Anal. Calcd. for $C_{24}H_{34}O_4$: C, 74.58; H, 8.87; O, 16.55. Found: C, 74.28; H, 8.89; O, 17.04.

The above enol ether XIII (1.0 g.) in 25 cc. of dioxane was added to 0.5 g. of calcium in 250 cc. of liquid ammonia and after stirring for 30 min., 4.0 g. of ammonium chloride was added and the product isolated in the usual manner. After heating under reflux for 1 hr. with 5 cc. of concd. hydrochloric acid, 10 cc. of water and 25 cc. of methanol, **19-norprogesterone** (VIII) (0.27 g., m.p. 140–142°) was obtained after passage through a short column of alumina and recrystallization from acetone–hexane.

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[CONTRIBUTION FROM THE SLOAN-KETTERING INSTITUTE FOR CANCER RESEARCH AND THE DIVISION OF PURE CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA][1]

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

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Characteristic absorption bands in the range 1350–650 cm.$^{-1}$ are reported for steroids hydroxylated at C(3), C(17) and C(20). The bands are observed in the monohydroxy compounds and in steroids containing additional hydroxy, acetoxy and ketonic groups, provided the functional groups are well separated. The general implications of these and similar bands in the spectra of ketones and acetates also are considered.

In preceding papers[2,3] it has been shown that many of the prominent bands occurring between 1350 and 650 cm.$^{-1}$ in the infrared spectra of steroid ketones and acetates depend specifically on the position and stereochemical arrangement of the functional group. Where the steroid contains two or more functional groups it is often possible to distinguish bands characteristic of each group. This applies most generally where the functional groups are well separated so that interaction effects are reduced. Examples have been given where one functional group is at C(3) and the other at C(17) or C(20).

The spectra of a large number of steroid alcohols have now been surveyed in a similar fashion, and for these compounds also many of the infrared absorption bands in the 1350–650 cm.$^{-1}$ range are observed to fall within narrow frequency ranges for steroids containing the same hydroxy substituent.

Experimental Methods and Results

The spectra were measured on Perkin–Elmer model 112 and model 21 spectrometers using sodium chloride prisms. The bands common to the various compounds of the same type are listed in Table I and the frequency ranges of the bands common to the compounds of the same type are summarized in Table II. A representative spectrum of each type of steroid alcohol is illustrated in Figs. 1–11. The common bands are cross-referenced between figures and tables by the letters A, B, etc., but it must be emphasized that these letters are assigned for identification purposes only, and no relationship is implied between bands carrying the same letter on different figures.

The bands are classified in Tables I and II into categories I, II and III. The basis of this classification was discussed in connection with ketone spectra.[2] Category I bands provide the main functional group identification; category II bands usually stand out in the spectra and are useful for secondary confirmation of the structure. The category III bands are generally weaker and tend to be obscured by other absorption in the spectra of steroids containing more than one functional group.

Most of the spectra were measured in carbon disulfide solution, but, because of the low solubility of many hydroxy steroids in this solvent, data for chloroform solutions at 1 mm. path length and for potassium bromide dispersions also are included in Table I. The spectra of some hydroxysteroids in potassium bromide disks have been shown to be sensitive to the conditions under which the disk is prepared[4]; therefore the frequency ranges given in Table II are based only on measurements in carbon disulfide solution.

The majority of the spectra discussed in this paper have been published in an atlas[5,6] and in the right hand column of Table I references are given to the corresponding atlas chart numbers. In some instances the band positions given in Table I are taken from measurements made with the model 112 spectrometer under higher resolution than the curves published in the atlas; this accounts for small frequency differences of the order of ±3 cm.$^{-1}$ between the band positions listed in Table I and those which would be interpolated from the atlas charts for the same compounds.

Discussion

3-Hydroxysteroids.—The most prominent band in the spectra of 3-hydroxysteroids occurs between 1056 and 999 cm.$^{-1}$. This band is outstandingly intense with $\epsilon_{\max}^{(a)}$ in the range 160–220. The corresponding bands in steroids hydroxylated at C(17) or C(20) have $\epsilon_{\max}^{(a)}$ in the range 60–120.

This band is presumed to involve principally a C-O stretching motion, and, in accordance with this, it is observed that the band position is affected only slightly by replacement of the hydroxy hydrogen atom with deuterium.[7] The position of the band within the range depends on the stereochemistry at C(3) and C(5).[8-10] The ranges previously assigned to this band in the various conformational isomers of 3-hydroxy steroids have been revised slightly as a result of the present investigation, and the new values are summarized in the second column of Table III.

3-Hydroxysteroids also exhibit several bands between 1015 and 890 cm.$^{-1}$; these, though weak, are usually sharp and can be useful as confirmatory

