442. *Optical Rotatory Dispersion: Further Applications of the Octant Rule to Structural and Stereochemical Problems.**

By CARL DJERASSI and W. KLYNE.

The octant rule is applied to hexahydroindanones, to ketones which show weak or no apparent Cotton effect, and to ketones with atoms in " front octants." Tables of further reference values for the contributions of substituents to the amplitudes of Cotton-effect curves are given.

IN an earlier paper [1] we considered many applications of the octant rule [2] to arrays of essentially unstrained cyclohexane rings carrying carbonyl groups, *i.e.*, extended cyclohexanones. In the present paper we deal with (1) hexahydroindanone types, (2) " front octant " effects, and (3) ketones which show weak or no apparent Cotton effects. We also give tables of reference values for the contributions of substituents to the amplitudes of Cotton-effect curves.

Symbols on Octant Projections. Symbols used in formulæ have the following meanings to indicate the contributions of atoms:

× × Atoms symmetrically disposed; contributions cancel.
● atom in back octant; positive contribution.
○ atom in back octant; negative contribution.
▲ atom in front octant; positive contribution.
△ atom in front octant; negative contribution.
* atom in vertical *xy* plane (no contribution).

(1) *Hexahydroindanone Types.*—Hexahydroindanones may be divided into two classes according to whether the ketone group is in a six-membered or a five-membered ring. The latter group cannot yet be considered adequately in terms of the octant rule; some very tentative suggestions have been made elsewhere.[3-5] The six-membered ring ketones (hexahydroindane-4- and 5-ones) can, however, be considered; the results, some of which have been presented previously,[6] show, in summary, that such a ketone gives a rotatory dispersion curve of the same sign and approximately the same amplitude as its decalone analogue.

Hexahydroindan-5-ones. The curve for 8-methyl-*trans*-hexahydroindan-5-one [6] (I; *a*, +47) agrees closely with that for the corresponding methyldecalone (II; *a*, +47), as would be expected from the projections.

(+)-8-Methyl-*cis*-hexahydroindan-5-one [7] has a negative Cotton curve,[6] very similar to that of 5β-cholestan-3-one. The absolute configuration (III) was therefore allotted to this enantiomer. However, this allocation is not unambiguous, since any *cis*-hexahydroindanone can exist in two conformations (in the same way as a *cis*-decalone). The corresponding (1*S*,8*S*)-*cis*-1-hydroxy-5-oxo-compound (IV) was found by Acklin and Prelog [8] to give a similar negative dispersion curve; this 1-hydroxy-5-oxo-compound was correlated,

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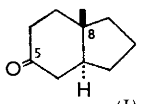
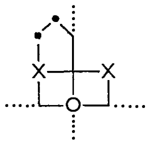
* This paper forms Part LXXVII in the series " Optical Rotatory Dispersion Studies " by Djerassi *et al.* (preceding paper, Bunnenberg, Djerassi, Mislow, and Moscowitz, *J. Amer. Chem. Soc.*, 1962, **84**, 2823, 5003 and Part VI in the series " Optical Rotatory Dispersion " by Klyne *et al.* (previous paper, Klyne and Robertson, *Experientia*, 1962, **18**, 413).

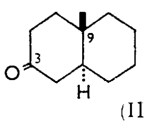
[1] Djerassi and Klyne, *J.*, 1962, 4929.
[2] Moffitt, Moscowitz, Woodward, Klyne, and Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 4013.
[3] Klyne, *Bull. Soc. chim. France*, 1960, 1396.
[4] Klyne, *Tetrahedron*, 1961, **13**, 29.
[5] Djerassi, Fishman, and Nambara, *Experientia*, 1961, **17**, 565.
[6] Djerassi, Marshall, and Nakano, *J. Amer. Chem. Soc.*, 1958, **80**, 4853.
[7] Conroy and Cohen, *J. Org. Chem.*, 1958, **23**, 616.
[8] Acklin and Prelog, *Helv. Chim. Acta*, 1959, **42**, 1239.

by an unusual 1,5-intramolecular hydride shift, with the (5*S*,8*S*)-5-hydroxy-1-ketone (V) from which the ketone (III) was subsequently obtained. The absolute configurations of the whole series were allotted by asymmetric synthesis, involving the 1-hydroxyl groups. The rotatory dispersion curve of compound (III) can therefore be used to assign the "steroid-like" conformation to this compound.



(I)





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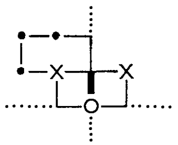

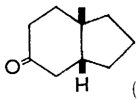

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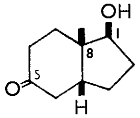

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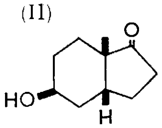
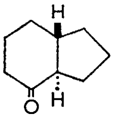
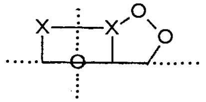


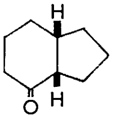
(V)

Hexahydroindan-4-ones. Schenker [9] has allotted the absolute configurations of simple hexahydroindan-4-ones (VI, VII) (obtained by microbiological routes) by analogy with those of the C–D steroid ketones (VIII) and (IX). The compounds (VI) and (VII) showed negative and positive curves, respectively; the samples were not optically pure, and the numerical values are therefore not significant.

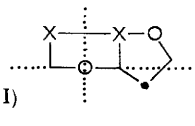


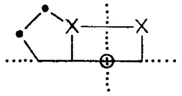
(VI)



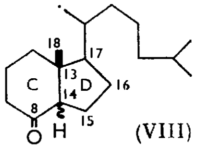


(VII)

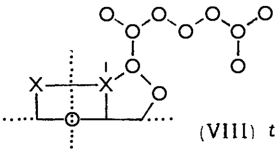




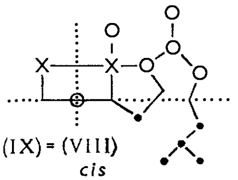
The *trans*- (VIII) and the *cis*-bicyclic ketone (IX) obtained by Inhoffen *et al.*[10] by oxidation of calciferol, consist of rings C and D of the steroid nucleus with the side-chain. Exact predictions of the size of the Cotton effect are impossible because of the large flexible side-chain, but an estimate may be made as shown in the following diagrams.



(VIII)



(VIII) *trans*



(IX) = (VIII) *cis*

In the *trans*-isomer (VIII), C-16,17,18 and the entire side-chain are all in the upper right-hand octant; a large negative Cotton effect would be predicted and is found (*a*, −129).[6] In the *cis*-isomer (IX) C-15 (now axial) has a large positive contribution, cancelling (roughly) those from C-17 and C-18; the two halves of the side-chain C-20,21,22 (upper right-hand octant) and C-24,25,26,27 (lower right-hand octant) may reasonably be expected to cancel. The very small Cotton effect (−9) can thus be rationalized.

