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The Infrared Spectra of Acetoxysteroids below 1350 Cm.$^{-1}$

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In the infrared spectra of acetoxysteroids several bands can be distinguished between 1350 and 650 cm.$^{-1}$, the positions of which serve to characterize the location of the acetoxy group and its relationship to neighboring centers of unsaturation. Many of these bands can be recognized also in the spectra of diacetates, hydroxyacetates and keto-acetates, provided the functional groups are well separated. The characteristic frequencies may be perturbed by substitution in rings B and C.

The region between 1350 and 650 cm.$^{-1}$ in the infrared spectra of steroids is often described as the fingerprint region, with the implication that this part of the spectrum is specific for each individual steroid. This generalization has been found to hold true for upwards of 2000 steroids that have been examined in these laboratories, although, in a few cases, the differences are small and may not be recognized on a casual inspection of the qualitative spectra. This applies principally to steroids that differ only in the homology or stereochemistry of the side chain.

This specificity suggested initially that the absorption in these low frequency regions arises from vibrations that involve significant motions of large parts of the molecule and that could not therefore be treated as group vibrations identifiable with more localized structural units. Empirical comparisons among the spectra of 3-, 17-, and 20-ketosteroids[3] have shown, however, that in a given stereochemical series most of the prominent bands are characteristic of the position of the ketone group and the unsaturation in its immediate neighborhood. Many of these bands are to be seen also in the presence of acetoxy, hydroxy or other ketone groups, provided the second substituent is located at a remote position so that interaction effects between the two substituents are kept small. These limitations have not yet been studied systematically, but it would seem that the perturbations between substituent groups are generally quite small when one functional group is in ring A and the second in ring D or on the side chain. The introduction of oxygen containing substituents into rings B or C can induce appreciable changes. The nature of the vibrations responsible for these low frequency group-specific bands is not yet known, but in the case of 3- and 17-ketosteroids it has been proposed that some of them arise from skeletal vibrations localized in the same ring as the functional groups, and others from C–H deformation vibrations of α-methylene groups.[4]

In the spectra of steroid acetoxyketones several prominent bands occur in addition to those that can be identified with the ketone group, and it seems reasonable to expect that some of these are specific to the acetate group. The strong absorption of acetates between 1290 and 1190 cm.$^{-1}$ has long been recognized, and has been used to characterize the stereochemical configuration of 3-acetoxysteroids.[5] More recently additional absorption bands characteristic of 3-acetoxy substitution have also been noted by Rosenkrantz and Skogstrom.[6]

A systematic survey has now been made of the spectra of steroids acetylated at positions 3, 17 and 20, and a large number of bands characteristic of the type and position of the acetate group has been identified. In this paper we shall deal only in an empirical manner with the practical potentialities of these bands for characterizing acetoxy groups in steroids, following the general pattern of the earlier ketone paper.[3] The strong bands at 1290–1190 cm.$^{-1}$ are known to involve C–O stretching vibrations and it may be possible to discuss the origin of the other characteristic acetate bands more effectively when comparisons can be made with the spectra of the corresponding trideuteroacetates; these are at present being prepared and studied.

Experimental Methods and Results

The spectra were determined in carbon disulfide solution on Perkin–Elmer Model 112 and Model 21 spectrometers using sodium chloride prisms. Many of the data are taken from curves which have been published previously[7] and to a few of these a minor scale correction of 2–4 cm.$^{-1}$ has been applied between 1350 and 1200 cm.$^{-1}$. Some of the monoacetate spectra have not yet been published and will be described in detail elsewhere.

The positions of the characteristic bands are listed for the individual compounds in Table I and are summarized in Table II. These bands are classified into categories I, II and III in accordance with their usefulness for identification purposes, the factors determining this classification being the same as were applied to the ketone bands discussed in reference 3. One representative example of each type of monoacetate spectrum is shown in Figs. 1–12, 14. The curves shown in Figs. 15–20 demonstrate the specificity of these bands in various types of diacetates and ketoacetates.

In preparing Tables I and II some additional bands were also surveyed, but rejected for their failure to appear clearly in one or more compounds, or for other reasons. The tables therefore do not pretend to present a complete picture of the absorption pattern associated with the steroid acetate groups, and additional bands may be added, or others withdrawn, as more information becomes available.

Discussion

3-Acetoxysteroids.—The spectra of the 3α- and 3β-monoacetates of 5α- and 5β-steroids have been examined in the C_{19}, C_{21} and C_{27} series as also have the 3β-Δ^5-steroids, which can conveniently be dis-

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(2) Mrs. H. Kaelber.

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(5) R. N. Jones, P. Humphries, F. Herling and K. Dobriner, *ibid.*, **73**, 3215 (1951).

(6) H. Rosenkrantz and P. Skogstrom, *ibid.*, **77**, 2237 (1955).

(7) K. Dobriner, E. R. Katzenellenbogen and R. N. Jones, "Infrared Absorption Spectra of Steroids—An Atlas," Interscience Pub., Inc., New York, N. Y., 1953.

TABLE I

CHARACTERISTIC GROUP FREQUENCIES IN THE INFRARED SPECTRA OF ACETOXYSTEROIDS BELOW 1350 CM.$^{-1}$

(Carbon disulfide solution)

Band Category[a]	A III	B III	C I	D I	E I	F II	G I	H III	I II	J II	K I	L III	M II	N I	O III	P III	Q III	R III
								3α-Acetoxy-5α-steroids										
Androstan-3α-ol acetate	1299	1282[e]	1259	1252	1238	1192	1160	1133	1116	1029	1018	1003	993	978	919	906	725	684
Allopregnan-3α-ol acetate	1298	1280[e]	1256	1246	1236	1190	1162	1133	1115	1031	1017	1002	985	978	917	904	728	685
Cholestan-3α-ol acetate	1300	1280[e]	1257	1248	1238	1188	1163	1133	1118	1033	1018	1005[e]	988	979	917	905	729	685
Androstan-3α-ol-17-one acetate	1300	1285[e]	1257	1244	1237	1195[e]	1165[q]	1132[e]	1120[q]	1025[e]		1016[q]...	990	978	916	903	727	684
Allopregnan-3α-ol-20-one acetate	1300[e]	1281[e]	1259[e]	1248[e]	1238	1190	1165	1130	1118	1030[e]	1018	1009[e]	993	979	919[n]	904	728	686
Androstane-3α,17β-diol acetate-3	1300	1280[e]	1257	1246	1236	1190	1162	1134	1117	1030	1018	1002[e]	990	978	918	906	728	684
Allopregnane-3α,20α-diol acetate-3	1298	1280[e]	1255	1245	1236	1190	1162	1134	1117	1033	1016[q]	1005[e]	988	977	917	906	726	685
Androstane-3α,17β-diol diacetate	1299[e]	1280[e]	1259[e]	1247[b]	1238[e]	1192	1162	1132[b]	1117[b]	1033[b]	1018	1006[e]	992	979[b]	919	*f*	727	*d*
Allopregnane-3α,20α-diol diacetate	1300[b,e]	1280[e]	1257[e]	1247[b]	1238[e]	1191[q]	1165[b]	*f*	1118[b]	1034[e]	1020[b]	1008[e]	990	978	918[e]	906[b]	725[b]	*d*

