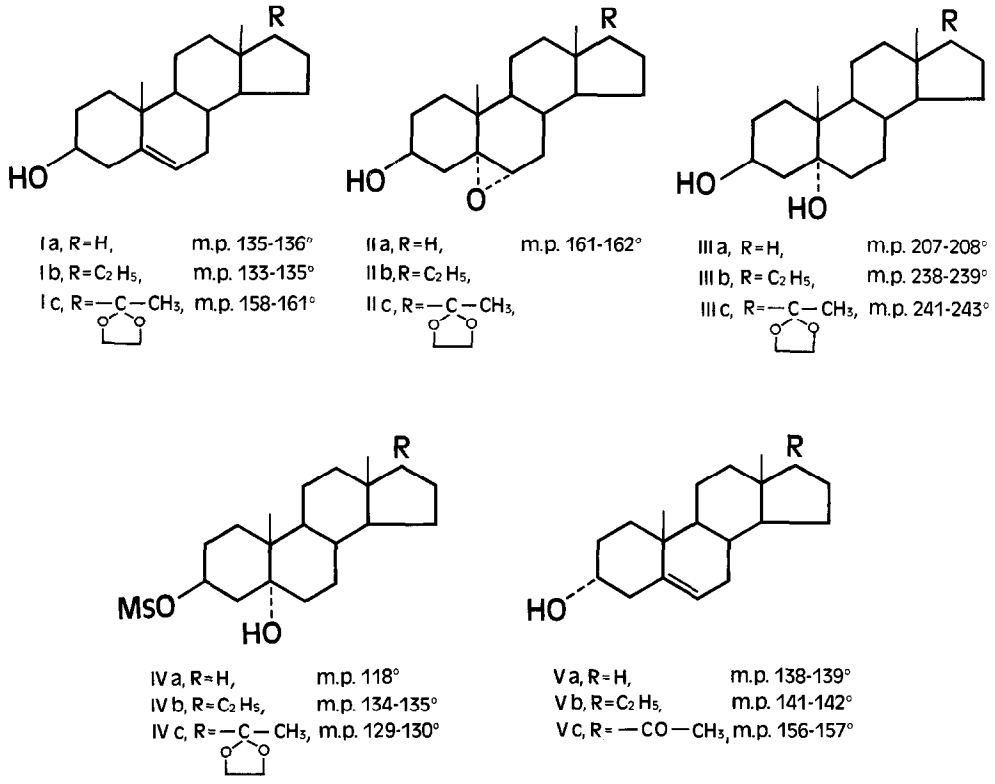


Fig. 1. Synthesis of $\Delta_5$-steroids.

terial was refluxed in benzene with ethylene glycol in the presence of p.toluenesulfonic acid according to the classic procedure. It is worth mentionning that 3$\beta$-hydroxypregn-5-ene-20-one required refluxing overnight to give the corresponding ethylene ketal Ic in 78 % yield while three hours are sufficient to obtain a similar yield of $C_{(17)}$ ethylene ketal.

Ethylene ketal (Ic) was cleaved by refluxing in acid medium after saponification of the epimerized corresponding product and without isolation of the intermediates.

## EXPERIMENTAL

### PREPARATION OF 3$\alpha$-HYDROXYANDROST-5-ENE

#### 3$\beta$-hydroxyandrost-5-ene (Ia)

To a solution of 3$\beta$-hydroxyandrost-5-ene-17-one (10 g) in diethylene glycol (150 ml) were added 98 % hydrazine hydrate (25 ml) and sodium hydroxide

(15 g). After refluxing for three hours, the water was drained from the condenser and the temperature allowed to rise to 195° ; refluxing was then continued for another five hours. The cooled solution was poured into ice and water, and one drop of concentrated hydrochloric acid was added. The precipitate was filtered and washed with water till neutral. Recrystallization from methanol yielded 7.6 g of 3β-hydroxyandrost-5-ene (Ia) m.p. 135-136° ; lit. (20) 136-137.