3-Oxo-B-norsteroids. Chemical evidence about the configuration at position 5 of the first-known isomer of this group has until recently been conflicting.[11,12] Djerassi *et al.*[6] suggested that this was the 5β-isomer (XI) because its dispersion curve was of the same sign and shape as that of 5β-cholestan-3-one (AB-*cis*). Recently both 5-epimers (X and

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[9] Schenker, Thesis, E.T.H., Zürich, 1960.

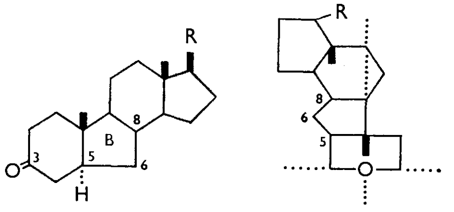
[10] Inhoffen, Quinkert, Schutz, Kampe, and Domagk, *Chem. Ber.*, 1957, **90**, 664.

[11] Fieser, *J. Amer. Chem. Soc.*, 1953, **75**, 4386.

[12] Dauben and Foncken, *J. Amer. Chem. Soc.*, 1956, **78**, 4736.

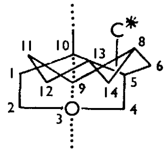
XI) have been prepared by Summers[13] and by Dauben *et al.*,[14] who have brought forward chemical evidence supporting the allotment of configurations made by Djerassi *et al.* Further, the dispersion curves of the two isomers have been measured in both our laboratories, and those of a similar pair of androstane derivatives[15] have also been measured. The results shown below, in conjunction with the predictions of the octant rule, fully support the previous allocation of configurations.[6]

The 5β-isomer could probably take up one of two conformations; in one, the A-ring has the same conformation (approximately) as in the 5α-isomer, and the Cotton effect would be positive. In the other conformer (XI), the conformation of the A-ring is reversed, and the general shape of the molecule approximates to that of the common 5β-steroid series. Here all of the B-, C-, and D-rings, except C-11 and C-12, are in the upper right-hand octant, and a negative Cotton effect would be predicted. Since a negative value is found, (XI) must represent the preferred conformation of the *cis*-isomer, and the data as a whole support the configurations shown.



(X) A, R = C_8H_{17}; B, R = OH

Predicted, positive. Found, A +73, B +68.



(XI) A, R = C_8H_{17}; B, R = OAc

* D-Ring lies behind C-13–14; omitted for clarity.

Predicted, negative. Found, A −55 (C. D.), −60 (W. K.); B −58.

The above formulæ show the normal (β) configuration at position 8. Shoppee and Sly[16] suggested that these B-nor compounds might have the 8α-configuration. This seems improbable on conformational grounds, because (unless ring C is a boat) it involves two unfavourable factors, (i) a $CH_2{:}CH_3$ diaxial interaction between positions 6 and 18, and (ii) an eclipsed conformation on the cyclopentane ring between C-19,10,9,11. The octant rule does not at present enable us to distinguish between the 8α- and the 8β-configuration, although it appears to support the latter.

Gibberellic acid derivatives. Extensive use has been made of rotatory dispersion evidence in allotting configurations to gibberellic acid derivatives (for reviews see Grove *et al.*[17]) both by the workers at Imperial Chemical Industries Limited and by Stork *et al.*[18]

Many hexahydroindan-5-ones are available in compounds of the types (XII) and (XIII) obtained by opening ring D (hydrofluorenones). These include compounds of B,C-*trans*- and B,C-*cis*-series (4bα and 4bβ) and also compounds in which ring A is either alicyclic or aromatic. Most of the data have been collected by Grove and Mulholland.[19] The B,C-*trans*-ketones (4bα, 8aβ) (*e.g.*, XII, *a*, +99!) generally show larger amplitudes than the B,C,-*cis*-ketones (4bβ, 8aβ) (*e.g.*, XIII, *a*, +35).

(2) *Front Octant Effects.*—It has been pointed out[2] that atoms lying in the front octants make contributions of opposite sign to those of atoms in the back octants. For most ketones the whole molecule (except the carbonyl-oxygen atom) lies in the back

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[13] Summers, *J.*, 1959, 2908.

[14] Dauben, Boswell, and Berezin, *J. Amer. Chem. Soc.*, 1959, **81**, 6082.

[15] Joska, Fajkoš, and Šorm, *Coll. Czech. Chem. Comm.*, 1960, **25**, 2341.

[16] Shoppee and Sly, *J.*, 1959, 345.

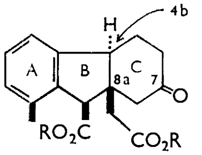
[17] Grove, *Quart. Rev.*, 1961, **15**, 56; Brian, Grove, and MacMillan, *Fortschr. Chem. Org. Naturstoffe*, 1960, **18**, 350; for *X*-ray evidence, see McCapra, Scott, Sim, and Young, *Proc. Chem. Soc.*, 1962, 185.

[18] Stork and Newman, *J. Amer. Chem. Soc.*, 1959, **81**, 3168.

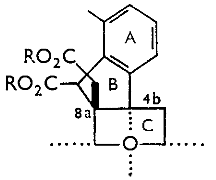
[19] Grove and Mulholland, *J.*, 1960, 3007.

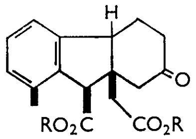
octants; but for some, particularly in polycyclic ketones whose carbonyl group is in a non-terminal ring, some parts of the molecule lie in the front octants and thus complicate the interpretation of dispersion curves.

We next comment on some steroid ketones which have atoms in a front octant. We stress, however, that there is as yet no clear example permitting even the roughest quantitative estimate of the magnitude of front-octant effects.

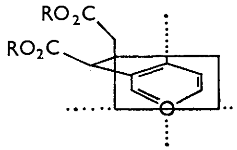


(XII) B,C-*trans*

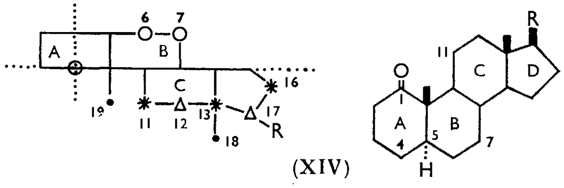




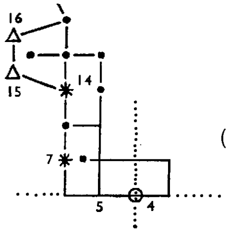
(XIII) B,C-*cis*



1-*Oxo*-5α-*steroid*. The 1-oxo-5α-steroid (XIV) is a compound which was previously reported[20] to give a curve without a marked peak or trough. Reconsideration of the data shows that 5α-cholestan-1-one (XIV; R = C_8H_{17}) has a weak negative Cotton effect (−25) superimposed on a strong positive background. (For recent work on circular dichroism of such compounds see ref. 21.) The corresponding decalone has a moderate positive Cotton effect (+32). The difference between the 1-oxo-5α-steroid and this decalone lies in the remote area of the C- and D-rings. C-12 and C-17 and the side-chain are clearly in the near right-hand lower octant (negative); C-18 and C-19 are in the far right-hand lower octant (positive). C-6 and C-7 are in the far right-hand upper octant (negative). C-11, C-13, and C-16 are nearly (if not exactly) in the vertical dividing surface. The resultant of these effects is apparently such as to render the total Cotton effect weakly negative.