Band Category	A III	B I	C III	D II	E II	F III	G III	H I	I III	J III	K III	L III	M III	N III	O III
							3β-Acetoxy-5α-steroids								
Androstan-3β-ol acetate	1296	1244	1169	1151	1133	1119	1081	1026	993	970	957	908	888	799	730
Allopregnan-3β-ol acetate	1297	1242	1178	1151[q]	1133	1121	1079	1027	993[e]	970	957	906	889	799	732
Cholestan-3β-ol acetate	1297	1243	1174	1152	1134	1120[e]	1076	1027	990[e]	969[e]	958	908	887	800	731
Δ^{14}-Cholesten-3β-ol acetate	1297[e]	1243	*f*	1152	1131	*f*	1072	1029	995	975	962	907	888	800[h]	731
Ergostan-3β-ol acetate	1298[e]	1242	1173	1151	1132	1121[e]	1074	1026	988	971	958	908	887	800	*d*
Androstan-3β-ol-17-one acetate	1296	1244	1182	1153	1132	1123[e,q]	1081	1023	988	968[q]	955	907	890[q]	801	730
Allopregnan-3β-ol-20-one acetate	1295[e]	1242	1178[n]	1152[n]	1132	1119	1079[q]	1027	990[e]	973	953[n]	907	889	800	*d*
Allopregnane-3β-20α-diol diacetate	1296[b,e]	1242[b,g]	1178	1152[b]	1132	1119[b,e]	1080[e]	1026[b]	988[e]	970	959[b]	908[b]	892	800	730
Allopregnane-3β,20β-diol diacetate	1297[b,e]	1243[h]	1180[b]	1152	1132	*f*	1077[b]	1027[b]	988[e]	972[e]	963[b]	908[b]	892	801	732
Allopregnane-3β,21-diol-20-one diacetate	1295[e,k]	1241	1173	1152	1133[k]	1118	1078[k]	1027	988[k]	971[k]	955	908[k]	893[e]	800	729
Δ^{16}-Androstene-3β,17-diol diacetate	1297[e,t]	1244	*o*	1151[t]	1132	1118[e]	1081	1027	*o*	970[e,t]	957[e]	903	887[e]	802[e]	732

Band Category	A II	B I	C II	D III	E III	F II	G I	H III	I II	J III	K III	L III	M II	N III
							3α-Acetoxy-5β-steroids							
Etiocholan-3α-ol acetate	1318	1243	1167	1108	1084	1063	1029	1015[e]	982	954	914	906	888	833
Pregnan-3α-ol acetate	1318	1242	1169	*f*	1087	1065	1028	1018[e]	983	950	914[e]	905	885[q]	831
Coprostan-3α-ol acetate	1318	1243	1169	1106	1089	1063	1028	1018[e]	983	950	914	906	887	827
Δ^{22}-5β-Ergosten-3α-ol acetate	1318	1242	1167	1108	1086	1064	1028	1015[e]	982	950	914	905	887	827
Etiocholan-3α-ol-17-one acetate	1318	1242	1170[p]	1106	1088	1062	1030	1010[q,p]	983	953	913[e]	907	890[q]	830[p]
Pregnan-3α-ol-20-one acetate	1318	1242	*l*	1108	1088[m]	1064	1029	1017[e]	983	950[q]	913[e]	906	886[q]	827
17-Isopregnan-3α-ol-20-one acetate	*f*	1243	*l*	1111[e]	1089	1063	1028	1015[e]	983	950	*f*	907	888	*f*
Etiocholane-3α-17β-diol diacetate	1318	1244[b]	1168	1109[b]	1087	1065[e]	1028[b]	*o*	983[b]	950[b]		912[q]...	887	833[b]
Pregnane-3α-, 20α-diol acetate	1318	1243	1169	*f*	1088	1065	1027[q]	*o*	982	950	913[e]	905	885	827
3α-Acetoxycholanic acid methyl ester	*f*	1243	1168[c]	1109[e]	1088[e]	1065	1028	1017[e]	983	950	914	905	885	830

TABLE I (*Continued*)

Band Category	A III	B I	C I	D I	E III	F II	G III	H I	I III	J II	K II	L III	M III	N III				
3β-Acetoxy-5β-steroids																		
Etiocholan-3β-ol acetate	1299	1253	1242	1236[e]	1176	1158	1045[e]	1023	985	972	958	788	735	687				
Pregnan-3β-ol acetate	1300	1253	1240	1233	1175[e]	1161	1050[e]	1025	988	976	960	789	737	688[g]				
Coprostan-3β-ol acetate	1300	1253	1242	1233	1173[e]	1161	1045[e]	1025	988	977	960	789	733	690				
Etiocholan-3β-ol-17-one acetate	1300[e]	1254[p]	1246[p]	1237	1171[p]	1159	1051[p]	1023	989	974	962[g]	788	737	*d*				
Pregnan-3β-ol-20-one acetate	1300[e]	1253	1241[e]	1232[m]	1176[m]	1161	1050[e]	1023	990	972[m]	957	788	732	*d*				
Etiocholane-3β,17β-diol diacetate	*f*	1250[b,g]	1240	1235[e]	*f*	1160	1048[b,e]	1023	991[b]	978[e]	960	789	*f*	688				
Pregnane-3β,20β-diol diacetate	1300[e]	1254[e]	1245	1233[e]	1175	1159	1047[e]	1023[g]	988	976	958	789	737	*d*				
Band Category	A III	B I	C III	D III	E II	F I	G III	H III	I III	J II	K III	L III	M II	N III	O II	P II	Q II	R III
3β-Acetoxy-Δ⁵-steroids																		
Δ⁵-Androsten-3β-ol acetate	1316	1243	1202[e]	1162	1137	1036	1023[e]	986	981	958	942	914	905	881[g]	843	816	796[g]	730[g]
Δ⁵-Pregnen-3β-ol acetate	1315	1243	1199[e]	1163	1135[g]	1033	1023[e]	990	978	956	935	913	903	875	839	811	799	737
Δ⁵-Cholesten-3β-ol acetate	1315	1242	1201	1167[g]	1136	1034	1027[e]	993	979	959	942	917	903	878	837[g]	812	800	734
Δ⁵-Androsten-3β-ol-17-one acetate	1316	1242	1199	1165[y]	1137	1030	*f*	984	976	954	940	916	903	875	842	810	798	737
Δ⁵-Pregnen-3β-ol-20-one acetate	1317	1242	1197[e]	1168[z]	1136	1032	1023[e]	990	978[z]	954	940[z]	918	902	878	834	808	798	733
Δ⁵-Nor-27-cholesten-3β-ol-24-one acetate	1317[e]	1242	1200	1162	1137	1034	1027[e]	993[e]	979	960[g]	942	917	903	878	838	810[e]	800	735[g]
Δ⁵-Nor-27-cholesten-3β-ol-25-one acetate	1314	1242	1199	1163[g]	1137	1033	1026[e]	993	980	961[g]	941	916	903	877	838	812	800	733[g]
Δ⁵,¹⁶-Pregnadien-3β-ol-20-one acetate	1317	1242	1204	1160	1137	1032	1018[e]	988[e]	974	957	944[g]	923	904	884	840	810	798	738
Δ⁵-Androstene-3β,17β-diol diacetate	1317	1244	1201	1160	1137	1034	1025[e]	995[e]	978	958	941[e]	919	904	877	844	812	799	*d*
17α-Ethynyl-Δ⁵-androstene-3β,17β-diol acetate-3	1318[e]	1241	1200	1163	1138	1037	1026[e]	995[e]	981	957	942	922	903	879	837	813	800	737
Δ⁵-Pregnene-3β,21-diol-20-one diacetate	1317	1243	1201	1162[e]	1137	1033	1023[e]	991	980	957	942	919[e]	903	878	837	811	799	730
3β-Acetoxy-Δ⁵-cholenic acid methyl ester	*f*	1244	1198	*c*	1138[e]	1034	1027[e]	993	980	960	942	916	903	*f*	837	811	800	733
Band Category	a III	b I	c II	d III	e III	f III	g II	h II	i I	j III	k III	l III						
17β-Acetoxy-5α-steroids																		
Androstan-17β-ol acetate	1290	1245	1220	1133	1118	1106	1075	1045	1032	985	960	832						
Androstan-17β-ol-3-one acetate	1288	1246	1220	1130[g]	1123[i]	1107	1079	1047	1033	980	957	835						
Androstane-3α,17β-diol acetate-17	1288[e]	1247	1222[e]	1132[g]	1116[g]	1105[e]	1074	1045[b]	1032	982	962	834[g]						
Androstane-3α,17β-diol diacetate	1287[e]	1247[b]	1220[e]	1132[b]	1117[b]	1107[e]	1073	1047	1033[b]	979[b]	961	833						
The following Δ⁴-3-ketosteroid shows anomalous high intensity absorption near 1044 cm.⁻¹																		
Δ⁴-Androsten-17β-ol-3-one acetate	1288	1247	1223[e]	1129[x]	1113[x]	*f*	1069	*1044*	1022[x]	980	959	831						
Band Category	A III	B I	C II	D III	E III	F III	G II	H II	I II	J I	K III	L III	M III	N III	O II	P III	Q II	R III
17β-Acetoxy-5β-steroids																		
Etiocholan-17β-ol acetate	1287	1247	1221	1132	1119	1111	1072	1048[e]	1040[e]	1030	990	983	952	940	920[e]	914	897	837
Etiocholane-3α,17β-diol acetate-17	1288	1245	1220	1134	1119	1109	1070	1049	1037[w]	1028	995[e]	982	947	938	920[e]	914	897	832
Etiocholane-3β,17β-diol acetate-17	1286[e]	1246	1219	1136	1117	1104	1073	1047[e]	1042[e]	1028	989	983[e]	951	934	913[g]		896	832
Etiocholane-3α,17β-diol diacetate	1288	1244[b]	1223[e]	1132	1117	1109[b]	1073	1047[e]	1042[e]	1028[b]	*f*	983[b]	950[b]	940	912[g]		898	833[b]
Etiocholane-3β,17β-diol diacetate	1288	1250[b,g]	1221	1135	1118[e]	1107	1073	1048[b,e]	1042[e]	1030[e]	991[b]	982	955[b,e]	937	916	907[e]	895	832
The following shows anomalous high intensity absorption near 1044 cm.⁻¹ (see text)																		
Etiocholan-17β-ol-3-one acetate	1288[i]	1245[i]	1219[i]	1133	1114	1104[i]	1072	*1047–1042*[g]	1027	996	983[e]	946	*f*	915[g]			898	829[i]