3β-hydroxy-5α,6α-epoxyandrostane (IIa)

p. Nitroperbenzoic acid (4 g or 22 mmoles) was added to a solution of 3β-hydroxyandrost-5-ene (6 g or 22 mmoles) in methylene chloride-benzene 9/1 and the mixture was stirred overnight at room temperature ; the insoluble material was filtered off and the filtrate washed twice with a 10 % potassium carbonate solution and twice with water, dried and evaporated. The resulting mixture (5.2 g), m.p.152-160°, was predominantly 3β-hydroxy-5α,6α-epoxyandrostane (IIa) which could be obtained in pure form by fractionnal crystallization from methanol or acetone. The analytical sample melted at 161-162°.

$\nu_{max.}^{CS_2}$ : 3610 ; $\nu_{max.}^{KBr}$ : 1160, 1091, 1060, 1038, 1015, 962, 918, 902, 871-864, 793 $cm^{-1}$.

Anal. Calcd. for $C_{19}H_{30}O_2$ : C, 78.57 ; H, 10.41
Found : C, 78.72 ; H, 10.59

Acetylation of IIa with acetic anhydride and pyridine in equal volume for two days at room temperature yielded 3β-acetoxy-5α,6α-epoxyandrostane, m.p.119-121°.

$\nu_{max.}^{KBr}$ : 1735, 1238, 1028, 960, 868, 800 $cm^{-1}$

Anal. Calcd. for $C_{21}H_{32}O_3$ : C, 75.86 ; H, 9.70
Found : C, 75.53 ; H, 9.74

3β,5α-dihydroxyandrostane (IIIa)

Crude 3β-hydroxy-5,6-epoxyandrostane (4 g) was refluxed for half an hour with lithium aluminium hydride (1.5 g) in anhydrous tetrahydrofuran freshly distilled from LAH. The excess reagent was destroyed with ethyl acetate, and a 10 % sodium hydroxide solution was added ; this formed a sludge which was separated from the solution by filtration. The sludge and the solution were extracted separately with ethyl acetate. The extracts were combined, washed with water till neutral, dried and the solvent was evaporated. Three crystallizations from acetone gave 2.4 g of 3β,5α-dihy-

droxyandrostane (IIIa) m.p.207-208°. Concentration of the mother liquor yielded an additional 0.9 g of IIIa, m.p. 203-205°.

$\nu_{max.}^{CS_2}$ : 3612; $\nu_{max.}^{KBr}$ : 1040, 1028, 998, 982, 960, 920, 910, 868, 818 $cm^{-1}$.

Anal. Calcd. for $C_{19}H_{32}O_2$ : C, 78.03 ; H, 11.03
Found : C, 78.15 ; H, 11.25

Acetylation of IIIa in the usual manner with acetic anhydride and pyridine gave 3β-acetoxy-5α-hydroxyandrostane, m.p. 164-165°.

$\nu_{max.}^{CS_2}$ : 3624, 3598, 3450 ; $\nu_{max.}^{KBr}$ : 1705, 1265, 1250, 1050, 1020, 962, 828 $cm^{-1}$.

Anal. Calcd. for $C_{21}H_{34}O_3$ : C, 75.40 ; H, 10.25
Found : C, 75.30 ; H, 10.27

3β-methanesulfonyloxy-5α-hydroxyandrostane (IVa)

Methanesulfonyl chloride (3 ml) was added to a cooled solution (10°) of 3β,5α-dihydroxyandrostane (2 g) in pyridine (50 ml) ; the mixture was allowed to stand at room temperature for two hours. After dilution with ice and water, the resultant mixture was extracted with ethyl acetate. The extract was washed successively with diluted sulfuric acid, diluted sodium hydroxide and then with water till neutral ; the solution was dried and the solvent evaporated. Trituration of the residue with a small portion of isooctane immediately gave silky crystals of 3β-methanesulfonyloxy-5α-hydroxyandrostane (IVa), (2.3 g) m.p. 118° with decomposition.