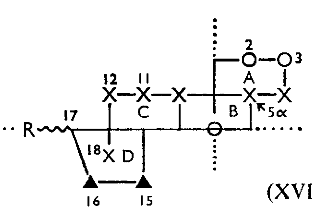
(XIV)



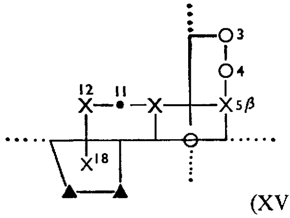
(XV)

4-*Oxo*-5β-*steroid*. The small observed Cotton effect[21] (+3) for compound (XV) is unexpected. The compound has a large number of atoms in the far upper left-hand octant (positive), with only two (C-7 and C-14) near the vertical plane and two (C-15 and C-16) in the near upper left-hand octant (negative); a large positive Cotton effect would be expected.

7-*Oxo-steroids*. In 5α-compounds[20] (XVI) the negative Cotton effect (−19) indicates that the atoms (C-2, C-3) in the far upper right-hand octant (negative) outweigh those (C-15, C-16) in the near lower left-hand octant (positive). C-17 is nearly in the horizontal symmetry plane and the position of the side-chain (R) is uncertain.



(XVI)



(XVII)

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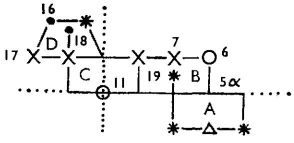
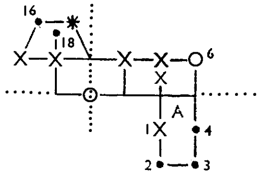
[20] Djerassi, Closson, and Lippman, *J. Amer. Chem. Soc.*, 1956, **78**, 3163.

[21] Djerassi, Riniker, and Riniker, *J. Amer. Chem. Soc.*, 1956, **78**, 6362.

In the 5β-isomer (XVII)[22] the positive Cotton effect (+30) is due essentially to the positive contribution (C-11) in the far upper left-hand octant, since the remaining contributions are either identical with those of the 5α-isomer (C-15, C-16) or very similar (C-4 and C-3 instead of C-2 and C-3).



(XVIII)



(XIX)

11-*Oxo-steroids.* The 11-oxo-5α-steroid (XVIII) shows a small positive Cotton effect (+15).[23] This is compatible with the fact that the effects of most of the atoms cancel in pairs. C-2 in the near lower right-hand octant must make a negative contribution. All the atoms in the two dividing planes (C-10,5,4,14,15) are without effect. C-1 and C-19 are nearly in the vertical dividing surface; and if they are not truly in it, their effects cancel

TABLE 1.

Contributions of α-methyl substituents.

Compound	Subst.	Amplitude *a*	Δ*a* for Me subst.	Ref.*
5α-Cholestan-3-one	None	+48, 54		
	2α-Me (*eq*)	+48, 57	0, +3	1/1
	2β-Me (*ax*)	+82, 79	+34, 25	
5α-Cholestan-2-one	None	+102, 94		
	3β-Me (*eq*)	+102	0	
5α-Androstan-3-one, 17β-acetoxy-	None	+54		
	4α-Me (*eq*)	+57	+3	
	4β-Me (*ax*)	+27	−27	
(9*R*)-*trans*-1-Decalone	None	−40		1/2
	9-Me (*ax*)	+27	+67	1/3
trans-2,5-Dimethylcyclohexanone		+26		1/4
2,2,5-Trimethylcyclohexanone		+81	+55 (*ax*)	1/5
2-Methylcyclohexanone		+12		1/4
trans-2,6-Dimethylcyclohexanone		+74	+62 (*ax*)	1/6
3-Methylcyclohexanone		+25		1/7
trans-2,5-Dimethylcyclohexanone		+26	+1 (*eq*)	1/4

* References in Table 1 are numbered 1/1, 1/2 . . ., in Table 2 are numbered 2/1, 2/2 . . ., etc., and back-references in other Tables are made in this form.

References: 1/1, Djerassi, Halpern, Riniker, and Riniker, *J. Amer. Chem. Soc.*, 1958, **80**, 4001. 1/2, Djerassi and Staunton, *ibid.*, 1961, **83**, 736. 1/3, Djerassi, Riniker, and Riniker, *ibid.*, 1956, **78**, 6362. 1/4, Beard, Djerassi, Elliott, and Tao, *ibid.*, 1962, **84**, 874. 1/5, Djerassi, Osiecki, and Eisenbraun, *ibid.*, 1961, **83**, 4433. 1/6, Beard, Djerassi, Sicher, Sipoš, and Tichý, *Tetrahedron*, in the press. 1/7, Djerassi, and Krakower, *J. Amer. Chem. Soc.*, 1959, **81**, 237.

TABLE 2.

Contributions of α-aryl substituents.

Compound	Subst.	Amplitude *a*	Δ*a* for aryl subst.
5α-Cholestan-2-one	3β-Ph (*eq*)	+53!, 45	−49!, 57
	3β-*p*-MeO·C_6H_4 (*eq*)	+13!	−89
	3α-Ph (*ax*)	+303, 379	+201, 277
	3α-*p*-MeO·C_6H_4 (*ax*)	+247	+147!
	3α-Ph (*ax*) 3β-Me (*eq*)	+398	+298
5α-Cholestan-3-one	2α-Ph (*eq*)	+23	−34

References: 2/1. Cookson and Hudec, *J.*, 1962, 429. 2/2, Moscowitz, Mislow, Glass, and Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1945. For unsubstituted compounds see Table 1.

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[22] Djerassi and Closson, *J. Amer. Chem. Soc.*, 1956, **78**, 3761.

[23] Djerassi, Osiecki, Riniker, and Riniker, *J. Amer. Chem. Soc.*, 1958, **80**, 1216.

TABLE 3.

Contributions of α-halogen substituents in oxo-steroids and related compounds.