TABLE I (*Continued*)

Band Category	a III	b III	c I	d III	e III	f III	g II	h II	i I	j II	k II	l III	m III	n III	o III	p III
20α-Acetoxy-5α-steroids																
Allopregnan-20α-ol acetate	1304	1274[e]	1247[g]	1160[e]	1150	1118[g]	1063	1052	1020	960	952	934[g]	905	838	825[g]	725
Allopregnan-20α-ol-3-one acetate	1305	1269[e,i]	1245[i]	1159[e]	1152[i]	1117[i]	1066	1048	1019	957	948[e]	934	903	842	820	723
Allopregnane-3α,20α-diol acetate-20	1303[e]	1275[e]	1246	1163	1153	1116	1060	1045	1018	962	953	933	906	843	825	725
Allopregnane-3α,20α-diol diacetate	1300[b,e]	1277[e]	1247[b]	1165[b]	1153[e]	1118[b]	1064	1048	1020[b]	962	954[e]	932	906[b]	838	825[e]	725[b]
Allopregnane-3β,20α-diol diacetate	1298[b,e]	1278[e]	1247[b,g]	1159[e]	1152[b]	1119[b,e]	1068	1052	1020[b,e]	959[b]	951	932	908[b]	841[g]	825[e]	725

Band Category	A III	B III	C III	D I	E II	F II	G III	H I	I I	J I	K II	L III	M II	N III	O III	P III	Q III
20β-Acetoxy-5α-steroids																	
Allopregnane-20β-ol acetate	1303[e]	1291[e]	1277[e]	1245	1181	1162	1127	1079	1051	1022	964	947	926	904	850	828	721
Allopregnane-20β-ol-3-one acetate	1298	1287[e]	1269[e,i]	1244[i]	1179[i]	1154[i]	1128[i]	1078[i]	1047	1022	962	942	925	902	851	828	725
Allopregnane-3β,20β-diol diacetate	1297[b,e]	1287[e]	1277[e]	1243[b]	1180[b]	1158	1127[e]	1077[b]	1048	1027[b]	963[b]	948	927	908[b]	848[g]	830	725

Band Category	A III	B III	C I	D II	E II	F III	G III	H I	I III	J III	K II	L II	M II	N III	O III	P III	Q III	R III	S III	T III	U III
Phenolic 3-acetoxysteroids																					
$\Delta^{1,3,5(10)}$-Estratrien-3-ol acetate	1281[e]	1251	1209	1177	1150	1115[e]	1047[g]	1012	984	962	943[e]	936	895	883[e]	824	819[e]	801	775[e]	747[g]	706	674
$\Delta^{1,3,5(10)}$-Estratrien-3-ol-17-one acetate (*Estrone acetate*)	1279[e]	1254	1204	1181	1149	1109	1051[u]	1014[e]	984	965	946	936	899	885	820	815[e]	794	777	747[g]	703	*d*
17-Acetyl-$\Delta^{1,3,5(10),16}$-estratetraene-3-ol acetate	1277	1252[e]	1207	1175	1151	1116	1045	1014	983[e]	*f*	942	938	897	886[e]	827[e]	818	793	778	747[g]	704	680
$\Delta^{1,3,5(10)}$-Estratrien-3,17α-diol diacetate (*17α-estradiol diacetate*)	1282[e]	*o*	1206	1178	1151	1118	1052[e]	1017	985	968	945	935	898	885[e]	824	820[e]	800	775	750[g]	705	*d*
$\Delta^{1,3,5(10)}$-Estratrien-3,17β-diol diacetate (*17β-estradiol diacetate*)	1281[e]	*o*	1209	1177	1151	1115	1046[e]	1012	982[e]	962	942	935	894	888	824[e]	817	792	775	747[g]	703	673
$\Delta^{1,3,5(10)}$-Estratrien-3,16α,17β-triol triacetate (*Estriol triacetate*)	*o*	*o*	1205	1178	1152	1122	*o*	1012	983[e]	*f*	948[g]	937[e]	895[g]		823	817[e]	796	780	748	707	*d*
$\Delta^{1,3,5(10)}$-Estratrien-3,16β,17β-triol triacetate	1277[e]	*o*	1206	1178	1152	1123[e]	*o*	1010	987[e]	967	946	937[e]	898	892[g]	824	817[e]	797	782	747[g]	706[g]	672