$\nu_{max.}^{KBr}$ : 1165, 1155, 998, 978, 935, 920, 868, 818 $cm^{-1}$

3α-hydroxyandrost-5-ene (Va)

Acetylchloride (25 ml) and diethylaniline (25 ml) were added to a solution of 3β-methanesulfonyloxy-5α-hydroxyandrostane (2.2 g) in chloroform (25 ml); the mixture was refluxed for five hours. The solution was then concentrated and extracted with ethyl acetate. The extract was washed successively with diluted sulfuric acid, diluted sodium hydroxide and then with water till neutral ; the solution was dried and the solvent evaporated. The greenish semicrystalline residue was directly saponified by refluxing with 10 % methanolic potassium hydroxide for thirty minutes. After concentration, the solution was extracted with ethyl acetate. The extract was washed twice with water and dried. Evaporation of the dried solution left a residue which, after crystallization from acetone, yielded 1.4 g of crude product ; this was passed through a short column of neutral alumina (Woelm) grade

III (15 g). The purified product (1.15 g) was carefully chromatographed on neutral alumina grade II (35 g) and eluted with hexane-benzene 9/1 (m.p. 135-137°). Recrystallization of the eluates from methanol gave 0.835 g of 3α-hydroxyandrost-5-ene, (138-139°).

Anal. Calcd. for $C_{19}H_{30}O$ : C, 83.15 ; H, 11.02
Found : C, 83.34 ; H, 11.11

A solution of Va in a mixture of acetic anhydride and pyridine in equal volume was refluxed for two hours and then allowed to stand overnight at room temperature. The usual work-up followed by recrystallization from methanol gave 3α-acetoxyandrost-5-ene, m.p. 129-131°.

Anal. Calcd. for $C_{21}H_{32}O_2$ : C, 79.70 ; H, 10.19
Found : C, 79.57 ; H, 10.20

## PREPARATION OF 3α-HYDROXYPREGN-5-ENE

### 3β-hydroxypregn-5-ene (Ib)

A mixture of 3β-hydroxypregn-5-ene-20-one (5 g), methanol (200 ml) and 98 % hydrazine hydrate (20 ml) was refluxed for three hours and then cooled in ice. The precipitate (2 g) was collected. The mother liquor was diluted and the precipitate obtained was filtered and recrystallized from methanol (2.9 g). The hydrazone (4.9 g) was dissolved in 98 % hydrazine hydrate (17 ml) and a solution of sodium in diethylene glycol (230 ml) was added. After refluxing for 24 hours and cooling, the mixture was poured into 600 ml of water and the whole extracted with ether. The extract was washed twice with water, dried, and the solvent evaporated. Recrystallization from methanol gave 3.1 g of 3β-hydroxypregn-5-ene (Ib) m.p. 133-135°; lit. (21) 134,5-135,5. Concentration of the mother liquor yielded an additional 0.65 g of Ib, m.p. 130-133°.

### 3β,5α-dihydroxypregnane (IIIb)

The transformation of Ib into Vb was carried out in the same manner as Ia-Va. In this instance, reduction of crude 3β-hydroxy-5,6-epoxypregnane (IIb), 2.6 g, m.p. 155-158°, gave 1.3 g of 3β, 5α -dihydroxypregnane (III b) m.p. 238-239° (60 % yield).

$\nu_{max.}^{CS_2}$ : 3612 ; $\nu_{max.}^{KBr}$ : 1040, 962, 952, 933, 916, 910, 869, 818 $cm^{-1}$

Anal. Calcd. for $C_{21}H_{36}O_2$ : C, 78.69 ; H, 11.32
Found : C, 78.52 ; H, 11.44

3β-methanesulfonyloxy-5α-hydroxypregnane (IVb)

m.p. 134-135° (90 % yield).