	Ketone without α-Hal	Ketone (XXI)			Ketone (XX)			
	a	Subst.	*a*	Δ*a*	Subst.	*a*	Δ*a*	Ref.
1-*Ketones* (5α)								
5α-Cholestan-1-one	−26				2α-Br (*eq*)			20, 3/1, 3/2
					2β-Br (*ax*)	−121	−95	
2-*Ketones* (5α)								
5α-Cholestan-2-one	+102	3α-I (*ax*)	+236	+134	1α-Br (*ax*)	−117	−219	3/3
		3α,3β-Br$_2$ (*a*)	+313	+211				3/4
		3α-Br (*ax*)	+262	+160				
		3β-Br (*eq*)	+119	+17				
3-*Ketones* (5α)								
5α-Cholestan-3-one	+48, 54	2α-Cl (*eq*)	+54	+6				23, 3/4
		2β-Br (*ax*)	+120	+66				
		2α-I (*eq*)	+104	+56				
5α-Androstan-3-one, 17β-acetoxy-	+54	2α-Br (*eq*)	+46	−8	4α-Br (*eq*)	+30	−24	3/5
		2β-Br (*ax*)	+174	+120	4β-Br (*ax*)	−160	−214	
4-*Ketones* (5α)								
5α-Cholestan-4-one, 7β-hydroxy-	−63	5α-Br (*ax*) (*b*)	+106	+169				3/6
5α-Cholestan-4-one	−94	5α-Br (*ax*)	+149	+243	3α-Br (*ax*)	−202	−108	3/7
4-*Ketones* (5β)					3,3-Br$_2$	−194	−100	
5β-Cholestan-4-one	+3				5β-Cl (*ax*) (*c*)	−235	−238	1/3
					5β-Br (*ax*)	−213	−216	
					3α (*eq*), 5β(*ax*)-Br$_2$	−110	−113	3/7
6-*Ketones* (5α)								
5α-Cholestan-6-one	−73, −78	7α-Br (*ax*)	+170	+248	5α-Br (*ax*)	−323	−245	23, 3/8, 3/9
		5α (*ax*), 7α (*ax*)-Br$_2$	−120	−42 (*d*)				
		7,7-Br$_2$	−98	−13 (*e*)				
5α-Cholestan-6-one, 3β-acetoxy-	−76, −68				5α-Br (*ax*)	−380	−312	23, 3/8, 3/9
					5α(*ax*), 7β(*eq*)-Br$_2$	−282	−214	
7-*Ketones* (5α)								
5α-Cholestan-7-one, 3β-acetoxy-	−16	6α-Br (*eq*)	−26	−10	8β-Br (*ax*)	−304	−288	20, 3/10, 1/1
		6β-Br (*ax*)	+193	+209 (*f*)				
7-*Ketones* (5β)								
7-Oxo-5β-cholanic acid, 3α,12α-diacetoxy ; Me ester	+17	6α-Br (*eq*)	+11	−6				3/11
		6β-Br (*ax*)	+96	+79				

Table 3. (*Continued.*)

	Ketone without α-Hal	Ketone (XXI)			Ketone (XX)			
	a	Subst.	*a*	Δ*a*	Subst.	*a*	Δ*a*	Ref.
11-*Ketones*								
5β-Androstan-11-one	+15							
5β-Androstan-11-one, 3α-hydroxy- or 3α-acetoxy-	+13	9α-Br (*ax*)	+203	+190	12α-Br (*ax*)	−206, −214	−219, −227	3/12
5β-Androstan-11-one, 3-ethylenedioxy-	+11	9α-Br (*ax*)	+247	+236	,,	−242	−231	3/12
5β-Androstane-3,11-dione	+15	9α-Br (*ax*)	+222	+207	,,	−199	−214	3/12
5α-Ergostan-11-one, 3β-hydroxy- or 3β-acetoxy-	+11	9α-Br (*ax*)	+250, +247	+239, 236	,,	−146	−157	23, 3/12, 3/13
5α-Ergostan-11-one, 3-ethylenedioxy-	+20	9α-Br (*ax*)	+250	+230				3/12
11-Oxo-5β-etianate, 3α-hydroxy- or 3α-acetoxy-; Me ester	0				12α-Br (*ax*)	−251	−251	3/14
12-*Ketones*								
12-Oxocholanic acid, 3α-acetoxy-; Me ester	+10				11α-Br (*eq*) 11β-Br (*ax*)	+15 −192	+5 −202	22, 23
3-*Oxofriedelanes*								
Friedelan-3-one	−109	4α-Br (*ax*)	+210D +209C	+319 +318	2α-Br (*ax*)	−261D	−152	23, 3/15
5-*Oxo-des-*A*-steroids*								
Des-A-androstan-5-one, 17β-acetoxy-	−39!	10β-Br (*ax*)	+244	+276!	6β-Br (*ax*) 6α-Br (*eq*)	−305 −54	−266! −22!	3/16
Des-A-androstan-5-one, 17β-benzoyloxy-	−48	10β-Br (*ax*)	+207	+255	6β-Br (*ax*)	−259	−211	,,
Des-A-cholestan-5-one	−76	10β-Br (*ax*)	+205!	+281!	6β-Br (*ax*) 6α-Br (*eq*)	−332 −88	−256 −14	,, ,,
Des-A-cholestan-5-one, 10α-2′-carboxyethyl-	+18				6α-Br (*eq*)	−21	−39	,,
Decalones (*g*)								
(9*S*)-*trans*-1-Decalone	+40	2-Br (*eq*) 2-Br (*ax*)	+44 +196	+4 +156	9-Br (*ax*)	−217	−257	1/2
(9*R*)-*cis*-1-Decalone	−14	9-Br (*ax*)	+223	+237	2-Br (*eq*) 2-Br (*ax*)	−4 −163	+10 −149	1/2

(*a*) *gem*-Dihalogeno-ketones; the effect of the equatorial halogen can in most cases be neglected, to a first approximation. (*b*) As 7-acetate. (*c*) With 7β-benzoyloxy-group. (*d*) Two axial bromine atoms, one on each side of carbonyl group; effects almost cancel. (*e*) *gem*-Dihalogeno-ketone. Difference in *a* from unsubstituted ketone is negligible. This may imply that the ring B has a " twist " conformation and that the two halogen atoms " straddle " the carbonyl. (*f*) Previous result (+143) (ref. 23) was for an impure sample. (*g*) Values corrected to 100% optical purity (see ref. 1/2).

