

very small acrosome meanwhile appears at the front end of the spermatid, *without any apparent connection with the Golgi bodies* (Italics mine). Further, NATH refers in some detail to ROGUE's⁶ paper on the cytoplasmic inclusions of the male germ-cells of *Helix*. This author finds no connection between acrosome-formation and any of the cytoplasmic inclusions (the so-called paranuclear bodies of this author, which must include the Golgi bodies also). NATH actually quotes ROGUE's own words to this effect.

As stated above, I have reinvestigated the male germ-cells of *Vaginula* by phase-contrast microscopy and I still find no evidence of the participation of any cytoplasmic inclusions in the acrosome-formation. This participation is not in evidence in any of GATENBY's figures^{7,8}, nor is it proved by NATH's¹ photographs despite his claim to have demonstrated it. At present, NATH, following Dr. BAKER⁹, does not accept that there is anything like a Golgi apparatus in animal cells, but it makes no difference to this discussion, whatever be the other name (lipochondria or any other term) that

NATH applies now to the structure which he used to name Golgi apparatus formerly.

Zusammenfassung. Der Verfasser macht am Golgi-körper der männlichen Geschlechtszellen von *Vaginula* eine Nachuntersuchung mit dem Phasenkontrastmikroskop und bestätigt, dass zwischen Golgikörperbildner und Akrosomgenese kein verwandtschaftlicher Zusammenhang besteht. Damit werden entgegenstehende Auffassungen von NATH widerlegt.

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Department of Zoology, University of Allahabad (India), May 11, 1962.

⁶ A. L. ROGUE, J. Roy. microscop. Soc. 74, 188 (1954).

⁷ J. B. GATENBY, Quart. J. microscop. Sci. 62, 555 (1917).

⁸ J. B. GATENBY, Quart. J. microscop. Sci. 63, 445 (1919).

⁹ J. R. BAKER, Proc. Linn. Soc. London 162, 67 (1950).

Rotatory Dispersion Curves of some Decalones of Microbiological Origin¹

The Octant Rule² provides a theoretical basis for the study of optical rotatory dispersion curves of ketones. The application of this rule to extensive collections of data for cyclohexanone types from Professor DJERASSI's laboratory

Decalones and related compounds
Amplitudes of rotatory dispersion curves (in methanol)

No.	Substituents	Amplitude <i>a</i>	Amplitude contributions Δa for substituents named	Refer- ences
(9 <i>R</i>)- <i>trans</i> -1-Decalones				
I	None	−40		⁸
II	(4 <i>R</i>)-4-OH	−43	Δa -OH (II-I) = −3	^{5,12,a}
III	(4 <i>S</i>)-4-OH	−37	Δa -OH (III-I) = +3	^{5,12,a}
IV	(5 <i>R</i>)-5-OH	−61	Δa -OH (IV-I) = −21	^{6,12,a}
V	(5 <i>S</i>)-5-OH	−50	Δa -OH (V-I) = −10	^{6,12,a}
(9 <i>R</i>)-9-Methyl- <i>trans</i> -Decalones				
VI	None	+27		⁹
VII	(5 <i>R</i>)-5-OH	+8	Δa -OH (VII-VI) = −19 Δa -Me (VII-IV) = +69	¹³
(9 <i>R</i>)-10-Methyl- <i>trans</i> -1-Decalones				
VIII	None	−32 ^b		¹⁰
IX	(5 <i>R</i>)-5-OH	−81	Δa -Me (IX-IV) = −20	¹³
X	(5 <i>S</i>)-5-OH	−72	Δa -Me (X-V) = −22	¹³
(9 <i>R</i>)- <i>trans</i> - Δ^6 -1-Octalones				
XI	(4 <i>R</i>)-4-OH	−6		¹⁴
XII	(4 <i>S</i>)-4-OH	−6		¹⁴
(9 <i>R</i>)- <i>cis</i> -1-Decalones				
XIII	None	−14		⁸
XIV	(4 <i>R</i>)-4-OH	−14	Δa -OH (XIV-XIII) = 0	^{5,12,a}
XV	(5 <i>R</i>)-5-OH	−2	Δa -OH (XV-XIII) = +12	^{6,12,a}

^a Curves for these compounds had previously been measured by Professor C. DJERASSI (then at Wayne State University, Detroit) but complete amplitudes were not obtained.

^b Amplitude incomplete; estimated from mixture of *cis* and *trans* isomers.

and from our own laboratory, has been described elsewhere³. It is becoming increasingly apparent that the amplitude⁴ of a Cotton effect curve is a useful measure of the asymmetry of the surroundings of the carbonyl group.