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TABLE 1.—CHARACTERISTIC GROUP FREQUENCIES IN THE

Compound	Solvent	Characteristic bands						
		A III	B III	C II	D II	E II	F III	G II
						I.	3α-Hydroxy-5α-	
Androstan-3α-ol (Fig. 1)	CS$_2$	1282	1242	1210	1162	1116	1070	1029
Allopregnan-3α-ol	CS$_2$	1283	1242	1216	1164	1112	1078	1031
Cholestan-3α-ol	CS$_2$	1283^{b}	1243	1216	1164	1120	1074	1033
Δ^{16}-Androsten-3α-ol	CS$_2$	1284	1242	1215	1165	1121^{c}	1065	1032
Androstan-3α-ol-17-one	CS$_2$	1288^{l}	1240^{b,l}	1212	1167^{l}	1121^{l}	1082	1027
Allopregnan-3α-ol-20-one	CS$_2$	1285	1240	1211^{m}	1164	1118	1071^{m}	1029
Androstane-3α,17β-diol 17-acetate	CS$_2$	1288^{o}	^{f}	1215	1166	1116^{o}	1074^{o}	1032^{n}
Allopregnane-3α,20α-diol 20-acetate	CS$_2$	^{h}	^{f}	1220^{c}	1163^{p}	1116^{p}	^{h}	1032
Androstane-3α,17β-diol	CHCl$_3$/KBr^{i}	^{h}	*1235*^{r}	*1215*	*1166*	1118	1067^{r}	1032^{r}
Allopregnane-3α,20α-diol	KBr	1275^{s}	1239^{s}	1211^{s}	1157	1120	1066^{s}	1037
		A III	B III	C III	D III	E III	F II	G II
						II.	3β-Hydroxy-5α-	
Androstan-3β-ol (Fig. 2)	CS$_2$	1295	1273	1250	1222	1210^{c}	1163	1132
Allopregnan-3β-ol	CS$_2$	1295^{c}	1274	1250	1222	1214	1167	1132
Cholestan-3β-ol	CS$_2$	1294	1270	1254	1223^{c}	1210	1168	1132
Ergostan-3β-ol	CS$_2$	1292	1270	1252	1222	1210	1168	1130
Δ^{22}-Stigmasten-3β-ol	CS$_2$	1293	1270	1252	1222	1210	1168	1132
Androstan-3β-ol-17-one	CS$_2$	1292^{l}	1272	1254^{l}	1219	1203^{l}	1170^{l}	1128^{l}
Allopregnan-3β-ol-20-one	CS$_2$	1289^{m}	1276	1256	1220	1211^{m}	^{h}	1134
Androstane-3β,17α-diol	CHCl$_3$/KBr^{i}	*1298*	*1275*	*1257*	^{h}	*1202*	*1170*	1135
Androstane-3β,17β-diol	CHCl$_3$	^{e}	^{e}	^{e}	^{e}	^{e}	^{e}	1132^{r}
Allopregnane-3β,20α-diol	CHCl$_3$/KBr^{i}	*1300*	*1278*	*1251*	^{h}	*1212*^{s}	*1167*^{s}	^{h}
		A III	B III	C III	D III	E II	F III	G III
						III.	3α-Hydroxy-5β-	
Etiocholan-3α-ol (Fig. 3)	CS$_2$	1278	1261	1250	1216	1170	1108	1079
Pregnan-3α-ol	CS$_2$	1278	1264	1250	1218	1171	1108^{c}	1082
Coprostan-3α-ol	CS$_2$	1273	1264	1256	1216	1169	1108	1088
Δ^{16}-Etiocholen-3α-ol	CS$_2$	1275	1263	1252	1219	1167	1105	1087^{c}
Etiocholan-3α-ol-17-one	CS$_2$	1282	1265^{c}	1255^{l}	1215^{c,j}	1168^{l}	1105^{c}	1083^{l}
Pregnan-3α-ol-20-one	CS$_2$	1280	1261	^{h}	1219^{m}	1175^{n}	1106	1088^{m}
17α-Pregnan-3α-ol-20-one	CS$_2$	1280	1260	1255	1217^{m}	1165	1110	1089^{m}
Etiocholane-3α,17β-diol 17-acetate	CS$_2$	^{h}	^{f}	^{f}	1220^{o}	1171	1109^{o}	1088
Etiocholan-3α,17α-diol	CHCl$_3$/KBr^{i}	*1270*	*1260*	^{h}	*1211*	*1162*	1108	1087
Etiocholane-3α,17β-diol	CHCl$_3$/KBr^{i}	*1280*^{r}	*1265*^{c,r}	*1244*^{r}	*1210*	*1165*^{c,r}	1110^{r}	1088
Pregnane-3α,20α-diol	CHCl$_3$/KBr^{i}	*1279*^{c}	*1262*	*1255*	*1217*^{c}	*1171*^{s}	1113	1090^{c}
		A III	B III	C II	D II	E II	F III	G III
						IV.	3β-Hydroxy-5β-	
Etiocholan-3β-ol (Fig. 4)	CS$_2$	1300	1270	1252	1218	1167	1135	1117
Pregnan-3β-ol	CS$_2$	1304	1276	1251	1220	1162	1138	1122
Coprostan-3β-ol	CS$_2$	1302	1276	1249	1215	1167	1134	1122
Δ^{16}-Etiocholen-3β-ol	CS$_2$	1301	1274	1249	1219	1162	1138	1120
Etiocholan-3β-ol-17-one	CS$_2$	1305	1278^{c}	1252^{l}	1218	1162	1134	1118^{c}
Pregnane-3β,17α-diol-20-one	CHCl$_3$/KBr^{i}	*1304*	^{h}	*1242*	*1225*	*1166*	1142	1115
Compound	Solvent	A III	B III	C III	D II	E III	F III	G III
						V.	3β-Hydroxy-Δ^{5}-	
Δ^{5}-Androsten-3β-ol (Fig. 5)	CS$_2$	1292	1268	1251	1217	1191	1172	1134
Δ^{5}-Pregnen-3β-ol	CS$_2$	1290	1272	1252	1216	1191	1172	1126
Δ^{5}-Cholesten-3β-ol	CS$_2$	1285	1272	1258	1220	1191	1170	1133
Δ^{5}-Stigmasten-3β-ol	CS$_2$	1286	1269	1251	1212	1189	1165	1130
Δ^{5}-17α-Pregnene-3β,17β-diol	CS$_2$	1288	1270	1252	1215	1193	1165	1139
Δ^{5}-Androsten-3β-ol-17-one	CS$_2$	1288^{l}	1265	1254^{l}	1216	1188	1170^{l}	1134
Δ^{5}-Pregnen-3β-ol-20-one	CS$_2$	1292^{m}	1273	1256	1217	1191^{m}	1171^{m}	1134
3β-Hydroxy-Δ^{5}-cholenic acid methyl ester	CS$_2$	1292	1268^{c}	1252	1215	1189	^{f}	1131^{c}
Δ^{5}-Androstene-3β,17α-diol	CHCl$_3$	^{e}	^{e}	^{e}	^{e}	^{e}	^{e}	1137
Δ^{5}-Androstene-3β,17β-diol	CHCl$_3$	^{e}	^{e}	^{e}	^{e}	^{e}	^{e}	1137^{r}
17-Ethynyl-Δ^{5}-androstene-3β,17β-diol	CHCl$_3$	^{e}	^{e}	^{e}	^{e}	^{e}	^{e}	1136
Δ^{5}-Androstene-3β,16α-diol	KBr	1287	^{h}	1250	1220	1192	1173	1136

INFRARED SPECTRA OF HYDROXYSTEROIDS BELOW 1350 CM.$^{-1}$

and categories[a]

H	I	J	K	L	M	N	O	P	Q	R	Chart number in steroid atlas[5,6]
I	II	II	II	II	III	III	III	III	III	III	

steroids

H	I	J	K	L	M	N	O	P	Q	R	Chart number in steroid atlas[5,6]
1001	973	952	927	907	896	886	825	796	722	701	23
1001	973	957	932	907	896	882	827	796	728	701	335
1002	974	960	934	909	901^{c}	886	826	796	728	701	38
1001	970	959	935	904	901	886	831	794	^{g}	^{g}	28
999	973	964^{l}	924	907	896	884	829^{l}	795	726	702	135
1001	973	962^{m}	928	907	895	882^{c}	828	795	728	700	444
1004	^{h}	962^{o}	928	908	900	^{d}	822	795	^{h}	699	..
1003	976	962^{p}	933^{p}	906^{p}	898	881	825	794	725^{p}	699	..
1001	975^{c}	960^{r}	*925*	906^{c}	900	885^{r}	*823*	*795*	^{h}	^{h}	65
1010^{s}	978^{s}	954^{s}	^{h}	909	901^{s}	877^{s}	832	797	724^{s}	696	369

H	I	J	K	L	M	N	O	P	Q	
II	I	III	II	II	II	II	III	III	III	

steroids

H	I	J	K	L	M	N	O	P	Q	
1072	1038	1009	990	975	953	934	903	796	733	25
1078	1037	1011	990	976	954	936	901	798	738	337
1072	1036	1010	990	975	954	936	904	795	734	40
1075	1037	1011^{c}	991	975	957	937	904	796	734	51
1074	1035	^{h}	991^{c}	^{g}	957	935	908	795	^{d}	59
1078^{c}	1037	1009^{l}	989	974	953	935	901	796	734	137
1075^{m}	1037	1010^{c}	993	978	951^{m}	936	900	796	732	150
1075	1035	1010	994	979	954	*936*	898	*801*	*727*	67
1069^{r}	1043	1012^{r}	992	977	954^{r}	^{e}	906^{c}	^{e}	^{e}	360
1070^{s}	1033	1010^{s}	994^{s}	978^{s}	954^{c,s}	*932*	905^{s}	799	736	74