References: 3/1, Shoppee, Roy, and Goodrich, *J.*, 1961, 1583. 3/2, Sigg and Tamm, *Helv. Chim. Acta*, 1960, **43**, 1402. 3/3, Cookson, unpublished work. 3/4, Bellas and Shoppee, *J*, 1963, in the press. 3/5, Malunowicz, Fajkoš, and Šorm, *Coll. Czech. Chem. Comm.*, 1960, **25**, 1359. 3/6, Summers, unpublished work. 3/7, Shoppee, Howden, Killick, and Summers, *J.*, 1959, 630; Shoppee and Lack, *J.*, 1961, 3271. 3/8, Shoppee, Jenkins, and Summers, *J.*, 1958, 1657. 3/9, Cookson, *J.*, 1954, 282; Cookson and Dandegaonker, *J.*, 1955, 352. 3/10, Cremlyn and Shoppee, *J.*, 1954, 3515. 3/11, Jones and Wluka, *J.*, 1959, 911. 3/12, *Idem, ibid.*, p. 907. 3/13, Henbest, Jones, Wagland, and Wrigley, *J.*, 1955, 2477; Henbest and Wrigley, *J.*, 1957, 4596. 3/14, Tobias, *Helv. Chim. Acta*, 1963, **46**, 159. 3/15, Shoppee and Johnston, *J.*, 1962, 1246. 3/16, Hartshorn and Jones, *J.*, 1962, 1312.

one another. C-3 is also nearly in this plane. The effect of C-7 cancels that of C-17. This leaves only the four atoms C-16 and C-18 (positive), C-6 (negative), and C-2 in the near lower right-hand octant (negative) to be considered. It might be expected from the octant projection that the 11-oxo-5β-steroid (XIX) would give a more positive curve (because of more contributions from ring A; C-2, -3, and -4), but in fact it does not.[24]

Branched-chain α-alkyl substituents. Some preliminary observations on front-octant effects due to isopropyl and t-butyl groups α to carbonyl in cyclohexanones have been presented elsewhere.[25]

(3) *Ketones with Weak or No Apparent Cotton Effect.*—Attention has been drawn [2] to the fact that certain ketones show curves which apparently lack a Cotton effect, or show only a very weak effect, *i.e.*, the curves have no distinct peaks or troughs. The explanation of this behaviour is simply that the contributions to the Cotton effect of different atoms and groups cancel each other. The best example is perhaps the 17a-oxo-D-homo-steroid [20] (cf. ref. 1); the 5α-1-oxo-steroid (XIV) [20] which is considered in this paper (p. 2394) is roughly, but not exactly, of enantiomeric type.

TABLE 4.

Contributions of substituents β to carbonyl.

For reference values for compounds without the named β-substituent, see Tables 1 and 2, also footnote *.

β-Subst.	Compound	Amplitude *a*	Δ*a* for subst.	Ref.
Me	5-Methyl-5α-cholestan-3-one	+73	+15	30
Me	5-Methyl-5β-cholestan-3-one	−18	+7	30
Me	3-Methyl-cyclohexanone	+25*	+25	1/7, 4/1
Me	3,9-Dimethyl(9*R*)-*trans*-1-decalone	+52 *	+25	4/1
$\mathrm{Bu^t}$	3-t-Butylcyclohexanone	+37	+37	4/2
$\mathrm{Bu^t}$	3-t-Butyl-9-methyl(9*R*)-*trans*-1-decalone	+66	+39	4/1
OH	5-Hydroxy-5α-cholestan-3-one	+69	+15	3/6
OH	6β-Acetoxy-5-hydroxy-5α-cholestan-3-one	+72!	+18!	3/6
CN	5-Cyano-5α-androstan-3-one	+58	+6	4/3
CN	5-Cyano-5α-cholestan-3-one	+45	−3	30
CN	5-Cyano-5β-androstan-3-one	−14	−11	4/3
CN	5-Cyano-5β-cholestan-3-one	−11!	+0!	30
CN	3-Oxo-19-nor-5α-androstan-17β-ol, 5-cyano-	+52	−12	4/4
CN	3-Oxo-19-nor-5β-androstan-17β-ol, 5-cyano-	−20	+10	4/4
SCN	5-Isothiocyanto-5α-cholestan-3-one	+30	−18	4/2
$\mathrm{CO_2Me}$	Me 3-oxo-5α-cholestane-5-carboxylate	+73	+25	30
$\mathrm{CO_2Me}$	Me 3-oxo-5β-cholestane-5-carboxylate	+45	−20	30

* Reference values for the corresponding compounds without the named β-substituent are: (9*R*)-9-methyl-*trans*-1-decalone, +27 (ref. 1/3); 3-oxo-19-nor-5α-, +64, and -5β-steroid, −30 (ref. 1).

References: 4/1, Djerassi, Lund, and Akhrem, *J. Amer. Chem. Soc.*, 1962, **84**, 1249. 4/2, Djerassi, Warawa, Wolff, and Eisenbraun, *J. Org. Chem.*, 1960, **25**, 917. 4/3, Henbest and Jackson, unpublished work. 4/4, Fishman, unpublished work.

In the past few years other examples have accumulated, as follows. (*a*) 3-Oxo-5α,10α-steroids: tetrahydro-4β-Me,6α(H),11α(H)-santonin.[1] (*b*) 11-Oxo-steroids: 3α,20β-diacetoxy-5β-pregnan-11-one,[26] 3β,20β-diacetoxy-5α-pregnan-11-one,[27] 3α,20β,21-triacetoxy-5β-pregnan-11-one,[28] and methyl 3α-hydroxy-11-oxo-5β-etianate.[29]

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[24] Djerassi, Mitscher, and Mitscher, *J. Amer. Chem. Soc.*, 1959, **81**, 947.

[25] Djerassi, Warawa, Berdahl, and Eisenbraun, *J. Amer. Chem. Soc.*, 1961, **83**, 3334.

[26] Jones *et al.*, unpublished work.

[27] Romo, Stock, Rosenkranz, and Djerassi, *J. Amer. Soc.*, 1952, **74**, 2918.

[28] Danilewicz and Klyne, unpublished work.

[29] Schindler, unpublished work.

The oxo-steroids which lack an apparent Cotton effect are interesting. The fundamental *a* values for 5α- and 5β-androstan-11-ones and -pregnan-11-ones (see p. 2394) without substituents[24] are: androstan-11-one, 5α +15, 5β +14; and pregnan-11-one, 5α +16, 5β +20!

TABLE 5.

Contributions of substituents γ to carbonyl.

Subst.	Compound	Amplitudes *a* (Subst.)	 *a* (Unsubst.)	Δ*a* for subst.	Ref.
OH	3β-Hydroxy-5α-cholestan-6-one	−69	−78, −73	+9, +4	—
OAc	3β-Acetoxy-5α-cholestan-6-one	−76, −70, −68		+2, +8, +10	20
OH + Me	6β-Hydroxy-6α-methyl-5α-cholestan-3-one	+68	+55	+13	3/6
OH	7β-Hydroxy-5α-cholestan-4-one	−64	−94	+30	3/6

TABLE 6.

Contributions of substituents δ to carbonyl.