$\nu_{max.}^{KBr}$ : 1162, 1155, 1001, 979, 940, 870, 818 $cm^{-1}$

3α-hydroxypregn-5-ene (Vb)

By recrystallization from methanol of the hexane-benzene 9/1 eluates, 3α-hydroxypregn-5-ene (Vb), m.p. 141-142° was obtained.

Anal. Calcd. for $C_{21}H_{34}O$ : C, 83.38 ; 11.33
Found : C, 83.41 ; 11.19

Vb was acetylated by the same procedure as Va. 3α-acetoxypregn-5-ene, m.p. 113-115° was obtained.

Anal. Calcd. for $C_{23}H_{36}O_2$ : C, 80.18 ; H, 10.53
Found : C, 79.99 ; H, 10.60

PREPARATION OF 3α-HYDROXYPREGN-5-ENE-20-ONE

3β-hydroxypregn-5-ene-20-one ethylene ketal (Ic)

To a solution of 3β-hydroxypregn-5-ene-20-one (6 g) in benzene (300 ml) was added ethylene glycol (9 ml) and p. toluenesulfonic acid (0.180 g). An azeotropic distillation was slowly performed overnight. The apparatus was designed to allow the solvent to be dried continuously over anhydrous sodium sulfate while refluxing [22]. Benzene was then washed with 2N sodium hydroxide and with water till neutral, dried and evaporated. From the first methanol crystallization, 4.7 g of 3β-hydroxypregn-5-ene-20-one ethylene ketal (Ic), m.p. 158-161° were obtained ; lit. (23) 160-161°.

3β,5α-dihydroxypregnane-20-one ethylene ketal (IIIc)

The transformation of Ic into Vc was carried out in the same manner as Ia-Va. Reduction of the crude epoxide, 3β-hydroxy-5,6-epoxypregnane-20-one ethylene ketal (IIc), m.p. 160-165°, by LAH gave 3β,5αdihydroxypregnane-20-one ethylene ketal, m.p. 241-243°.

$\nu_{max.}^{CS_2}$ : 3612 ; $\nu_{max.}^{KBr}$ : 1260, 1233, 1210, 1123, 1062, 1042, 1015, 944, 919, 880 $cm^{-1}$.

Anal. Calcd. for $C_{23}H_{38}O_4$ : C, 72.97 ; H, 10.11
Found : C, 73.12 ; H, 10·25

Epimerization was performed on 3β-methanesulfonyloxy-5α-hydroxy-pregnane-20-one ethylene ketal, (IVc) m.p. 129-130°.

$\nu_{max.}^{KBr}$ : 1170, 1068, 1050, 1030, 962, 930, 864, 829 $cm^{-1}$

3α-hydroxypregn-5-ene-20-one (Vc)

After saponification of the resulting product of epimerization, ethylene ketal was cleaved by refluxing (15 minutes) in the presence of concentrated hydrochloric acid (1 ml). Crystallization from isooctane of hexane-benzene 5/5 and 4/6 eluates gave 3α-hydroxypregn-5-ene-20-one (Vc), m.p. 156-157°; lit. (7) 148-152.

Anal. Calcd. for $C_{21}H_{32}O_2$ : C, 79.70 ; H. 10.19
Found : C, 79.74 ; H, 10.25

Vc, acetylated by the procedure described above, gave 3α-acetoxypregn-5-ene-20-one, m.p. 146-148° ; lit. (7) 147°.

The melting points were taken on a micro-hot stage Rotax (A. Balzer) and corrected. Organic solutions were dried over anhydrous sodium sulfate and solvents removed with a rotating film evaporator at the water pump. All solvents used were previously purified.

## II. - INFRARED SPECTRA

### Experimental method and results.

The spectra were measured in carbon disulfide solution and in potassium bromide dispersion on Perkin-Elmer spectrometer using lithium fluoride prism (range 3700-3500 $cm^{-1}$) or sodium chloride prism (range 1800-780 $cm^{-1}$). The position of the characteristic bands for the individual compounds are listed in Table I and summarized in Table II. Representative spectra are shown in Figs. 2 and 3.