H	I	J	K	L	M	N	
II	I	II	II	II	II	III	

steroids

H	I	J	K	L	M	N	
1063	1035	1009	952	912	898	834	31
1066	1038	1014	945	912	899	832	345
1066	1037	1012	946	913	900	831	49
1065	1038	1010	943	916	893	835	34
1060	1038	1007^{l}	947	920	898	829^{l}	144
1066	1035	1012	952^{c}	908^{o}	899	^{d}	156
1066	1037	1012	952	908	899	838	452
1070^{o}	1037^{o}	1013	947^{o}	914^{o}	897^{o}	833^{o}	..
1063	1034	1012	949	*912*	899	*841*	364
1069^{r}	1032^{r}	1007^{c}	946^{r}	*917*^{r}	898^{r}	*830*^{r}	71
1067^{s}	1030	1011^{s}	946	*914*^{s}	898^{s}	*829*	77

steroids

H	I	J	K	L	M	N	O	P	Q	R	S	T	U	
III	III	I	III	II	II	III	III	II	III	III	III	III	III	
1074	1060	1030	998	983	960	949	932	908	879	832	782	732	700	33
1076	1062	1032	1000	986	960	950	928	913	881	830	788	740	703	37
1072	1060	1033	1000	984	959	950^{c}	928	916	880	828	787	735	702	50
^{h}	^{h}	1033	1002	982	962	952^{c}	925	906	880	834	^{h}	745	703	..
1075^{c}	1065^{c}	1033	1006^{l}	980	959	946	930	910	879	825^{l}	788	740	708^{l}	146
1083^{m}	1061	1031	*1002*	985	966	955^{c}	*931*	912	880	*830*	^{h}	^{h}	*704*	180

H	I	J	K	L	M	N	O	P	Q	R	S	
III	III	I	II	III	II	II	III	II	II	II	III	

steroids

H	I	J	K	L	M	N	O	P	Q	R	S	
1109	1079	1050	1019	1007	978	954	941	840	812	796	735	27
1111	1082	1049	1019	1007	982	953	935	840	806	798	740	339
1109	1082	1049	1023	1007	986	954	936	840	804^{c}	798	736	41
1105	1080^{c}	1051	1022	1007	986	953	934	838	805^{c}	800	740	58
1094^{b}	1094^{b}	1040	1020	1005	988	956	932^{c}	836	806	798	740	368
1110^{l}	1084	1056^{l}	1025	1006^{l}	979	954	938	841	805	798	742	139
1109	^{h}	1047	1021	1007	985	953	^{h}	^{d}	805^{c}	798	738	..
1110^{c}	1082^{c}	1054	1020	1008	986	958	933	838	809^{c}	800	739	235
1102	1079^{c}	1045	1021	1008	971	955	^{e}	835	^{e}	^{e}	^{e}	68
1100^{c}	1077^{c}	1050^{r}	1028^{r}	1010^{c}	980^{r}	955^{r}	939	837	^{e}	^{e}	^{e}	69
1105^{c}	1085	1046	1021	1006	986	955	^{e}	835	^{e}	^{e}	^{e}	..
1102	1083	1055	1026	1012	977	957	937	832	805	798	..	359

(TABLE I.

		A	B	C	D	E	F	G
		III	II	II	I	II	III	II
						VI.	17β-Hydroxy-5α-	
Androstan-17β-ol (Fig. 6)	CS_2	1246	1134	1085	1046	1025	1008^c	984
Androstan-17β-ol-3-one	CS_2	1250^k	1135^l	1077	1059	1027	1011	981
Δ¹-Androsten-17β-ol-3-one	CS_2	1242	1133^k	1082	1059	1024	1011	982
Androstane-3α,17β-diol	$CHCl_3/KBr^i$	*1253*	*1135*	1067^q	1049	1032^q	1010^c	985
Androstane-3β,17β-diol	$CHCl_3$	^{e}	1132^q	1069^q	1059	1027	1012^q	^{e}
Androstane-6β,17β-diol	$CHCl_3$	^{e}	1134	1068	1046	1025	1012	989
		A	B	C	D	E	F	G
		III	III	III	III	II	II	II
						VII.	17β-Hydroxy-5β-	
Etiocholan-17β-ol (Fig. 7)	CS_2	1288	1263	1246	1163	1135	1116	1067
Etiocholan-17β-ol-3-one	CS_2	1288^k	1264^k	1250^k	1167^k	1136	1117	1070
Etiocholane-3α,17β-diol	$CHCl_3/KBr^i$	*1280*^{q}	*1265*^{c,q}	1244^q	*1167*^{q}	1132	1110^q	1069^q
		A	B	C	D	E	F	G
		III	III	III	I	I	III	III
						VIII.	Δ⁴-, Δ⁵- and Δ¹˒⁴-17β-	
Δ⁴-Androsten-17β-ol-3-one	CS_2	1249	1130^k	1075	1057	1022	982	957^k
Δ¹˒⁴-Androstadien-17β-ol-3-one	CS_2	1249^c	1132^c	1075^c	1057	1020	982	957^k
Δ⁵-Androstene-3β,17β-diol	$CHCl_3$	^{e}	1137^q	$1077^{c,q}$	1050^q	1028^q	980^q	955^q
		A	B	C	D	E	F	G
		III	II	III	II	III	III	II
						IX.	20α-Hydroxy-5α-	
Allopregnan-20α-ol (Fig. 8)	CS_2	1265	1244	1210	1174	1148	1112	1099
Allopregnan-20α-ol-3-one	CS_2	1270^k	1239	1210	1172^k	1152^k	1114^k	1096
Allopregnane-3α,20α-diol 3-acetate	CS_2	^{f}	^{f}	1212	^{h}	1150^c	1117^n	1097
Allopregnane-3α,20α-diol	KBr	1275^q	1239^q	1211^q	1169	1150^c	1112	1097
Allopregnane-3β,20α-diol	$CHCl_3/KBr^i$	*1267*	^{h}	*1212*^{q}	*1167*^{q}	*1153*	1119	1098^c
		A	B	C	D	E	F	G
		III	III	III	III	III	II	III
						X.	20β-Hydroxy-5α-	
Allopregnan-20β-ol (Fig. 9)	CS_2	1272	1244	1172	1158	1120	1100	1044^b
Allopregnan-20β-ol-3-one	CS_2	1270^k	1242	1170^k	1150^k	1126^k	1098	1044
		A	B	C	D	E	F	G
		III	II	III	II	III	III	III
						XI.	20α-Hydroxy-5β-	
Pregnan-20α-ol (Fig. 10)	CS_2	1268	1240	1194	1172	1147	1114	1105
Pregnan-20α-ol-3-one	CS_2	1266^k	1244^k	$1190^{c,k}$	1168^k	1147^k	1112	1102^k
Pregnane-3α,20α-diol	$CHCl_3/KBr^i$	*1262*	*1240*	*1189*	*1171*^{q}	*1148*	1113^q	1102
		A	B	C	D	E	F	G
		III	III	III	I	III	II	III
						XII.	20β-Hydroxy-5β-	
Pregnan-20β-ol (Fig. 11)	CS_2	1270	1166	1147	1100	1064	1032	1008
Pregnan-20β-ol-3-one	CS_2	1266^k	1168^k	1148^k	1099^k	1060	1032	1000