Band Category	A III	B III	C I	D I	E I	F II	G II	H II	I III	J III	K II	L II	M III	N III	O III
Δ^2-3-Acetoxy-5α-steroids															
Δ^2-Cholesten-3-ol acetate	1294	1269	1219	1158	1110	1050	1010	963	947	934	917	904	748[g]	726	705
Δ^2-Androsten-3-ol-17-one acetate	1294[g]	1269	1218	1158	1110	1051[q]	1007[q]	964[g,q]	944[e]	935	917	906	747	722	703[e]
$\Delta^{2,16}$-Androstadiene-3,17-diol diacetate	1298[r]	1268[e,r]	1218	1160	1107[e]	1051	1010[r]	966[r]	950	938[r]	917[r]	904	745	725	705[r]

Band Category	a III	b III	c III	d III	e I	f III	g III	h II	i I	j II	k III	l III	m III	n III	o II	p II	q III
Δ^{16}-17-Acetoxysteroids																	
Δ^{16}-Androsten-17-ol-acetate	1312[e]	1303	1273	1253	1206	1199[e]	1185	1153	1098	1011	965	937	916	877	833	813	705
Δ^{16}-Androstene-3β,17-diol diacetate	1309	1300[g,s]	1273[e]	*o*	1207	1198[e]	1187[e]	1151[s]	1098	1013[e]	966	938	920	877[e]	833	812	705
$\Delta^{2,16}$-Androstadiene-3,17-diol diacetate	1309	1298[r]	1268[e,r]	1252	1208	1200[e]	1187[e]	1155[e]	1099	1010[r]	966[r]	938[r]	917[r]	879	834	812	705[r]
$\Delta^{3,5,16}$-Androstatriene-3,17-diol diacetate	1308	1296	1271	1254	1204		1184	1154	1096	1013[g]	968	934[g]	920	*f*	829[g]	813	712

TABLE I (*Concluded*)

Band Category	a III	b II	c I	d III	e III	f III	g I	h I	i III	j III	k III	l II	m III	n II	o II
21-Acetoxy-20-keto-5α-steroids															
Allopregnan-21-ol-20-one acetate	1293[g]	1269	1230	1201	1129	1110	1078	1055	1020	992	971	911	905[g]	837	762
Allopregnan-21-ol-3,20-dione acetate	1290	1268	1230	1200[g]	1127[i]	1111	1077	1053	1017	988	968	910	903[g]	840	763
Δ^1-Allopregnen-21-ol-3,20-dione acetate	1292[g]	1269[g,v]	1231	1203	1127	1112[w]	1073	1053	1017	987	*f*	911	903	*f*	763[g]
Allopregnane-3β,21-diol-20-one diacetate	1292[g,s]	1267[e]	1231	1202[g]	1133[g]	1110	1078[g]	1055	1017[g]	988[g]	971[g]	908[g,s]	904[g]	837	762

[a] For definitions of categories see reference 3. [b] A band at this position is associated with both acetate groups. [c] This region obscured by strong carbomethoxy group absorption. [d] This region of the spectrum was not measured. [e] Inflection. [f] Band not observed. [g] Broad band. [h] A band at this position is also associated with the Δ^{14}-group. [i] A band at this position is also associated with 3-keto-5α-steroids. [j] A band at this position is also associated with 3-keto-5β-steroids. [k] A band at this position is also associated with 21-acetoxy-20-keto-5α-steroids. [l] Obscured by strong absorption associated with the 20-ketone group. [m] A band at this position is also associated with 20-keto-5β-steroids. [n] A band at this position is also associated with 20-keto-5α-steroids. [o] Obscured by strong absorption associated with a second acetate group. [p] A band at this position is also associated with 17-keto-5β-steroids. [q] A band at this position is also associated with 17-keto-5α-steroids. [r] A band at this position is associated with both enol-acetate groups. [s] A band at this position is also associated with 3β-acetoxy-5α-steroids. [t] A band at this position is also associated with Δ^{16}-17-acetoxysteroid group. [u] A band at this position is also associated with 17-ketosteroids containing an aromatic A ring. [v] A band at this position is also associated with 3-keto-Δ^1-5α-steroids. [w] A band at this position is also associated with 3α-hydroxy-5β-steroids. [x] A band at this position is also associated with 3-keto-Δ^4-steroids. [y] A band at this position is also associated with 17-keto-Δ^5-steroids. [z] A band at this position is also associated with 20-keto-Δ^5-steroids.

cussed at the same time. Representative spectra are shown in Figs. 1–5. The most prominent bands lie between 1250 and 1200 cm.$^{-1}$ and have been described by several investigators.[5,6,8,9] The most interesting feature of this absorption is the fact that the axial 3-acetates (3α-acetoxy-5α-steroids and 3β-acetoxy-5β-steroids) show a complex group of bands, and the equatorial 3-acetoxysteroids a single band of simple contour. The complex band system of the axial acetates is usually a triplet. If consideration is limited to 3-axial acetates containing no other functional substituents, it is observed that the center band of the triplet is the most intense in the 5β-series (band C, Fig. 4) while in the 5α-series the triplet band of lowest frequency is the strongest (band E, Fig. 1). This holds in the C_{21} and C_{27} series as well as in the C_{19} series shown in Figs. 1 and 4. Changes in the relative intensities of these bands do occur on the introduction of ketone groups at C_{17} or C_{20} and consideration of the absolute band intensities suggest that this is a real intensity change, not merely an additive effect produced by superposition of ketonic absorption.[10]

The second most prominent band in the 3-monoacetate spectra occurs near 1025 cm.$^{-1}$. The position of this band varies slightly with the stereochemistry of ring A, as has been noted by Rosenkrantz and Skogstrom.[6] These stereochemical shifts show parallelism with the 1052–996 cm.$^{-1}$ absorption bands of 3-hydroxysteroids.[11] Both sets of bands move in the same sense (Table III) with the A-ring stereochemistry, but the displacements are larger for the hydroxyl than for the acetate bands. Several other bands characteristic of 3-acetoxysteroids are also listed in Tables I and II, and of these, the following are most useful for identification purposes:

3α-acetoxy-5α-steroid	1162, 978 cm.$^{-1}$
3β-acetoxy-5α-steroid	1152, 1133 cm.$^{-1}$
3α-acetoxy-5β-steroid	1063, 982, 888 cm.$^{-1}$
3β-acetoxy-5β-steroid	1160, 975, 960 cm.$^{-1}$
Δ^5-3β-acetoxysteroid	1136, 957, 903, 840, 812, 798 cm.$^{-1}$

In most Δ^5-3β-acetoxysteroids the pair of bands near 812 and 798 cm.$^{-1}$ stand out fairly prominently, and have been noted previously by Hirshmann.[12,13]

17β-Acetoxysteroids.—The 17β-acetoxysteroids also have their most prominent absorption near 1245 cm.$^{-1}$ with strong secondary absorption near 1030 cm.$^{-1}$ and several weaker characteristic bands. The 17β-acetates of the 5α- and 5β-series exhibit significant differences that are easily recognized in the monoacetates, but which tend to be obscured when other functional groups are also present. These differences are more notable between 1100 and 1000 cm.$^{-1}$. In addition to the

(8) A. Fürst, H. H. Kuhn, R. Scontoni, Jr., and Hs. H. Günthard, *Helv. Chim. Acta*, **74**, 5206 (1952).