Subst.	Compound	Amplitude *a*	Δ*a* for subst.	Ref.
MeO	7α-Methoxy-5β-cholestan-3-one	−20	+5	6/1
AcO	3β-Acetoxy-5α-cholestan-7-one	−16, −18	+3, +1	20
HO	3β-Hydroxy-5α-cholestan-7-one	−28	−9	—

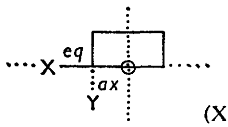
Reference values: 5β-cholestan-3-one, −25; 5α-cholestan-7-one, −19.

Reference: 6/1, Henbest and Jones, *J.*, 1948, 1798.

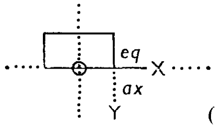
In the compounds for which *a* is almost zero, this result may be due either to a simple mass effect [increase in effect of the side-chain, considered in its (unknown) preferred conformation] or to a more subtle effect such as hydrogen-bonding or solvent-bonding between groups in the side-chain and the 11-oxo-group. The last factor could be explored by studying the effect of different solvents on the dispersion curves.

(4) *Amplitude Contributions for Substituents in the Neighbourhood of the Carbonyl Group.*—In Tables 1—6 the contributions made to the amplitudes (*a*) of carbonyl Cotton effects by substituents in the neighbourhood of the carbonyl are listed. The contributions (Δ*a* values) are amplitudes for substituted ketones *minus* amplitude for unsubstituted ketone.

Where references to the literature are not given, the values are from unpublished observations in one of our laboratories, as indicated in the Experimental section of this paper or of ref. 1.



(XX)



(XXI)

No comment is needed for Tables 1—3 except as in footnotes. For β-substituents (Table 4) the Δ*a* values are generally small, and in many cases the sign of the Cotton effect is sufficient for allocation of configurations at the β-centre (see, *e.g.*, Nagata *et al.*[30]).

Formulæ (XX) and (XXI) illustrate α-substituents to left and right of the carbonyl group, as required for Table 3.

Some examples of decalones produced by microbiological action are discussed elsewhere.[31]

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[30] Nagata, Hirai, Hazaki, and Takeda, *Annalen*, 1961, **641**, 184, 196.

[31] Klyne and Robertson, *Experientia*, 1962, **18**, 413.

TABLE 7.

Molecular rotations and Cotton effects.

Observer *	Compound	Extrema				Amplitude a	Solvent	Ref. and source	
		$[\phi]$	λ (mμ)	$[\phi]$	λ (mμ)				
	Hexahydroindanones								
D	*trans*-Hexahydro-8-methylindan-5-one (I)	−2140°	310	+1960°	272·5	−41	M	6	—
D	*cis*-Hexahydro-8-methylindan-5-one (III) †	−290	315	+670	280	−10	D	6, 7	A
K	*trans*-Hexahydroindan-5-one	+2440	310	−2820	265	+53	M	7/1	B
D	(1*R*,8*R*)1-(1,5-Dimethylheptyl)-*trans*-hexahydroindan-4-one (VIII)	−5510	305	+10,000	270	−155	M	6, 10	C
D	*cis*-Isomer of above (IX)	+240	302·5	+1150!	292·5	−9!	M	6, 10	C
D	B-Nor-5α-cholestan-3-one (X)	+4380	312·5	−5280	270	+97	M	14	D
K		+3470	310	−3790!	260	+73!	M	13	E
D	B-Nor-5α-androstan-3-one, 17β-acetoxy-	+3950	312·5	−1870!	285	+58!	M	15	F
D	B-Nor-5β-cholestan-3-one (XI)	−1640	310	+3830	265	−55	M	14	D
K		−1830	310	+4080!	265	−59!	M	13	E
D	B-Nor-5β-androstan-3-one, 17β-acetoxy-	−2290	310	+3430	270	−57	M	15	F
K	9β-Carboxy-4bα,5,6,7,8,8a-hexahydro-1-methyl-7-oxo-fluoren-8aβ-xylacetic acid (Me$_2$ ester) (B,C-*trans*) (XII)	+3780	315	−6080!	270	+99!	M	19	B
K	Isomer of preceding, 4bβ(H) (B,C-*cis*) (XIII)	+3860	310	+380	280	+35	M	19	B
	Miscellaneous steroids								
D	5α-Cholestan-1-one (XIV)	+1410	317·5	+4100	285 (infl.)	−25	M	20, 3/1	—
D	5β-Cholestan-4-one (XV)	+1230	300	+920	277·5	+3	M	20	—
K	5α-Cholestan-7-one (XVI)	−1060	307	+880	270	−19	M	3/10	E
		−1380	305	+1190	275	−26	M		
D	7-Oxo-5β-cholanic acid, 3α-hydroxy- (XVII)	+370	312	−2630	264	+30	M	22	G
D	5α-Androstan-11-one (XVIII)	+890	325	−610	307·5	+15	M	—	H
D	5β-Androstan-11-one (XIX)	+1160	322·5	−260	282·5	+14	M	—	H
D	5α-Pregnan-11-one	+820	325	−770	285	+16	M	—	H
K		+790	320	+120!	280	+7!	M	—	—
D	5β-Pregnan-11-one	+900	317·5	−1120!	297·5	+20!	M	24	H
	Compounds with and without α-alkyl substituents								
D	5α-Cholestan-3-one	+2320	308	−2470	268	+48	M	20	—
K		+3050	307·5	−2380	265	+54	M		
K		+3160	310	−2300	262·5	+55	M		—
D	2α-Methyl- ,,	+3040	307·5	−1760	262·5	+48	M	1/1	K
K		+2620	305	−3040	275	+57	M		E
D	2β-Methyl- ,,	+6170	305	−2080	265	+82	M	1/1	K
K		+4080	310	−3840	270	+79	M		E
D	5α-Androstan-3-one, 17β-acetoxy-	+2420	310	−2950	267·5	+54	M	—	—
D	4α-Methyl- ,, ,,	+2520	302·5	−3220	265	+57	M	—	H
D	4β-Methyl- ,, ,,	+1280	307·5	−1380	265	+27	M	—	H
D	5α-Cholestan-2-one	+4830	310	−4540	267·5	+94	M	20	—
K		+4860	310	−5230	267·5	+101	M		L
K	3β-Methyl-5α-cholestan-2-one	+4900	307·5	−5350	280	+102	M	2/1	L
D	*trans*-2,5-Dimethylcyclohexanone	+1030	310	−1520	270	+26	M	1/4	—
D	2,2,5-Trimethylcyclohexanone	+4030	311	−4070	270	+81	M	1/5	—
D	*trans*-2,6-Dimethylcyclohexanone	+3900	310	−3460	272	+74	M	1/6	—
	Compounds with α-aryl substituents								
D	3α-Phenyl-5α-cholestan-2-one	+19,400	322	−18,500	287	+379	M	2/1, 2/2	L
D	3β-Phenyl- ,,	+2250	318	−2260	279	+45	M	2/1, 2/2	L
K	3β-*p*-Methoxyphenyl-5α-cholestan-2-one	+1090	320	−230!	300	+13!	M	2/1	L
K	2α-Phenyl-5α-cholestan-3-one	+690	315	−1630	280	+23	M	2/1	L