[a] For significance of categories see text. [b] Broad band. [c] Inflection. [d] The absorption in this region was not measured. tion obscured by the strong band associated with the unsaturated group. [h] Band not observed. [i] Figures for measure- associated with the 3-ketone group.[2] [l] Also associated with the 17-ketone group.[2] [m] Also associated with the 20-ketone with the 20-acetoxy group.[3] [q] Also associated with the 3-hydroxy group (see this table, sections I–V). [r] Also associated sections IX–XII).

evidence for the stereochemistry at C(3) and C(5). Some of these bands have been noted previously by Rosenkrantz and Skogstrom, and they are summarized in the columns to the right of Table III. The Δ⁵-3β-hydroxysteroids also have characteristic bands between 850 and 790 cm.$^{-1}$ associated with the unsaturated linkage.[11]

17-Hydroxysteroids.—Our observations on steroids hydroxylated at C(17) are restricted to the 17β-hydroxy compounds of the C_{19}-series. The spectra of androstan-17β-ol and etiocholan-17β-ol are shown in Figs. 6 and 7. All the 17β-hydroxy compounds have a medium-strong band between 1059 and 1046 cm.$^{-1}$ (band D of Fig. 6 and band H of Fig. 7); this is probably a "C–O stretching band" and is useful for differentiating these compounds from those hydroxylated at C(3). The position of this band is not significantly different in compounds of the 5α- and 5β-series, or in compounds containing a Δ⁴- or Δ⁵-bond. The spectra shown in Figs. 6 and 7 are readily distinguished, but the differences between them depend mainly on small frequency shifts and intensity changes and are not consistent when other functional groups are also present. The infrared spectrum therefore does not provide a satisfactory means for differentiating between 17β-hydroxy compounds of the 5α- and 5β-series.

20-Hydroxysteroids.—The spectra of the 20β-hydroxysteroids we have examined are dis-

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(11) H. Hirschmann, THIS JOURNAL, **74**, 5357 (1952).

Continued)

H II	I III	J III	K III	
steroids				
956	916	889	824	29
953	913	^{h}	828	128
957^{k}	917	^{h}	827	. .
962^{q}	^{h}	885^{q}	*829*^{q}	65
954^{q}	^{e}	889	^{e}	360
960	920	890	^{e}	362

H I	I II	J II	K III	L III	M III	N III	
steroids							
1052	1030	985	950	918	898	830	35
1050	1028	985^{c}	950	918	898	828^{b,k}	142
1054	1032^{q}	*987*	946^{q}	*917*^{q}	898^{q}	*830*^{q}	71

H III	I III	
Hydroxysteroids		
915	828	130
920^{c}	828	427
914	^{e}	69

H II	I I	J III	K III	L I	M III	N III	O III	P III	Q III	
steroids										
1067	1012	996^{c}	976	957	929	906	889	875	725	341
1067	1010	999	^{h}	954	930^{c}	902	890	^{d}	727	441
1067	1016^{b,n}	988^{n}	977^{n}	956	928	906^{n}	888	877	726^{n}	. .
1066	1010^{r}	995^{c}	978^{q}	954	920	901^{q}	888	877^{q}	724^{q}	369
1070	1010	994	978	954^{c}	*932*^{q}	902	888	872	^{h}	74

H III	I III	J III	K I	L III	M III	N III	O III	P III	
steroids									
1030	1012	1002	965	936	908	876	830	722	343
1028	1010	998	962	932	904	882	826^{b}	722	442

H II	I II	J I	K III	L I	M III	N III	O III	P III	
steroids									
1088	1064	1008	987	952	910	895	876	725	348
1091	1072	1012	990	956	916	898	^{d}	725	. .
1090^{c,s}	1067^{q}	1011^{q}	990^{c}	958	*914*^{q}	898^{q}	875	^{h}	77

H II	I II	J III	K III	L III	M III	
steroids						
998	970	952	897	877	828^{b}	350
992	968	952	899	877	828^{k}	. .

[e] The absorption in this region was obscured by the solvent. [f] Absorption obscured by the strong ester band. [g] Absorpments made on KBr disks are italicized. [i] This band was not resolved in the curve shown in the "Steroid Atlas."[5,6] [k] Also group.[2] [n] Also associated with the 3-acetoxy group.[3] [o] Also associated with the 17-acetoxy group.[3] [p] Also associated with the 17-hydroxy group (see this table, sections VI–VIII). [s] Also associated with the 20-hydroxy group (see this table,

tinguished by the medium-strong band at 1100-1090 cm.$^{-1}$; these show predominantly in the spectra of the mono-alcohols (band F of Fig. 9 and band D of Fig. 11). The 20α-hydroxy steroids have no comparable band in this part of the spectrum and their strongest band appears at 1016-1008 cm.$^{-1}$ (band I of Fig. 8 and band J of Fig. 10). The 20α-hydroxysteroids of both the 5α- and 5β-series have a characteristic band at 957-952 cm.$^{-1}$ (band L of Figs. 8 and 10). The 20β-hydroxysteroids of the 5α-series have a strong band at 965–962 cm.$^{-1}$ (band K of Fig. 9), but in the 5β-series this band is not so prominent (band I of Fig. 11). These differences in the spectra of 20α- and 20β-hydroxysteroids between 970 and 950 cm.$^{-1}$ have been noted also by Wiggins and Klyne.[12]

No systematic differences are observed between the spectra of 20α-hydroxysteroids of the 5α- and 5β-series and the situation is similar to that of the 17β-hydroxy compounds discussed above. The spectra of the 20β-hydroxysteroids of the 5α- and 5β-series show more pronounced differences, notably between 1050 and 900 cm.$^{-1}$ where the 5β-compound shows a series of sharp peaks (bands F-H, J, K of Fig. 11). The spectra of the 20β-hydroxysteroids therefore appear to be more sensitive to the stereochemistry at C(5) than do either the