(9) A. R. H. Cole, *J. Chem. Soc.*, 4969 (1953).

(10) For example see Charts 136, 147, 159 and 163 of reference 7.

(11) A. R. H. Cole, R. N. Jones and K. Dobriner, THIS JOURNAL, **74**, 5571 (1952).

(12) H. Hirschmann, *ibid.*, **74**, 5357 (1952).

(13) The relative intensities of these two bands vary in a seemingly erratic manner with the molecular structure. A closer study of the spectra of Δ^5-3β-acetoxysteroids suggests that in addition to the three bands at 840, 812 and 798 cm.$^{-1}$ shown in Tables I and II there may also be a fourth band near 835 cm.$^{-1}$. Measurement in this region is complicated by solvent absorption.

TABLE II

SUMMARY OF ACETOXYSTEROID GROUP FREQUENCIES

(Carbon disulfide solution)

Band	Frequency range, cm.$^{-1}$	Category[a]
3α-Acetoxy-5α-steroid		
A	1300–1298	III
B	1285–1280	III
C	1259–1255	I
D	1252–1244	I
E	1238–1236	I
F	1195–1188	II
G	1165–1160	I
H	1134–1130	III
I	1118–1115	II
J	1034–1029	II
K	1020–1016	I
L	1009–1002	III
M	993– 985	II
N	979– 977	I
O	919– 916	III
P	906– 903	III
Q	729– 725	III
R	686– 684	III
3β-Acetoxy-5α-steroid		
A	1297–1295	III
B	1244–1241	I
C	1182–1169	III
D	1153–1151	II
E	1134–1131	II
F	1123–1118	III
G	1081–1072	III
H	1029–1023	I
I	995– 988	III
J	975– 968	III
K	963– 953	III
L	908– 903	III
M	893– 887	III
N	802– 799	III
O	732– 729	III
3α-Acetoxy-5β-steroid		
A	1318	II
B	1244–1242	I
C	1170–1168	II
D	1111–1106	III
E	1089–1084	III
F	1065–1062	II
G	1030–1027	I
H	1018–1012	III
I	983– 982	II
J	954– 950	III
K	914– 913	III
L	907– 905	III
M	890– 885	II
N	833– 827	III
3β-Acetoxy-5β-steroid		
A	1300–1299	III
B	1254–1250	I
C	1246–1240	I
D	1237–1232	I
E	1176–1171	III
F	1161–1158	II
G	1051–1045	III
H	1025–1023	I
I	991– 985	III
J	978– 972	II
K	962– 957	II
L	789– 788	III
M	737– 732	III
N	690– 687	III
3β-Acetoxy-Δ^5-steroid		
A	1318–1314	III
B	1244–1241	I
C	1204–1197	III
D	1168–1160	III
E	1138–1135	II
F	1037–1030	I
G	1027–1018	III
H	995– 984	III
I	981– 974	III
J	961– 954	II
K	944– 935	III
L	923– 913	III
M	905– 902	II
N	884– 875	III
O	844– 834	II
P	816– 808	II
Q	800– 796	II
R	738– 730	III
17β-Acetoxy-5α-steroid		
a	1290–1287	III
b	1247–1245	I
c	1222–1220	II
d	1133–1130	III
e	1123–1116	III
f	1107–1105	III
g	1079–1073	II
h	1047–1045	II
i	1033–1032	I
j	985– 979	III
k	962– 957	III
l	835– 832	III
17β-Acetoxy-5β-steroid		
A	1288–1286	III
B	1250–1244	I
C	1223–1219	II
D	1136–1132	III
E	1119–1117	III
F	1111–1104	III
G	1073–1070	II
H	1049–1047	II
I	1042–1037	II
J	1030–1028	I
K	995– 989	III
L	983– 982	III
M	955– 947	III
N	940– 934	III
O	920– 916	II
P	914– 907	III
Q	898– 895	II
R	837– 832	III
20α-Acetoxy-5α-steroid		
a	1305–1298	III
b	1277–1269	III
c	1247–1245	I
d	1165–1159	III
e	1153–1150	III
f	1119–1116	III
g	1068–1060	II
h	1052–1045	II
i	1020–1018	I
j	962– 957	II
k	954– 948	II
l	934– 932	III
m	908– 903	III
n	843– 838	III
o	825– 820	III
p	725– 723	III
20β-Acetoxy-5α-steroid		
A	1303–1297	III
B	1291–1287	III
C	1277–1269	III
D	1245–1243	I
E	1181–1179	II
F	1162–1154	II
G	1128–1127	III
H	1079–1077	I
I	1051–1047	I
J	1027–1022	I
K	964– 962	II
L	948– 942	III
M	927– 925	II
N	908– 902	III
O	851– 848	III
P	830– 828	III
Q	725– 721	III
Phenolic 3-acetoxysteroid		
A	1282–1277	III
B	1254–1251	III
C	1209–1204	I
D	1181–1175	II
E	1152–1149	II
F	1123–1109	III
G	1052–1045	III
H	1017–1010	I
I	987– 982	III
J	968– 962	III
K	948– 942	II
L	938– 935	II
M	899– 894	II
N	892– 883	III
O	827– 820	III
P	820– 815	III
Q	801– 792	III
R	782– 775	III
S	750– 747	III
T	707– 703	III
U	680– 672	III
Δ^2-3-Acetoxy-5α-steroid		
A	1298–1294	III
B	1269–1268	III
C	1219–1218	I

TABLE II (*Continued*)

Band	Frequency range, cm.$^{-1}$	Category[a]
D	1160–1158	I
E	1110–1107	I
F	1051–1050	II
G	1010–1007	II
H	966– 963	III
I	950– 944	III
J	938– 934	III
K	917	II
L	906– 904	II
M	748– 745	III
N	726– 722	III
O	705– 702	III
Δ^{16}-17-Acetoxysteroid[b]		
a	1312–1308	III
b	1303–1296	III
c	1273–1268	III
d	1254–1252	III
e	1208–1204	I
f	1200–1198	III
g	1187–1184	III
h	1155–1151	II
i	1099–1096	I
j	1013–1010	II
k	968– 965	III
l	938– 934	III
m	920– 916	III
n	879– 877	III
o	834– 829	II
p	813– 812	II
q	712– 705	III
21-Acetoxy-20-keto-5α-steroid		
a	1293–1290	III
b	1269–1267	II
c	1231–1230	I
d	1203–1200	III
e	1133–1127	III
f	1112–1110	III
g	1078–1073	I
h	1055–1053	I
i	1020–1017	III
j	992– 987	III
k	971– 968	III
l	911– 908	II
m	905– 903	III
n	840– 837	II
o	763– 762	II

[a] For definitions of categories see reference 3. [b] Based on measurements on steroids in the 5α-, and $\Delta^{3,5}$-series.

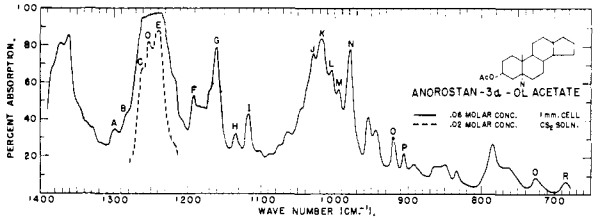

Fig. 1.—Characteristic infrared bands for 3α-acetoxy-5α-steroid.