TABLE 7. (*Continued.*)

Observer *	Compound	Extrema				Amplitude *a*	Solvent	Ref. and source	
		$[\phi]$	λ (mμ)	$[\phi]$	λ (mμ)				
	Compounds with and without α-halogen substituents								
D	2β-Bromo-5α-cholestan-1-one	−4880	345	+7210	280	−121	M	3/1	—
D	1α-Bromo-5α-cholestan-2-one	−4550	327·5	+7170	282·5	−117	M	—	—
K	3α-Bromo- ,,	+12,200	337·5	−14,400	287·5	+266	M	3/4	M
D	,, ,,	+13,100	335	−13,100	285	+262	M	3/4	M
D	3β-Bromo- ,,	+5140	318	−6750	266	+119	M	3/4	M
K	3,3-Dibromo- ,,	+14,800	335	−16,500	285	+313	M	3/4	M
O	3α-Iodo- ,,	+13,200	346	−10,400	290	+236	D	—	—
D	2α-Chloro-5α-cholestan-3-one	+3140	310	−2250	265	+54	M	23	—
K	2β-Bromo- ,,	+6370	335	−5620	275	+120	M	3/4	M
D	2α-Iodo- ,,	+3250	315	−6850	270	+104	D	—	—
D	2α-Bromo-5α-androstan-3-one, 17β-acetoxy-	+2060	307·5	−2510	265	+46	M	3/5	F
D	2β-Bromo- ,, ,,	+8220	332·5	−9200	282·5	+174	M	3/5	F
D	4α-Bromo- ,, ,,	+700	302·5	−2260	255	+30	M	3/5	F
D	4β-Bromo- ,, ,,	−7400	332·5	+8630	285	−160	M	3/5	F
K	5α-Cholestan-4-one, 7β-hydroxy-	−2260	307·5	+4100	272·5	−63	M	3/6	E
K	3α-Bromo-5α-cholestan-4-one	−8250	332·5	+12,000	282·5	−202	M	3/7	M
K	5-Bromo-5α-cholestan-4-one, 7β-acetoxy-	+11,300	330	+660	287·5	+106	M	3/6	E
K	5-Bromo-5α-cholestan-4-one	+7050	332·5	−7830	287·5	+149	M	3/7	M
K	5-Bromo-5β-cholestan-4-one	−8900	335	+12,400	287·5	−213	M	3/7	M
K	5-Chloro-5β-cholestan-4-one, 7β-benzoyloxy-	−9550	325	+13,900	285	−235	M	3/6	E
D	3α,5-Dibromo-5β-cholestan-4-one	−9400	330	+1520	285	−109	M	3/7	M
D	5α-Cholestan-6-one	−2470	310	+4850	270	−73	M		
K		−3500	310	+4300	265	−78	M	3/8, 3/15	M
K	5-Bromo-5α-cholestan-6-one	−13,500	330	+18,800	285	−323	M	3/8, 3/15	M
K	7α-Bromo- ,,	+7200	332·5	−9800	285	+170	M	3/8, 3/15	M
K	5,7α-Dibromo- ,,	−6050	360	+5950	312·5	−120	M	3/8, 3/15	M
K	7,7-Dibromo- ,,	−5010	312·5	+4760	275	−98	M	3/8, 3/15	M
D	5α-Cholestan-6-one, 3β-acetoxy-	−3580	306	+4050	270	−76	M	3/8	
K		−3120	305	+3720	272·5	−68	M		E
K		−3660	310	+3300	267·5	−70	M		
K	5-Bromo- ,, ,,	−16,700	307·5	+21,300	285	−380	M	3/8	E
D	5,7β-Dibromo-	−11,700	330	+16,500	280	−282	M	23, 3/9	L
D	5α-Cholestan-7-one, 3β-acetoxy-	−1520	310	+70	274	−16	M	20	—
K		−1270	310	+220	277·5	−15	M	3/10	M
D	6α-Bromo- ,, ,,	−1740	300	+880	260	−26	M	23	N
D	6β-Bromo- ,, ,,	+8170	335	−11,100	287·5	+193	M	23	N
D	8β-Bromo- ,, ,,	−13,100	335	+17,300	287·5	−304	M	23	N
K	7-Oxo-5β-cholanic acid, 3α,12α-diacetoxy-, Me ester	+2360	307·5	+660	275	+17	M	3/11	J
K	6α-Bromo-7-oxo- ,, ,, ,,	+630	330	−470	300	+11	M	3/11	J
K	6β-Bromo-7-oxo- ,, ,, ,,	+5310	330	−4250	285	+96	M	3/11	J
K	5β-Androstan-11-one, 3β-acetoxy-	+1690	320	+380	280	+13	M	3/12	J
K	9α-Bromo- ,, ,,	+9300	342·5	−11,000	295	+203	M	3/12	J
K	12α-Bromo- ,, ,,	−8550	335	+12,900	290	−214	M	3/12	J
K	12α-Bromo-5β-androstan-11-one, 3β-hydroxy-	−8500	337·5	+12,100	290	−206	M	3/12	J
K	5β-Androstan-11-one, 3-ethylenedioxy-	+1600	325	+530	285	+11	M	3/12	J
K	9α-Bromo- ,, ,,	+9900	342·5	−14,800	295	+247	M	3/12	J
K	12α-Bromo- ,, ,,	−9950	337·5	+14,200	290	−242	M	3/12	J
K	5β-Androstane-3,11-dione	+1950	327·5	+410	285	+15	M	3/12	J
K	9α-Bromo- ,,	+9700	340	−12,500	297·5	+222	M	3/12	J
K	12α-Bromo- ,,	−9100	342·5	+10,800	285	−199	M	3/12	J

TABLE 7. (*Continued.*)