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

TABLE II

SUMMARY OF HYDROXYSTEROID CHARACTERISTIC FREQUENCIES

Band	Frequency range, cm.$^{-1}$	Category^{a}	Band	Frequency range, cm.$^{-1}$	Category^{a}
	3α-Hydroxy-5α			3β-Hydroxy-5α	
A	1288–1282	III	A	1295–1289	III
B	1243–1240	III	B	1276–1270	III
C	1220–1210	II	C	1256–1250	III
D	1167–1162	II	D	1223–1219	III
E	1121–1112	II	E	1214–1203	III
F	1082–1065	III	F	1170–1163	II
G	1033–1027	II	G	1134–1128	II
H	1004–999	I	H	1078–1072	II
I	976–970	II	I	1038–1035	I
J	962–952	II	J	1011–1009	III
K	935–927	II	K	993–989	II
L	909–904	II	L	978–976	II
M	901–895	III	M	957–951	II
N	886–881	III	N	937–934	II
O	831–822	III	O	908–900	III
P	796–794	III	P	798–795	III
Q	728–722	III	Q	738–732	III
R	702–699	III			
	3α-Hydroxy-5β			3β-Hydroxy-5β	
A	1282–1273	III	A	1305–1300	III
B	1265–1260	III	B	1278–1270	III
C	1256–1250	III	C	1252–1249	II
D	1220–1215	III	D	1220–1215	II
E	1175–1165	II	E	1167–1162	II
F	1110–1105	III	F	1138–1134	III
G	1089–1079	III	G	1122–1117	III
H	1070–1060	II	H	1076–1072	III
I	1038–1035	I	I	1062–1060	III
J	1014–1007	II	J	1033–1030	I
K	952–943	II	K	1006–998	III
L	920–908	II	L	986–980	II
M	900–893	II	M	962–959	II
N	838–829	III	N	952–946	III
			O	932–925	III
	17β-Hydroxy-5α		P	916–908	II
A	1250–1242	III	Q	881–879	III
B	1135–1133	II	R	834–825	III
C	1086–1077	II	S	788–782	III
D	1059–1046	I	T	745–732	III
E	1027–1024	II	U	708–700	III
F	1011–1008	III			
G	984–981	II		3β-Hydroxy-Δ^5	
H	957–953	II	A	1292–1285	III
I	917–913	III	B	1272–1265	III
J	889	III	C	1258–1251	III
K	828–824	III	D	1220–1212	II
			E	1191–1188	III
	17β-Hydroxy-5β		F	1172–1165	III
A	1288	III	G	1134–1126	III
B	1264–1263	III	H	1111–1105	III
C	1250–1246	III	I	1084–1079	III
D	1167–1163	III	J	1056–1047	I
E	1136–1135	II	K	1025–1019	II
F	1117–1116	II	L	1008–1006	III
G	1070–1067	II	M	986–978	III
H	1052–1050	I	N	958–953	II
I	1030–1028	II	O	941–933	II
J	985	II	P	841–838	II
K	950	III	Q	812–805	II
L	918	III	R	800–796	II
M	898	III	S	742–735	III
N	830–828	III			
	20β-Hydroxy 5α			20α-Hydroxy-5α	
A	1272–1270	III	A	1270–1265	III
B	1244–1242	III	B	1244–1239	II
C	1172–1170	III	C	1212–1210	III
D	1158–1150	III	D	1174–1172	II
E	1126–1120	III	E	1152–1148	III
F	1100–1098	II	F	1117–1112	III
G	1044	III	G	1099–1096	II
H	1030–1028	III	H	1067	II
I	1012–1010	III	I	1016–1010	I
J	1002–998	III	J	999–988	III
K	965–962	I	K	977–976	III
L	936–932	III	L	957–954	I
M	908–904	III	M	930–928	III
N	882–876	III	N	906–902	III
O	830–826	III	O	890–888	III
P	722	III	P	877–875	III
			Q	727–725	III
	20β-Hydroxy-5β			20α-Hydroxy-5β	
A	1270–1266	III	A	1268–1266	III
B	1168–1166	III	B	1244–1240	II
C	1148–1147	III	C	1194–1190	III
D	1100–1099	I	D	1172–1168	II
E	1064–1060	III	E	1147	III
F	1032	II	F	1114–1112	III
G	1008–1000	III	G	1105–1102	III
H	998–992	II	H	1091–1088	II
I	970–968	II	I	1072–1064	II
J	952	III	J	1012–1008	I
K	899–897	III	K	990–987	III
L	877	III	L	956–952	I
M	828	III	M	916–910	III
			N	898–895	III
	Δ^4-, Δ^5-, and $\Delta^{1,4}$-17β-Hydroxy		O	876	III
A	1249	III	P	725	III
B	1132–1130	III			
C	1075	III			
D	1057	I			
E	1022–1020	I			
F	982	III			
G	957	III			
H	920–915	III			
I	828	III			

[a] For significance of categories see text.

TABLE III

BANDS USEFUL FOR CHARACTERIZING THE STEREOCHEMISTRY OF 3-HYDROXYSTEROIDS

Structure	Main band, cm.$^{-1}$	Additional bands, cm.$^{-1}$
3α-Hydroxy-5α	1004– 999	976–970, 962–952, 935–927, 909–904
3β-Hydroxy-5α	1038–1035	993–989, 978–976, 957–951, 937–934
3α-Hydroxy-5β	1038–1035	1014–1007, 952–943, 920–908, 900–893
3β-Hydroxy-5β	1033–1030	986–980, 962–959, 916–908
3β-Hydroxy-Δ^5	1056–1047	1025–1019, 989–978, 958–953, 841–838, 812–805, 800–796

20α-hydroxy or 17β-hydroxy compounds. This is notable in view of the large distance separating the hydroxy groups from the center of stereoisomeric change.

General Conclusions

It is extremely unlikely that the complex spectra of such large molecules will ever be fully interpreted by the application of the conventional methods of

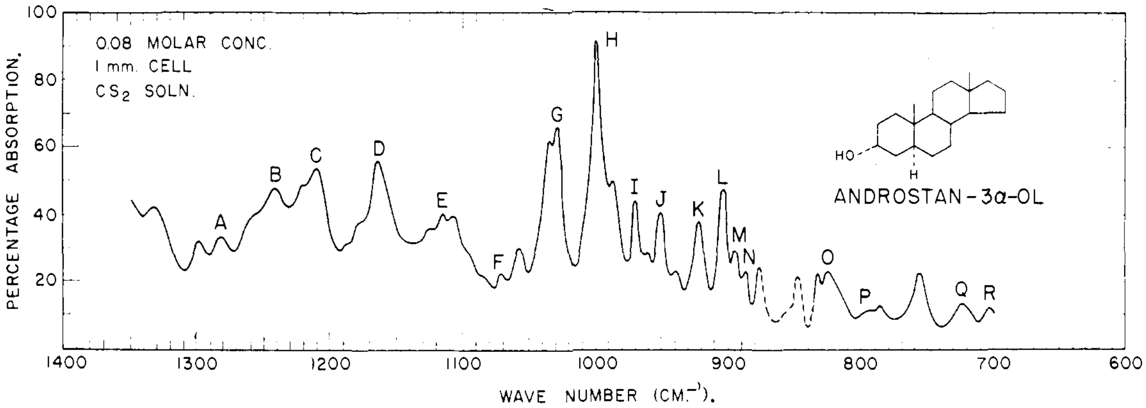

Fig. 1.