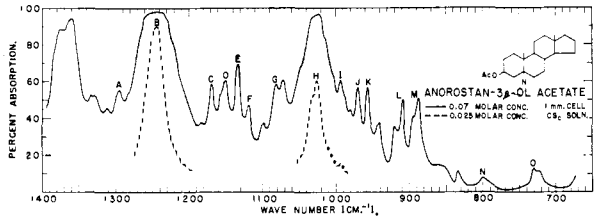

Fig. 2.—Characteristic infrared bands for 3β-acetoxy-5α-steroid.

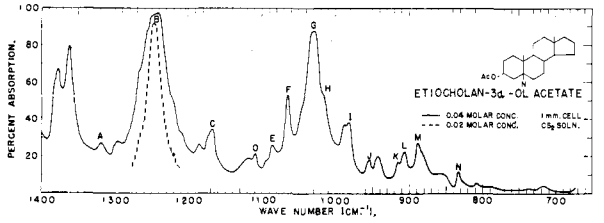

Fig. 3.—Characteristic infrared bands for 3α-acetoxy-5β-steroid.

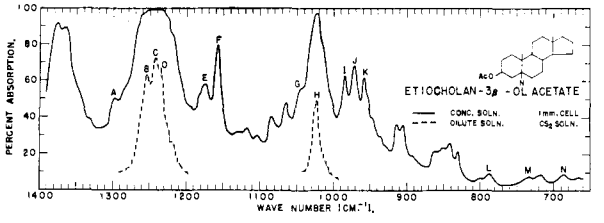

Fig. 4.—Characteristic infrared bands for 3β-acetoxy-5β-steroid.

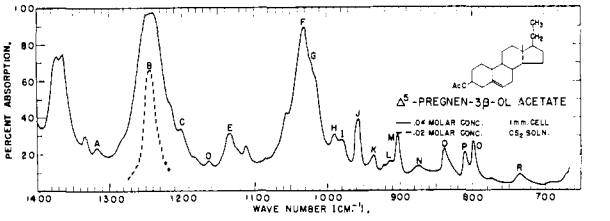

Fig. 5.—Characteristic infrared bands for 3β-acetoxy-Δ^5-steroid.

strong band near 1030 cm.$^{-1}$ both the 17β-acetoxy-5α- and the 17β-acetoxy-5β-steroids show secondary bands near 1075 and 1047 cm.$^{-1}$. The 1075 cm.$^{-1}$ band is stronger in the 5α- than in the 5β-compounds (*cf.* Figs. 6, 7); the 5β have an additional band near 1040 cm.$^{-1}$.

TABLE III

COMPARISON OF STEREOCHEMICAL EFFECTS ON THE SPECTRA OF 3-HYDROXY- AND 3-ACETOXYSTEROIDS BETWEEN 1052 AND 996 CM.$^{-1}$[a]

A-ring stereochemistry	C_3-bond conformation	Acetate frequency, cm.$^{-1}$	Hydroxyl frequency, cm.$^{-1}$
3α-5α	Axial	1020–1016	1002– 996
3β-5β	Axial	1025–1023	1036–1032
3β-5α	Equatorial	1029–1023	1040–1037
3α-5β	Equatorial	1030–1027	1044–1037
3β-Δ^5-	Equatorial	1037–1030	1052–1050

[a] Carbon disulfide soln.

In the 5α-series this absorption is not significantly perturbed by substitution at C_3 (Figs. 15, 18). In the 5β-series hydroxylation or acetylation at C_3 also produces no appreciable effects on the 17β-acetate bands, but the introduction of the 3-ketone group induces a new intense band near 1040 cm.$^{-1}$ as is illustrated in the spectra of etiocholan-17β-ol-3-one acetate and Δ^4-etiocholen-17β-ol-3-one acetate shown in Charts 131 and 143 of reference 7.[14]

(14) It is interesting in this connection to note that a strong anomalous band appears near 1015 cm.$^{-1}$ in the spectrum of etiocholane-3,17-dione, but not in the spectrum of androstane-3,17-dione (see reference 4).

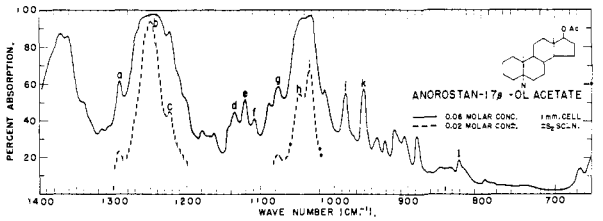

Fig. 6.—Characteristic infrared bands for 17β-acetoxy-5α-steroid.

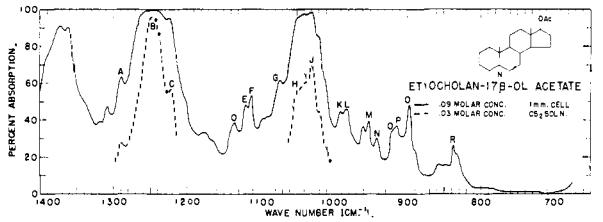

Fig. 7.—Characteristic infrared bands for 17β-acetoxy-5β-steroid.

20 - Acetoxysteroids.—The 20 - acetoxysteroids have been studied only in the 5α-series (Figs. 8, 9). Both the 20α- and the 20β-isomers show a strong band of simple contour near 1245 cm.$^{-1}$ and a number of secondary bands, the more prominent of which are:

20α-acetoxy-5α-steroids	1065, 1048, 1019, 960, 950 cm.$^{-1}$
20β-acetoxy-5α-steroid	1078, 1049, 1024, 963, 926 cm.$^{-1}$

Most of these can be recognized without difficulty in the presence of A-ring substitution (*cf.* Fig. 16).

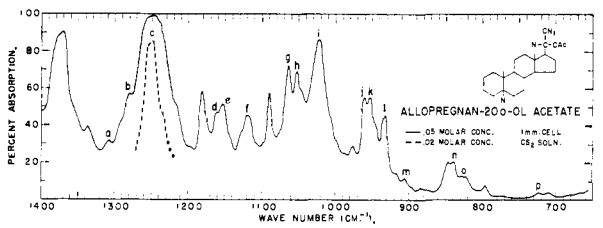

Fig. 8.—Characteristic infrared bands for 20α-acetoxy-5α-steroid.

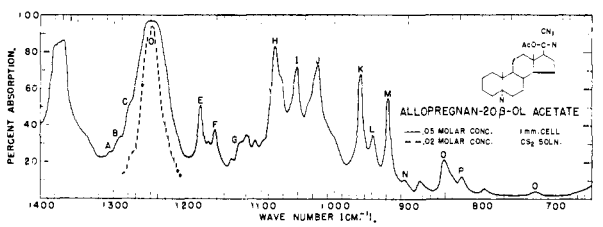

Fig. 9.—Characteristic infrared bands for 20β-acetoxy-5α-steroid.

