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OPTICAL ROTATORY DISPERSION CURVES OF SOME 9,10-DIMETHYL-1-DECALONE TYPES[1]

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Recent studies[2,3] of the sesquiterpene ketone valeranone (I) have drawn attention to the rather rare occurrence in nature of the decalin system in which both ring-junctions are substituted by alkyl groups.

The preparation[4] of 5-methyl-4-oxo-steroids (II and III; X=Y=Me), which represent authentic 9,10-dimethyl-1-decalone types (both cis and trans), enables us to give optical rotatory dispersion data for these two rare types. The 5-methyl-5α- and 5β-cholestan-4-ones give Cotton effects with amplitudes[5] of -18 and -75, respectively; the Octant diagrams[5] for these two compounds are as shown in IIa and IIa, X=Y=Me).

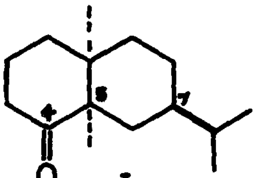
The 5α-methyl-4-ketone (II, X=Y=Me) provides an interesting addition for the reference series of trans-decalones summarised elsewhere[6]. A further member of this series (kindly provided by Dr. S. Szpilfogl of N.V. Organon, Oss, The Netherlands) is the 19-nor-4-ketone (II, X=Y=H). The series of 4-oxo-steroids may now be presented as follows.

	Compound	X	Y	Amplitude *a*	Structural difference	Δ*a* for Me*
	5α-Steroid					
IIA	19-nor-4-one	H	H	-68		
IIB	4-one	Me	H	-91	(B-A)3ax-Me	-23
IIC	*E*(D-homo-17*a*-one)†	H	Me	0	(C-A)2ax-Me	+68
IID	5-Me-4-one	Me	Me	-18	((D-C)3ax-Me ((D-B)2ax-Me	-18 +73
	5β-Steroid					
IIIB	4-one	Me	H	+ 8		
IIID	5-Me-4-one	Me	Me	-75	(D-B)2ax-Me	-83

*Cf. reference values in ref. 6, and data given by Djerassi *et al.*[7]

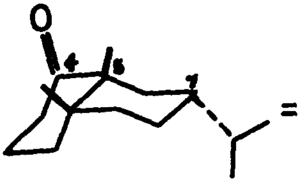
†The value entered for IIC is that for the enantiomer (*E*) of a 17*a*-oxo-*D*-homo-steroid; this is the closest analogue available for a 5α-methyl-19-nor-4-ketone, which does itself not exist. The amplitude '0' indicates that this curve is in fact a *plain* one, as first found by Djerassi[8].

Valeranone (I) is noteworthy for the large amplitude (*a*, -166) of its Cotton effect. Search of the literature has revealed another *cis*-1-decalone of high amplitude[9]; this is the 1-oxo-5β-steroid (IV; *a*, -136). In this compound the carbonyl group is joined to the neighbouring ring-junction by an equatorial bond (IVa; Octant Projection IVb). Presumably the preferred conformation of valeranone is related to the two-chair form (Ia, Ib) in which the carbonyl

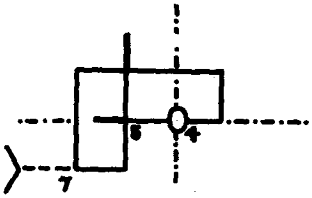


I

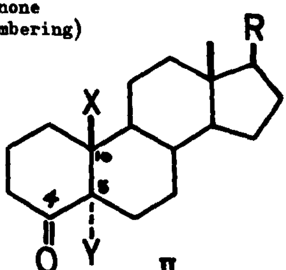
Valeranone
(steroid numbering)



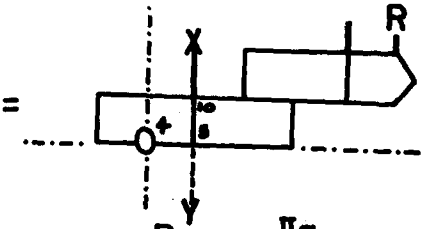
Ia



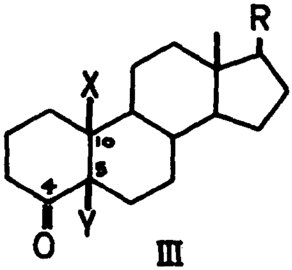
Ib



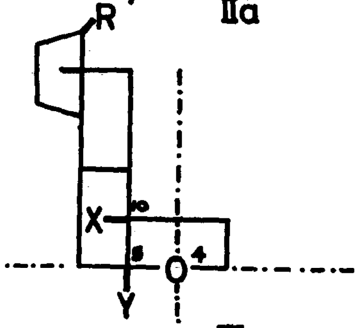
II



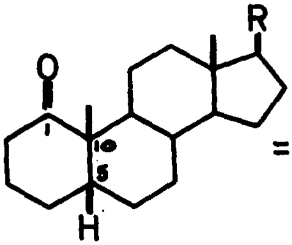
IIa



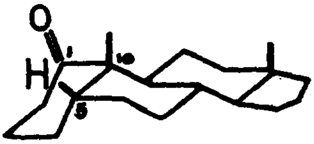
III



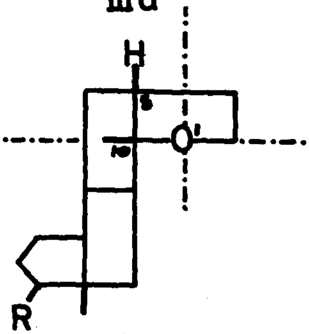
IIIa



IV



IVa



IVb

ring-junction bond is equatorial, so as to keep the 7-isopropyl group equatorial; the resemblance of Ib to IVb is striking. It must be assumed that in each of those compounds the carbonyl-carrying A ring adjusts its conformation in such a way as to minimise non-bonded interactions (cf. recent studies on cyclohexanone conformations[10,11]), and that this modified conformation is responsible for the abnormally large amplitude.

Addendum

One of us (W.K.) begs to draw attention to the fact that in our previous note[2] insufficient emphasis was given to the work of the Japanese authors on valeranone[3], which did in fact constitute a proof of its absolute stereochemistry. We apologise for not pointing this out clearly. The significance of the O.R.D. work lay in the fact that the enantiomeric curves for the keto-esters obtained from valeranone and from eudesmol are more extensive evidence for the enantiomeric nature of these compounds than the monochromatic data previously presented. We regret also that by an oversight we omitted to mention that the sample of the keto-ester from β-eudesmol was kindly provided by Dr. H. Hikino and Prof. T. Takemoto.

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