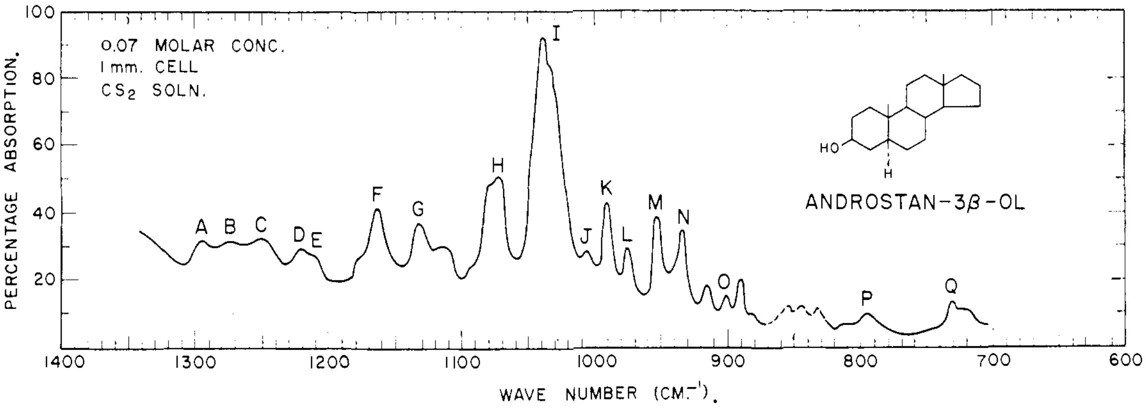

Fig. 2.

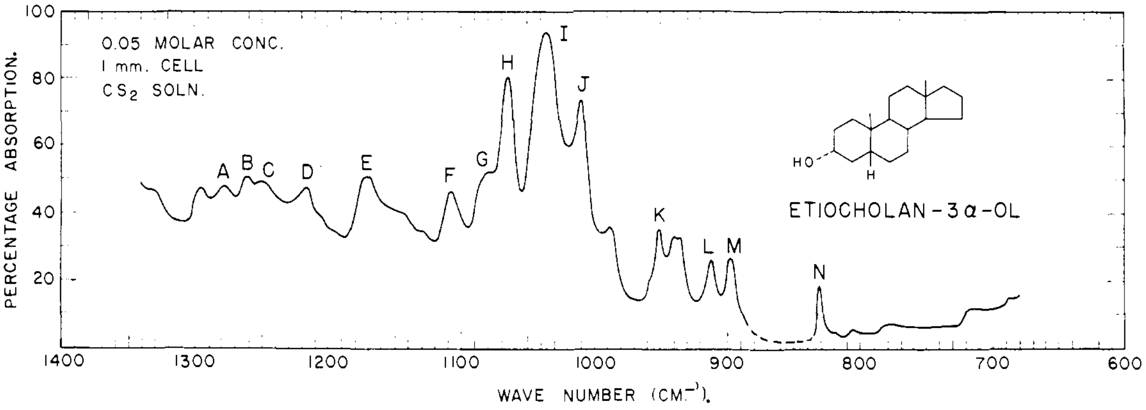

Fig. 3.

molecular vibrational analysis which were developed to deal with small polyatomic molecules. The characteristic frequencies tabulated for the various types of steroid alcohols, ketones and acetates in this and the two earlier papers[2,3] were derived by a purely empirical method of surveying the spectra of a large number of steroids of related structure and selecting the bands that appeared consistently within narrow frequency ranges.

The steroids of the types considered in these papers can be regarded as derived from androstane and etiocholane by substitution in the ring system, or by addition of a side chain at C(17). In a like manner their spectra can be regarded as derived from the spectra of these hydrocarbons by a modulating effect of the substituent. Expressed in these terms the problem is to determine the extent to which this modulation conforms to a standard pattern for a given type of substituent and also to determine the extent to which the modulation following the introduction of two or more substituents can be treated as the sum of the effects produced by each substituent acting separately. These concepts will be examined in more detail elsewhere.

The empirical band analyses reported in these papers enable us to look at steroid spectra in a little more rational manner than heretofore. It is clear that the various types of functional groups exercise their principal effects on different regions of the spec-

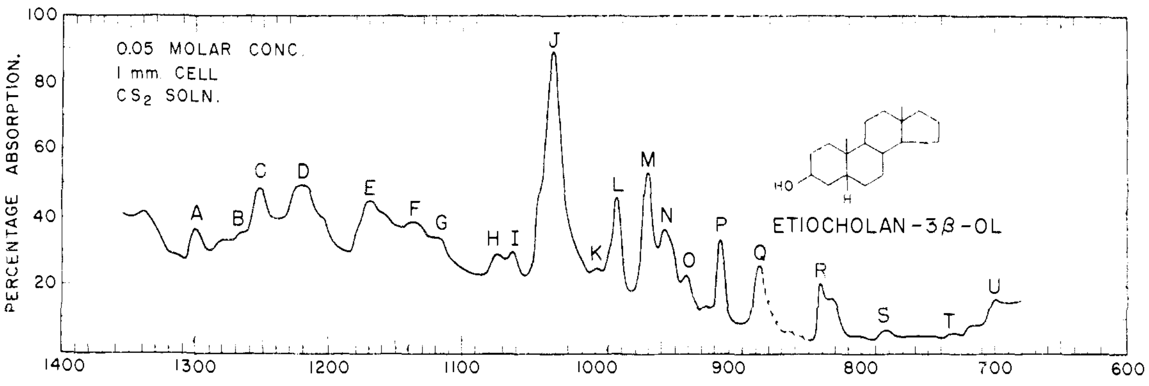

Fig. 4.

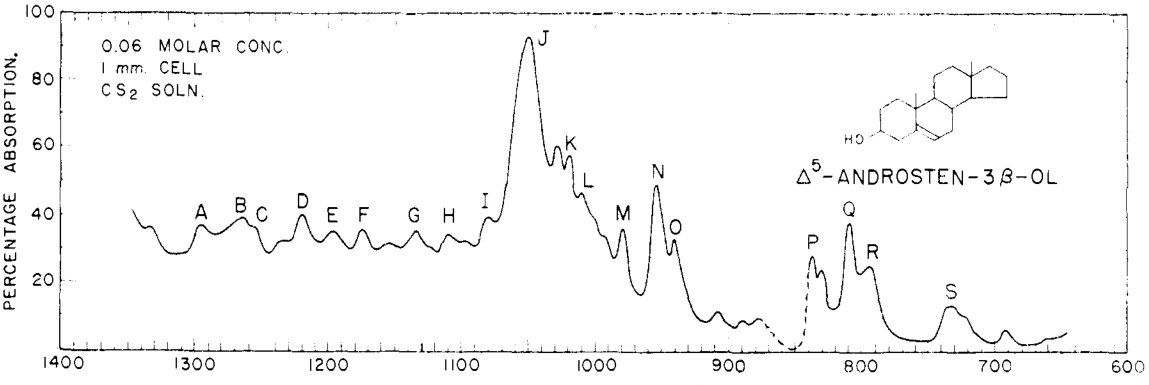

Fig. 5.