### Discussion.

#### 3-HYDROXY $\Delta_5$-STEROIDS

In the range of 3700-3500 $cm^{-1}$, where absorption associated with an

TABLE I. - CHARACTERISTIC GROUP FREQUENCIES IN THE INFRARED

| Compounds | Solvent | Characteristic bands ($cm^{-1}$) | | | | |
|---|---|---|---|---|---|---|
| 3α-hydroxyandrost-5-ene | $CS_2$ | 3605 | 3578 | 1177 | 1162 | 1140 |
| | KBr | | | 1190 | 1164 | 1140 |
| 3α-hydroxypregn-5-ene | $CS_2$ | 3605 | 3578 | 1179 | 1163 | 1140 |
| | KBr | | | 1188 | 1168 | 1141 |
| 3α-hydroxycholest-5-ene | $CS_2$ | 3605 | 3578 | 1180 | 1164 | 1140 |
| | KBr | | | 1189 | 1163 | 1140 |
| 3α-hydroxyandrost-5-ene-17-one | $CS_2$ | 3606 | 3582 | 1180 | 1165 | 1140 |
| | KBr | | | 1191 | 1162 | 1138 |
| 3α-hydroxypregn-5-ene-20-one | $CS_2$ | 3606 | 3582 | 1180 | 1165 | 1140 |
| | KBr | | | 1186 | | 1143 |
| 3α-acetoxyandrost-5-ene | $CS_2$ | 1250 | 1239 | 1225 | 1148 | 1110 |
| | KBr | 1259 | 1241 | 1231 | 1148 | 1110 |
| 3α-acetoxypregn-5-ene | $CS_2$ | 1245 | 1235 | 1222 | 1145 | 1110 |
| | KBr | 1258 | 1240 | 1228 | 1150 | 1113 |
| 3α-acetoxycholest-5-ene | $CS_2$ | 1245 | 1238 | 1228 | 1149 | 1110 |
| | KBr | 1259 | 1239 | 1230 | 1148 | 1109 |
| 3α-acetoxyandrost-5-ene-17-one | $CS_2$ | 1242 | 1235 | 1220 | 1148 | 1105 |
| | KBr | 1252 | 1234 | 1228 | 1150 | 1108 |
| 3α-acetoxypregn-5-ene-20-one | $CS_2$ | 1245 | 1230 | | 1145 | 1108 |
| | KBr | 1249 | 1220 | | 1140 | 1105 |

O-H stretching motion occurs, 3α-hydroxy $\Delta_5$-steroids show a doublet while the other 3-hydroxysteroids exhibit a single band of simple contour ; changes in the relative intensities of these two bands occur on the introduction of a ketone group at $C_{(17)}$ or $C_{(20)}$.