The two stereochemical series can best be distinguished by the 1065 cm.$^{-1}$ band in the 20α-acetates and the 1078 cm.$^{-1}$ band in the 20β-acetates (*cf.* bands g and H in Figs. 8 and 9). The strong band at 1080–1068 cm.$^{-1}$ in the 20β-acetate has been noted also by Wiggins and Klyne.[15]

Conjugated Acetoxysteroids.—Conjugated acetoxy groups are encountered in 3-acetoxy estrogenic steroids (Fig. 10) and in enol acetates, of which examples are given for the Δ^2-3-acetate and Δ^{16}-17

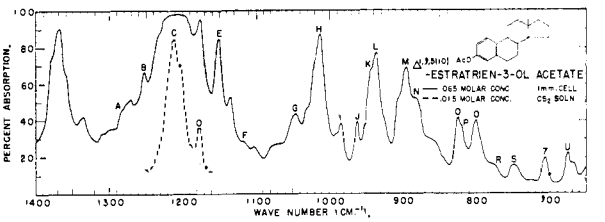

Fig. 10.—Characteristic infrared bands for phenolic 3-acetoxysteroid.

acetate groups (Figs. 11, 12). Most characteristic of these compounds is the displacement of the ma-

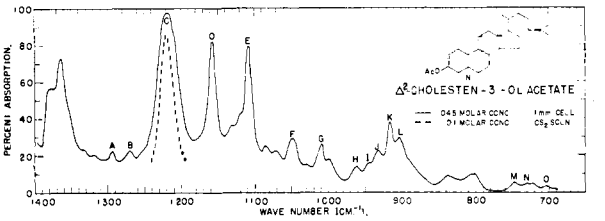

Fig. 11.—Characteristic infrared bands for Δ^2-3-acetoxysteroid.

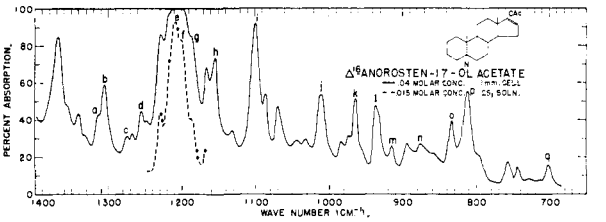

Fig. 12.—Characteristic infrared bands for Δ^{16}-17-acetoxysteroid.

jor C—O stretching band downwards from 1250–1240 cm.$^{-1}$ to the region of 1220–1200 cm.$^{-1}$ and it

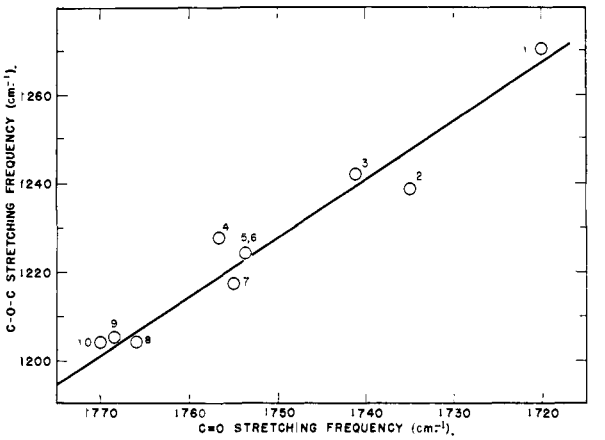

Fig. 13.—Diagram showing inverse relationships between C=O and C—O stretching frequencies for steroid esters: (1) 3-benzoxysteroid; (2) equatorial 3-acetoxysteroid; (3) 17β-acetoxysteroid; (4) 21-acetoxy-20-ketosteroid; (5) $\Delta^{17(20)}$ - 20 - acetoxysteroid; (6) $\Delta^{20(21)}$ - 20 - acetoxysteroid; (7) Δ^2-3-acetoxysteroid; (8) phenolic 3-acetoxysteroid; (9) Δ^{16}-17-acetoxysteroid; (10) naphtholic 3-acetoxysteroid (carbon disulfide solution).

(15) H. S. Wiggins and W. Klyne, *Chemistry and Industry*, 1448 (1955).

is interesting to note that the frequency of this band varies in an approximately inverse linear relationship with the C=O stretching frequency as is demonstrated in Fig. 13.

Both the phenolic and the enolic acetates show much additional characteristic structure, the most notable bands being at 1013 cm.$^{-1}$ in phenolic 3-acetates, 1160 and 1108 cm.$^{-1}$ in Δ^2-3-acetates and at 1097 cm.$^{-1}$ in Δ^{16}-17 acetates. These bands show up quite characteristically when other functional groups are also present, as is demonstrated in Fig. 19 where most of the Δ^2-3-acetate and Δ^{16}-17-acetate bands can be recognized in the spectrum of $\Delta^{2,16}$-androstadiene-3,17-diol diacetate.

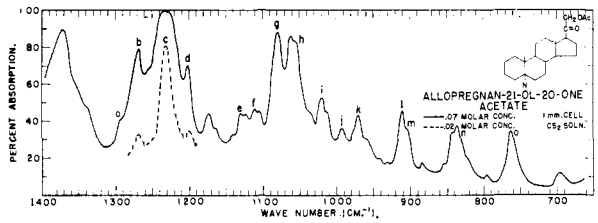

Fig. 14.—Characteristic infrared bands for 21-acetoxy-20-keto-5α-steroid.

Di- and Polysubstituted Steroids.—Examples of diacetate spectra are shown in Figs. 15 and 16, and provided the two acetoxy groups are at well separated positions the bands assignable to each functional group can be distinguished. The same holds true for the 3-acetoxy-17-ketosteroid, and 17-acetoxy-3-ketosteroid spectra shown in Figs. 17 and 18, where the ketone-characteristic bands are also indicated.

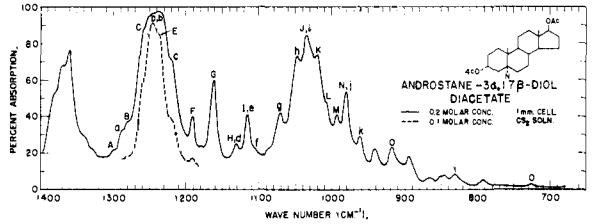

Fig. 15.—Infrared spectrum of 3α,17β-diacetoxy-5α-steroid: bands A–Q characterize the 3α-acetoxy group and bands a–l the 17β-acetoxy group (*cf.* Figs. 1 and 6).

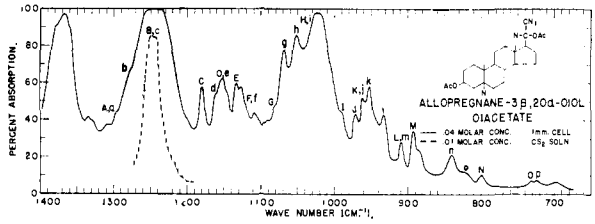

Fig. 16.—Infrared spectrum of 3β,20α-diacetoxy-5α-steroid: bands A–O characterize the 3β-acetoxy group and bands a–p the 20α-acetoxy group (*cf.* Figs. 2 and 8).

The 21-acetoxy-20-ketone system is of particular interest in view of its occurrence in the adrenocortical hormone acetates and the spectrum of the model compound, allopregnan-21-ol-20-one acetate, is shown in Fig. 14. In view of the known perturbation between the C=O stretching vibrations in 21-

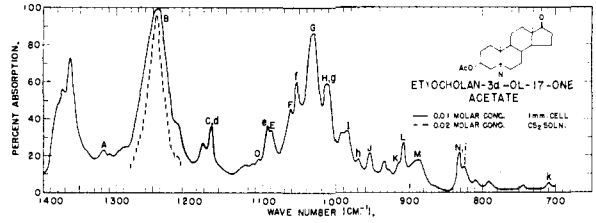

Fig. 17.—Infrared spectrum of 3α-acetoxy-17-keto-5β-steroid: bands A–N characterize the 3α-acetoxy group and bands d–k the 17-ketone group (*cf.* Fig. 3). (Bands d–k correspond with bands D–K in Fig. 8 of reference 3.)