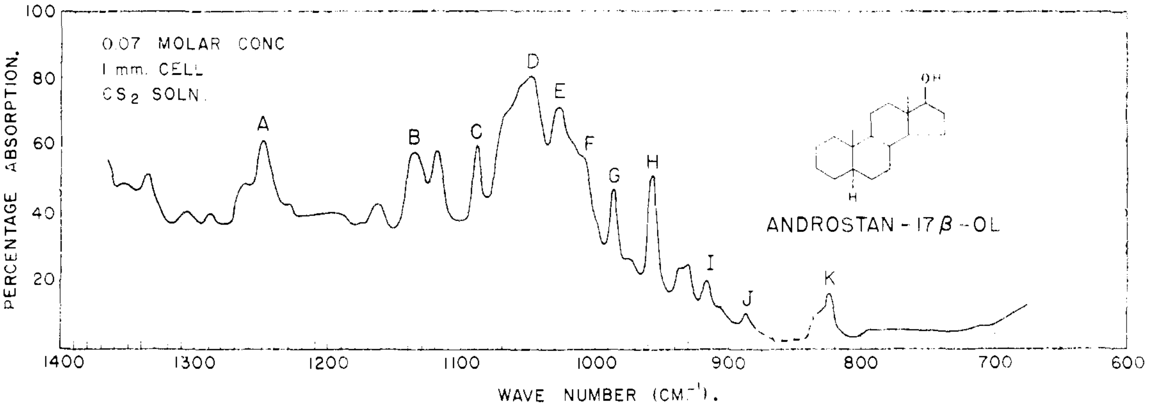

Fig. 6.

trum. In saturated 6-membered ring ketones and linear ketones the main effects of the substituents, which produce the bands of categories I and II, are observed in the 1300-1150 cm.$^{-1}$ region and also below 850 cm.$^{-1}$. The absorption in the higher frequency range probably involves skeletal vibration of the carbonyl group and of the carbon atoms attached directly to it; the weaker absorption below 850 cm.$^{-1}$ probably is associated with C-H bending vibrations of the α-methylene groups.[13] In 17-ketosteroids the strong skeletal modes are displaced to the 1100-1000 cm.$^{-1}$ region. In steroid acetates the main absorption bands occur near 1240 cm.$^{-1}$ and between 1100 and 1000 cm.$^{-1}$ and both probably involve stretching motions of the strongly polarized C-O bonds of the ester groups. The principal effect of the hydroxyl group also occurs between 1100 and 1000 cm.$^{-1}$ with pronounced secondary effects between 1000 and 900 cm.$^{-1}$. Where the functional groups are conjugated with ethylenic double bonds additional characteristic absorption appears below 900 cm.$^{-1}$ probably associated with the out-of-plane C-H deformation motions of the ethylenic hydrogen atoms.

The above generalization covers practically all of the prominent bands of ketones, alcohols and acetates that have been classified into categories I or II as being of practical use for purposes of struc-

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(13) R. N. Jones, B. Nolin and G. Roberts, THIS JOURNAL, **77**, 6331 (1955).

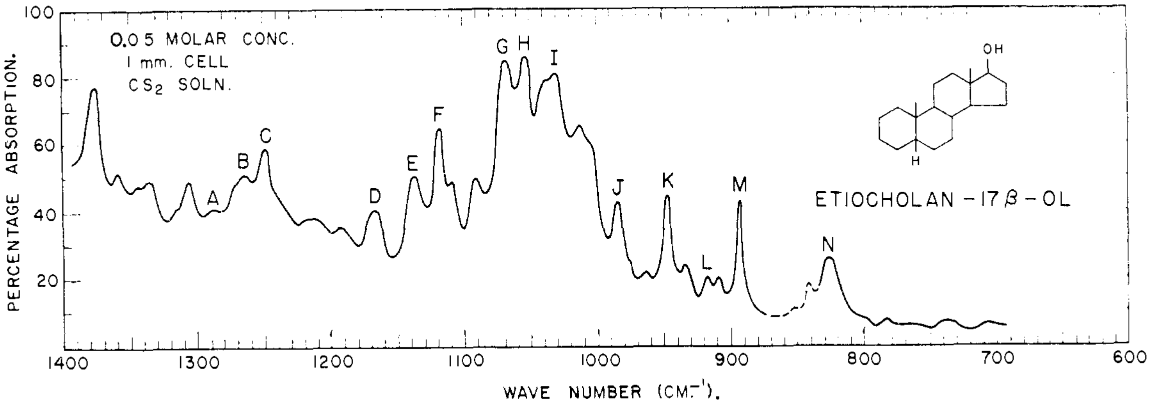

Fig. 7.

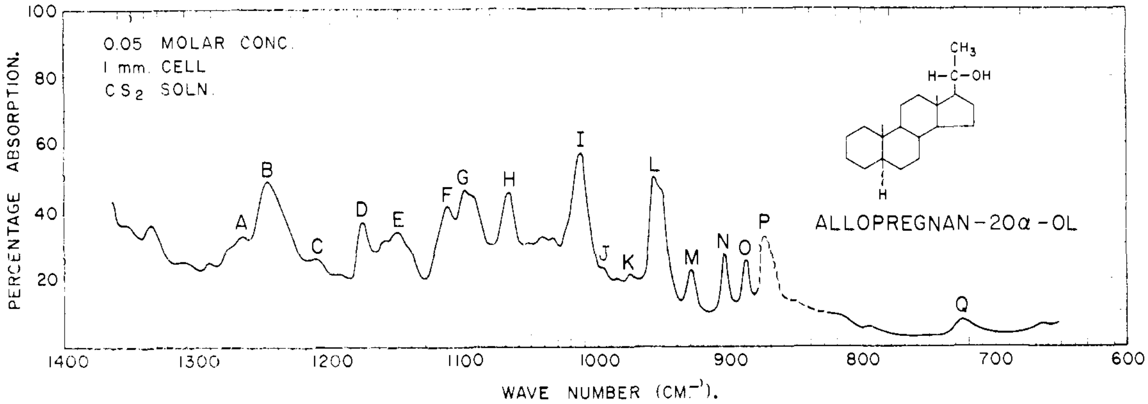

Fig. 8.