In the range of 1050-1000 $cm^{-1}$, where 3-hydroxysteroids exhibit only

OF 3α-HYDROXY $\Delta_5$-STEROIDS AND 3α-ACETOXY $\Delta_5$-STEROIDS

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1020 | 1003 | 994 | 978 | 960 | 938 | | | | | |
| 1021 | 1004 | 996 | 983 | 960 | 938 | 874 | 840 | 828 | 815 | 792 |
| 1022 | 1005 | 994 | 977 | 958 | 938 | | | | | |
| 1024 | 1006 | 994 | 980 | 960 | 939 | 878 | 837 | 825 | 813 | 791 |
| 1025 | 1008 | 995 | 978 | 960 | 940 | | | | | |
| 1022 | 1006 | 993 | 982 | 959 | 940 | 878 | 839 | 828 | 819 | 792 |
| 1022 | 1004 | 996 | 980 | 961 | 938 | | | | | |
| 1022 | 1007 | 997 | 979 | 963 | 940 | 880 | 841 | 828 | 810 | 794 |
| 1024 | 1008 | 994 | 978 | 960 | 939 | | | | | |
| 1025 | 1010 | 996 | 983 | 962 | 942 | 874 | 837 | | 818 | 792 |
| 1040 | 1018 | 982 | | | | | | | | |
| 1040 | 1018 | 982 | 946 | 929 | 909 | 864 | 828 | 815 | 794 | |
| 1035 | 1015 | 985 | | | | | | | | |
| 1039 | 1018 | 987 | 950 | 935 | 910 | 864 | 828 | 814 | 794 | |
| 1042 | 1018 | 990 | | | | | | | | |
| 1042 | 1021 | 992 | 956 | 928 | 912 | 862 | 833 | 813 | 792 | |
| 1035 | 1013 | 983 | | | | | | | | |
| 1035 | 1018 | 984 | 950 | 930 | 913 | 853 | 830 | 813 | 795 | |
| 1045 | 1018 | 990 | | | | | | | | |
| 1047 | 1019 | 990 | 948 | 930 | 916 | 862 | 829 | 814 | 793 | |

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one prominent band presumed to involve principally a C-O stretching motion [4], 3α-hydroxy $\Delta_5$-steroids show a complex group of three prominent bands at 1025-1020, 1010-1003 and 997-993 $cm^{-1}$; their relative intensities vary in a seemingly erractic manner with molecular structure and physical state.

TABLE II. - SUMMARY OF CHARACTERISTIC FREQUENCIES

| | Frequency range, $cm^{-1}$ | |
|---|---|---|
| | Carbon disulfide solution | Potassium bromide dispersion |
| 3α-HYDROXY $\Delta_5$-STEROIDS | 3606-3605 | |
| | 3582-3578 | |
| | 1180-1177 | 1191-1186 |
| | 1165-1162 | 1164-1162 |
| | 1140 | 1143-1148 |
| | 1025-1020 | 1025-1021 |
| | 1008-1003 | 1010-1004 |
| | 996-994 | 997-993 |
| | 980-978 | 983-979 |
| | 961-958 | 963-959 |
| | 940-938 | 942-938 |
| | | 880-874 |
| | | 841-837 |
| | | 828-825 |
| | | 819-810 |
| | | 794-791 |
| 3α-ACETOXY $\Delta_5$-STEROIDS | 1250-1242 | 1259-1249 |
| | 1239-1230 | 1241-1234 |
| | 1228-1222 | 1231-1220 |
| | 1149-1145 | 1150-1140 |
| | 1110-1105 | 1113-1105 |
| | 1045-1035 | 1047-1035 |
| | 1018-1013 | 1021-1018 |
| | 990-982 | 992-982 |
| | 956-946 | 956-946 |
| | | 935-928 |
| | | 916-909 |
| | | 864-853 |
| | | 833-828 |
| | | 815-813 |
| | | 795-792 |

Between 1200 and 780 $cm^{-1}$, 3α-hydroxy $\Delta_5$-steroids have other bands which can be useful as confirmatory evidence for stereochemistry ; the prominent bands which occurs below 850 $cm^{-1}$ are associated with unsaturated linkage, and , therefore , are highly characteristic.