Observer *	Compound	Extrema				Amplitude a	Solvent	Ref. and source	
		[ϕ]	λ (mμ)	[ϕ]	λ (mμ)				
	Compounds with and without α-halogen substiuents								
D	5α-Ergostan-11-one, 3β-acetoxy-	+1260	322·5	+120	282·5	+11	M	23, 3/13	P
K	9α-Bromo- ,, ,,	+11,050	345	−12,900	292·5	+240	M	3/12	J
D		+11,300	347·5	−13,400	297·5	+247	M	23, 3/13	P
D	12α-Bromo- ,, ,,	−7150	342·5	+7420	292·5	−146	M	23, 3/13	P
K	Ergostan-11-one, 3-ethylenedioxy-	+1630	317·5	−350	280	+20	M	3/12	J
K	9α-Bromo- ,, ,,	+11,400	345	−13,600	290	+250	M	3/12	J
K	12α-Bromo-11-oxo-5β-etianic acid, 3α-acetoxy-, Me ester	−10,600	340	+14,500	295	−251	M	3/14	Q
D	12-Oxo-5β-cholanic acid, 3α-acetoxy-, Me ester	+3450	305	+2440	272·5	+10	M	22	Q
D	11α-Bromo-12-oxo- ,, ,,	+2620	295	+1110	270	+15	M	23	R
D	11β-Bromo-12-oxo- ,, ,,	−5350	337·5	+13,800	280	−192	M	23	QR
D	4α-Bromofriedelan-3-one	+10,300	335	−10,800	290	+211	D	23	—
K		+9300	332·5	−11,600	285	+209	C	3/15	M
D	2α-Bromo- ,,	+12,600	335	+13,700	285	−263	D	23	—
K	6β-Bromodes-A-androstan-5-one, 17β-acetoxy-	−14,550	327·5	+15,950	287·5	−305	M	3/16	J
K	10β-Bromo- ,, ,,	+11,350	350	−13,100	282·5	+244	M	3/16	J
K	6α-Bromodes-A-androstan-5-one, 17β-benzoyloxy-	−5040	305	+340!	280	−54!	M	3/16	J
K	6β-Bromo- ,, ,, ,,	−11,610	325	+14,300	285	−259	M	3/16	J
K	10β-Bromo- ,, ,, ,,	+9780	327·5	−10,900	282·5	+207	M	3/16	J
K	6α-Bromodes-A-cholestan-5-one	−3920	310	+4850	270	−88	M	3/16	J
K	6β-Bromo- ,,	−14,700	327·5	+18,550	280	−333	M	3/16	J
K	10β-Bromo- ,,	+15,000	330	−5550!	290	+205!	M	3/16	J
K	6α-Bromodes-A-cholestane-5-one, 10-2′-carboxyethyl-	−230	317·5	+1880	277·5	−21	M	3/16	J
	Compounds with substituents β to carbonyl								
D	5-Methyl-5α-cholestan-3-one	+4000	305	−3320	267·5	+73	M	30	S
D	5-Methyl-5β- ,,	+120	307·5	+1960!	255	−18!	M	30	S
K	5-Hydroxy-5α- ,,	+3540	300	−3400	267·5	+69	M	3/6	E
K	5-Hydroxy-5α-cholestan-3-one, 6β-acetoxy-	+2340	305	−4900!	255	+72!	M	3/6	E
K	5-Cyano-5α-androstan-3-one	+2580	310	−3280	267·5	+58	M	4/3	P
D	5-Cyano-5α-cholestan-3-one	+2650	310	−1850	270	+45	M	30	S
K	5-Cyano-5β-androstan-3-one	−440	307·5	+1000	267·5	−14	M	4/3	P
D	5-Cyano-5β-cholestan-3-one	+820	307·5	+1890!	260	−11!	M	30	S
D	5-Cyano-3-oxo-19-nor-5α-androstan-17β-ol	+2560	304	−2660	260	+52	M	4/4	R
D	5-Cyano-3-oxo-19-nor-5β-androstan-17β-ol	−480	304	+1500	265	−20	M	4/4	R
D	5-Isothiocyanato-5α-cholestan-3-one	+2660	305	−270!	260	+29!	M	4/2	S
D	5-Methoxycarbonyl-5α-cholestan-3-one	+3060	305	−4270	257·5	+73	M	30	S
D	5-Methoxycarbonyl-5β-cholestan-3-one	+490	300	+5000!	250	−45!	M	30	S
	Compounds with and without substituents γ and δ to carbonyl group								
K	3β-Hydroxy-5α-cholestan-6-one	−3500	307·5	+3420	267·5	−69	M	—	—
K	6β-Hydroxy-6α-methyl-5α-cholestan-3-one	+2640	305	−4160	265	+68	M	3/6	E
K	7β-Hydroxy-5α-cholestan-4-one	−2260	307·5	+4100	272·5	−64	M	3/6	E
D	5α-Cholestan-4-one	−3020	307·5	+6410	267·5	−94	M	20	T, U
K	7α-Methoxy-5β-cholestan-3-one	−640	310	+1410	285	−20	M	6/1	P
K	3β-Hydroxy-5α-cholestan-7-one	−2300	307·5—305	+450	270	−28	M	—	T

* D = Djerassi or co-worker, K = Klyne, or co-worker. † Perhaps incompletely resolved.

Reference: 7/1, Bourn and Klyne, *J.*, 1960, 2044.

EXPERIMENTAL

Rotatory dispersion curves were measured with Rudolph photoelectric spectropolarimeters. Experimental details are as in ref. 1; the solvent was methanol (M) or, less commonly, dioxan (D) or chloroform (C); $l = 0{\cdot}5$ or 1 dm.; 18—25°, c 0·1 mg. or less/c.c. New values are listed in Table 7, as molecular rotations.

Sources of Compounds.—If no source is given, compounds were taken from the authors' collections. Others are: (A) Dr. H. Conroy, Yale. (B) Mr. J. F. Grove, Imperial Chemical Industries Limited, Akers Research Laboratories, Welwyn Garden City, Herts. (C) Prof. H. H. Inhoffen, Braunschweig, Germany. (D) Prof. W. G. Dauben, University of California, Berkeley, California. (E) Dr. G. H. R. Summers, Swansea. (F) Prof. F. Šorm, Czecholovak Academy of Science, Prague. (G) Prof. S. Bergström, Karolinska Institutet, Stockholm. (H) Dr. A. (Bowers and others), Syntex S.A., Mexico City. (J) Prof. E. R. H. Jones, Oxford. (K) Prof. A. Nickon, Johns Hopkins University, Baltimore, Md. (L) Prof. R. C. Cookson, Southampton. (M) Prof. C. W. Shoppee, Sydney, N.S.W. (N) Prof. E. J. Corey, Harvard (formerly University of Illinois). (P) Prof. H. B. Henbest, Belfast. (Q) Prof. T. Reichstein and Dr. O. Schindler, Basle. (R) Dr. T. F. Gallagher and Dr. J. Fishman, Sloan Kettering Institute, New York. (S) Dr. W. Nagata, Shionogi and Co., Osaka, Japan. (T) Prof. D. H. R. Barton, Imperial College, London. (U) Prof. L. F. Fieser, Harvard. We are greatly indebted to these colleagues for the use of samples.

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