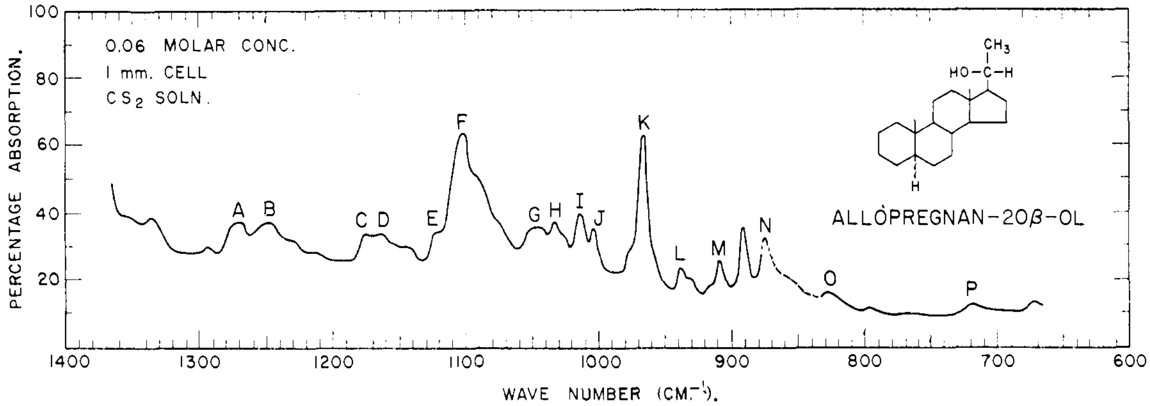

Fig. 9.

tural identification. There remain in addition the numerous weaker bands that we have put into category III. These are observed persistently in the various types of substituted steroids; their intensity is more variable and for the most part they fall outside of the frequency ranges discussed in the preceding paragraph. Very probably some of these bands are associated with vibrations localized in the neighborhood of the functional groups and are essentially similar to the bands of categories I and II. It is notable, however, that some of these bands appear in the same spectral region of steroids containing different functional groups; thus, for example, many types of steroids exhibit absorption near 1170 cm.$^{-1}$ and in the ranges 980-950 and 910-890 cm.$^{-1}$. These are the regions of strongest absorption below 1350 cm.$^{-1}$ in the spectra of androstane and etiocholane. They may be associated with vibrations that are characteristic of the ring system and persist in the spectra of the simpler mono- and disubstituted steroids because they arise from centers in the molecule that are remote from the positions of substitution with which we have been concerned in these papers, such as the angular methyl groups. The category III bands, together with other weak bands in the spectra of these compounds, are at present being examined from this point of view, and in a later paper we hope to discuss both their position and intensity in more detail.

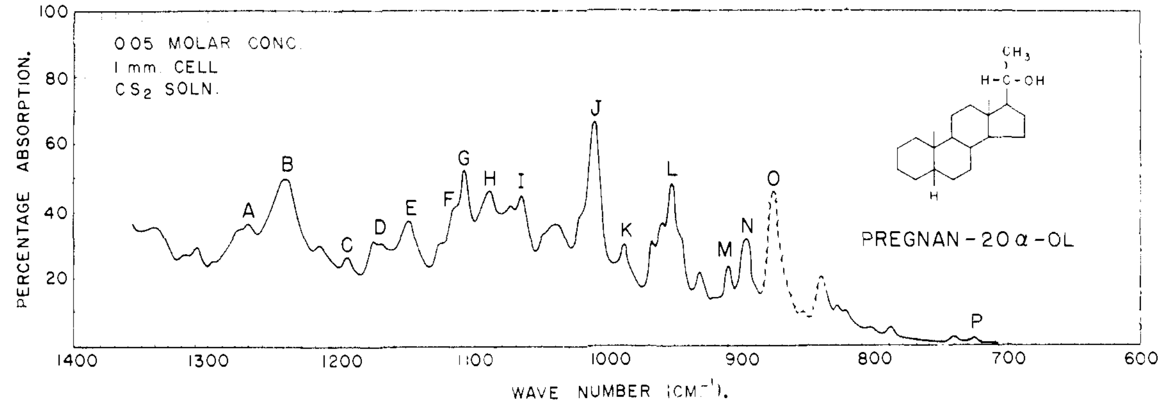

Fig. 10.

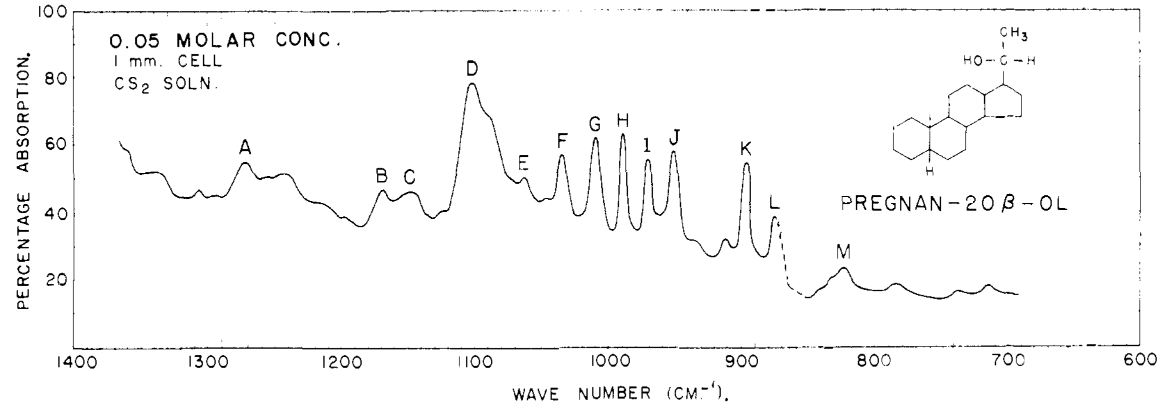

Fig. 11.

Acknowledgments.—We wish to thank Dr. E. M. Augdahl and Dr. A. Nickon who synthesized a number of the compounds of the C(21) series. We also wish to acknowledge the technical assistance of Mrs. M. A. MacKenzie, Miss Beate Spiegel and Miss Doris Leskin who measured a number of the spectra supplementing those published in the two volumes of the atlas of steroid spectra.[5,6]

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[Contribution from the Research Department, R. J. Reynolds Tobacco Co.]

Flue-cured Tobacco. III. Solanachromene and α-Tocopherol

By R. L. Rowland

Received April 7, 1958

A high molecular weight phenol, solanachromene, has been isolated from aged flue-cured tobacco leaf in 0.05% of the dry weight of the leaf. Structural studies indicate that solanachromene is 2,7,8-trimethyl-6-hydroxy-2(4',8',12',16',20',24',28',32',36'-nonamethyl-3',7',11',15',19',23',27',31',35'-heptatriacontanonenyl)-1,2-benzopyran (V, $R_1 = R_2 = CH_3$, $R_3 = H$). α-Tocopherol was isolated from aged tobacco leaf in an amount 0.01–0.02% of the dry weight of the leaf.

In a study of the ether-soluble compounds extracted from aged flue-cured tobacco, we have recently reported the isolation of solanesol[1] and neophytadiene.[2] We now wish to report the isolation of two phenol fractions, α-tocopherol and a high molecular weight unsaturated phenol to which we have given the name solanachromene. Isolation of these two compounds was accomplished by repeated chromatography using silicic acid.

Solanachromene, which constituted about 0.05% of the dry weight of the tobacco leaf, is a colorless oil which, after solidification at reduced temperature, melted at 16-19°. The infrared absorption is shown in Fig. 1. Absorption at 3 μ indicated the presence of a hydroxyl group, absorption at 6 μ indicated unconjugated double bonds of the type present in solanesol and absorption at 6.3 μ sug-

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[1] R. L. Rowland, P. H. Latimer and J. A. Giles, This Journal, **78**, 4680 (1956).

[2] R. L. Rowland, *ibid.*, **79**, 5007 (1957).