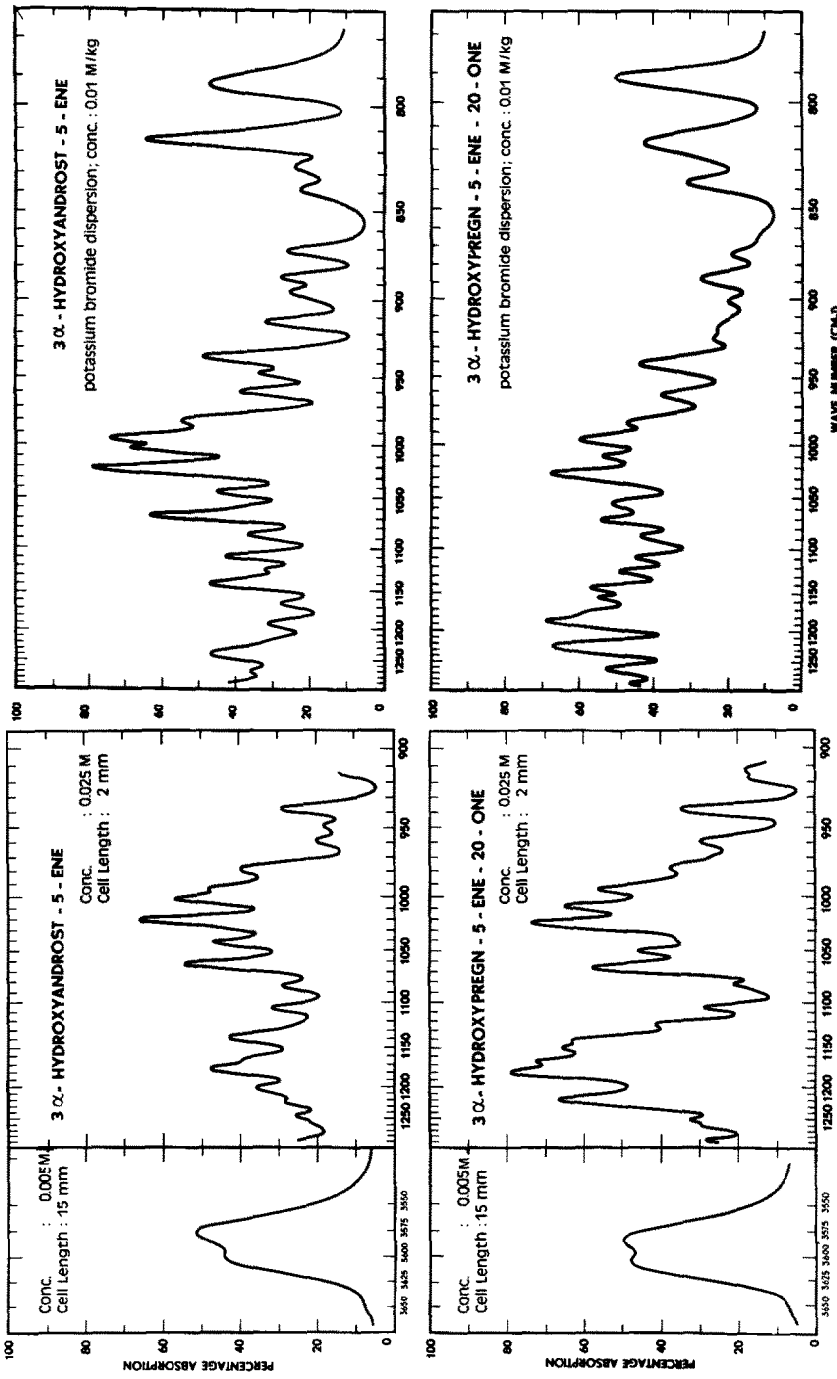


Fig. 2.- Infrared spectra of 3α-hydroxyandrost-5-ene and 3α-hydroxypregn-5-ene-20-one

(carbon disulfide solution and potassium bromide dispersion)