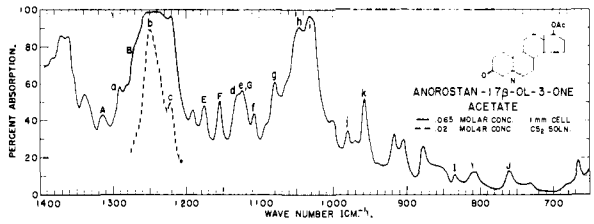

Fig. 18.—Infrared spectrum of 17β-acetoxy-3-keto-5α-steroid: bands a–l characterize the 17β-acetoxy group and bands A, B, E–G, I, J the 3-ketone group (*cf.* Fig. 6). (Bands A–J correspond with bands a–j in Fig. 2 of reference 3.)

actoxy-20-ketones,[16] it is unlikely that this system would show low frequency bands separately characteristic of the 20-ketone and 21-acetate groups and it is more realistic to consider the 21-acetoxy-20-ketone as an independent "chromophoric" system. On this basis we can recognize the bands listed in the last section of Table II as characterizing this group. Most notable is the downward displacement of the C–O stretching band to 1230 cm.$^{-1}$; this has been pointed out previously[5] and is consistent with the C=O/C–O stretching frequency relationships illustrated in Fig. 13.

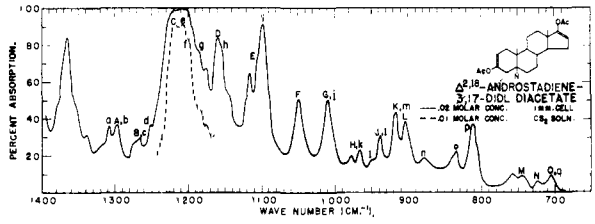

Fig. 19.—Infrared spectrum of $\Delta^{2,16}$-3,17-diacetoxy-5α-steroid: bands A–O characterize the Δ^2-3-acetoxy group and bands a–q the Δ^{16}-17-acetoxy group (*cf.* Figs. 11 and 12).

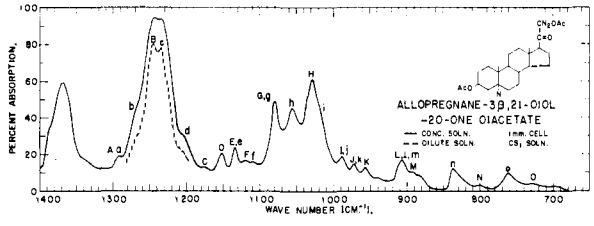

Fig. 20.—Infrared spectrum of 3β,21-diacetoxy-20-keto-5α-steroid: bands A–O characterize the 3-acetoxy group and bands a–o the 21-acetoxy-20-ketone group (*cf.* Figs. 2, 14).

(16) R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner THIS JOURNAL, **70**, 2024 (1948).

In Fig. 20 is shown the spectrum of allopregnane-3β-21-diol-20-one acetate in which most of the major bands are assignable to one or other of the functional systems. This constitutes the most complex structure to which this type of band analysis has yet been applied.

Concluding Remarks.—From the point of view of the organic chemist, the value of these curve analyses is restricted at present by the exclusion of compounds substituted in rings B and C. The logical approach to this problem involves a preliminary study of the spectra of monoalcohols, monoacetates and monoketones substituted only in the B or C rings, and studies directed to this end are in progress.

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The Preparation of 17β-Methyl-Δ⁵-androsten-3β-ol

BY MILTON HELLER AND SEYMOUR BERNSTEIN

RECEIVED OCTOBER 17, 1955

17β-Methyl-Δ⁵-androsten-3β-ol (IIa) has been unequivocally prepared from 17-methyl-Δ⁵,¹⁶-androstadien-3β-ol 3-acetate (I). The physical constants of IIa do not coincide with those reported for Serposterol.

The report by Ghosh and Basu[1] of a new steroid (Serposterol) isolated from the oleoresin fraction of *Rauwolfia serpentina* roots, which was postulated to have the structure 17β-methyl-Δ⁵-androsten 3β-ol (IIa), prompted us to synthesize the latter compound for comparison purposes.

An appropriate starting material was the already known 17-methyl-Δ⁵,¹⁶-androstadien-3β-ol 3-acetate (I).[2] Preferential reduction of the Δ¹⁶-double bond with 5% palladium-on-carbon in absolute alcohol was achieved readily[3] to give the 17β-methyl-3-acetate IIb. It was assumed that the hydrogenation had taken place from the rear as postulated previously.[2,4]

Saponification of IIb with 5% potassium hydroxide in methanol yielded 17β-methyl-Δ⁵-androsten-3β-ol (IIa). The 3-benzoate IIc was prepared in the usual manner. The structure of IIa was further verified by reducing the Δ⁵-double bond of the acetate IIb in acetic acid with Adams catalyst to afford 17β-methyl-androstan-3β-ol 3-acetate (IV) which compared well with a sample prepared from the Δ⁵,¹⁶-diene I in the authentic fashion.[2] Retention of the Δ⁵-3β-ol grouping in IIa was confirmed by its transformation into 17β-methyl-Δ⁴-androsten-3-one (III) (λ_{max} 241 mμ) through an Oppenauer oxidation.

It is important to notice the disparity of physical constants given by Ghosh and Basu[1] for their compound and derivatives and our compounds as shown in Table I.

TABLE I

	Ghosh and Basu[1] M.p., °C.	(CHCl₃) $[\alpha]_D$	This paper M.p., °C.	(CHCl₃) $[\alpha]_D$
17β-Methyl-Δ⁵-androsten-3β-ol (IIa)	152–154	−47°	164–165	−63°
17β-Methyl-Δ⁵-androsten-3β-ol 3-acetate (IIb)	136–138	...	123.5–124.5	−68
17β-Methyl-Δ⁵-androsten-3β-ol 3-benzoate (IIc)	142–144	...	193–194	−26

It is apparent from these figures that the compound isolated by Ghosh and Basu[1] is otherwise than as indicated by the structure IIa. It may finally be pointed out that the infrared absorption spectrum of IIa contains *one* medium strong band at 10.5 μ in contradistinction to the doublet at 10.3 and 10.4 μ reported for Serposterol.[1]

Androgen Assay.[5]—Subcutaneously as measured by the weight of the ventral prostate in the castrated male rat (single dose in sesame oil, 72 hours) both 17β-methyl-Δ⁵-androsten-3β-ol (IIa) and 17β-methyl-Δ⁴-androsten-3-one (III) were inactive.

(1) B. P. Ghosh and R. K. Basu, *Naturwiss.*, **42**, 130 (1955).

(2) S. A. Julia and H. Heusser, *Helv. Chim. Acta*, **35**, 2080 (1952).

(3) E. B. Hershberg, E. P. Oliveto, C. Gerold and L. Johnson, THIS JOURNAL, **73**, 5073 (1951), show many examples of preferential reductions of this type.

(4) L. Ruzicka, P. Meister and V. Prelog, *Helv. Chim. Acta*, **30**, 867 (1947).

(5) We are indebted to Dr. F. I. Dessau and his associates for these results.