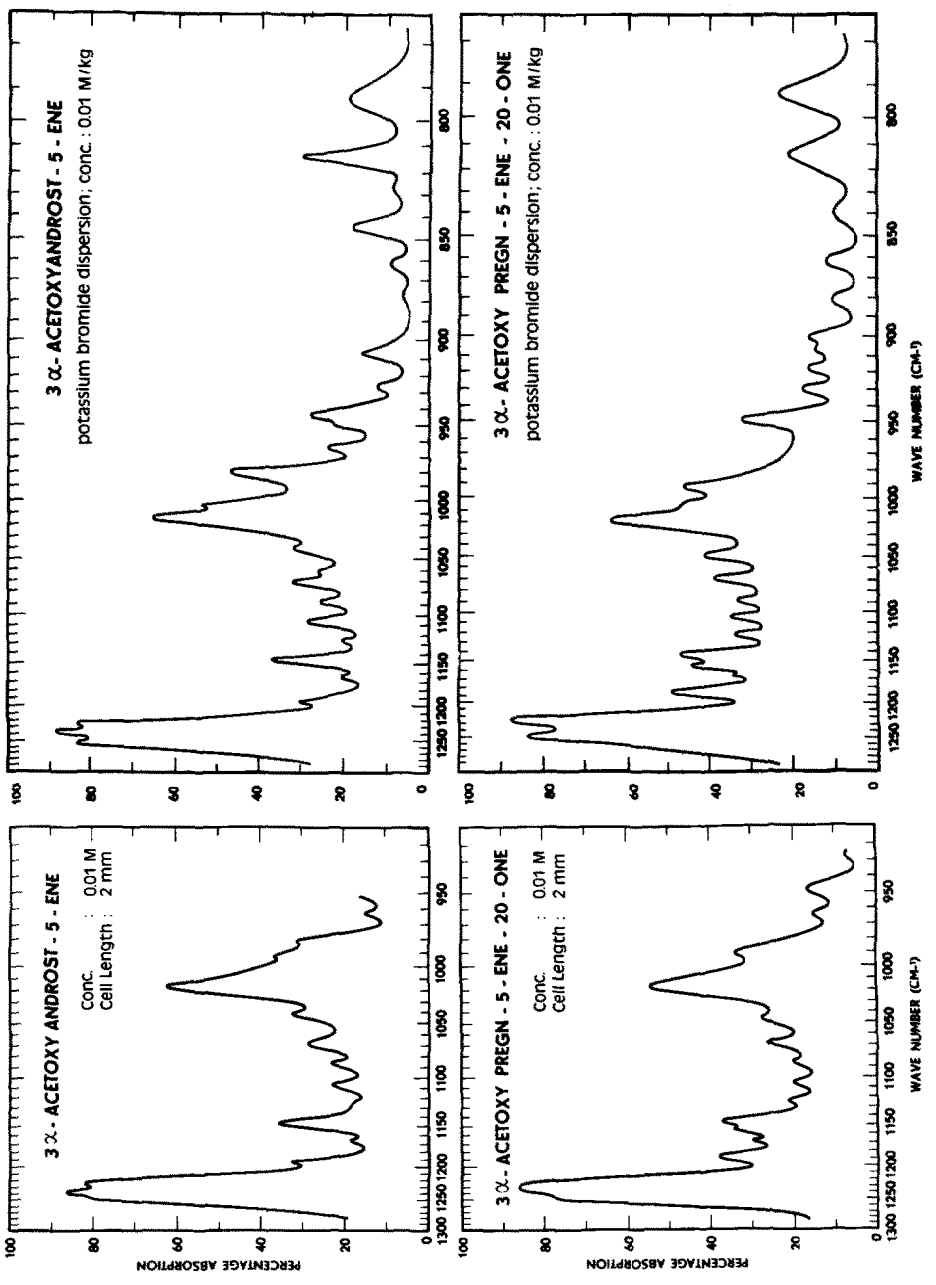


Fig. 3.- Infrared spectra of 3α-acetoxy-androst-5-ene and 3α-acetoxy-pregn-5-ene-20-one (carbon disulfide solution and potassium bromide dispersion)

## 3-ACETOXY $\Delta_5$-STEROIDS

Like all 3-axial acetoxysteroids, 3$\alpha$-acetoxy $\Delta_5$-steroids show a strong band at 1020-1010 $cm^{-1}$ and a characteristic group of two or three prominent peaks between 1260 and 1220 $cm^{-1}$, the center band of the triplet being the most intense in all compounds discussed here. Below 870 $cm^{-1}$, several bands can be distinguished, which, though weak, seem specific to the acetoxy group at $C_{(3)}$ in relation to the neighboring center of unsaturation at $C_{(5)}$.

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