The decalone derivatives prepared by microbiological oxidations and reductions at the ETH, Zürich, in the laboratory of Professor V. PRELOG⁵⁻⁷, provide an excellent series, from which reference values have been obtained illustrating the semi-quantitative application of the Octant Rule.

The amplitudes obtained in this work, together with some values previously obtained by DJERASSI et al.⁸⁻¹⁰, are collected in the Table. All results are expressed for the 9*R*-series for the sake of ready comparison (although some were actually measured with the 9*S*-compounds).

The conclusions may be briefly presented as follows: (i) The differences Δa (II-I) and Δa (III-I) represent the contribution to the Cotton effect of hydroxyl groups in a symmetry plane (at C-4). They are, as expected, negligible. (ii) The differences Δa (IV-I) and Δa (V-I) relate to hydroxyl groups in a negative octant. They are, as expected, negative. (iii) The difference Δa (VII-VI) is Δa for an axial methyl group in the 2-position relative to a cyclohexanone carbonyl. The value (+69) agrees well with

¹ Paper V of the series 'Optical Rotatory Dispersion'. For Paper IV see C. DJERASSI and W. KLYNE, Proc. Nat. Acad. Sci. Washington, in press (1962).

² W. MOFFITT, R. B. WOODWARD, A. MOSCOWITZ, W. KLYNE, and C. DJERASSI, J. Amer. chem. Soc. 83, 4013 (1961).

³ C. DJERASSI and W. KLYNE, J. chem. Soc. 1962, in press.

⁴ Amplitude (*a*) = 10^{−2} (Molecular rotation at *extremum* (peak or trough) of longer wavelength *minus* molecular rotation at *extremum* of shorter wavelength). The measurements were made, in methanol solution, on a Rudolph spectropolarimeter generously provided by the Wellcome Trust.

⁵ P. BAUMANN and V. PRELOG, Helv. chim. Acta 41, 2362 (1958).

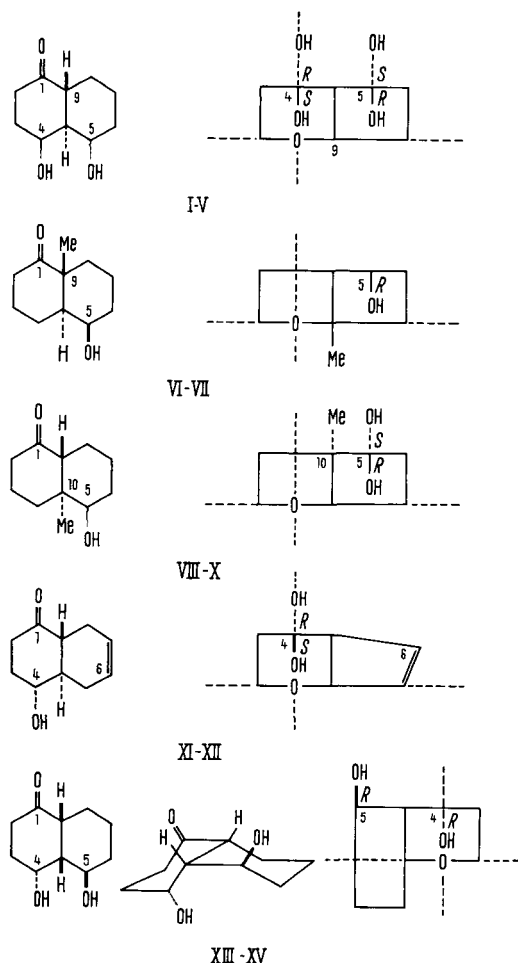
⁶ P. BAUMANN and V. PRELOG, Helv. chim. Acta 41, 2379 (1958).

⁷ V. PRELOG et al., Helv. chim. Acta 39, 748 (1956); 41, 1416, 1424, 1428, 2396 (1958); 42, 736, 1239, 1862, 2624 (1959).

⁸ C. DJERASSI and J. STAUNTON, J. Amer. chem. Soc. 83, 736 (1961).

⁹ C. DJERASSI, R. RINIKER, and B. RINIKER, J. Amer. chem. Soc. 78, 6362 (1956).

¹⁰ C. DJERASSI and D. MARSHALL, J. Amer. chem. Soc. 80, 3986 (1958).



Note: In order to save space, each basic formula shows *all* relevant substituents. The compounds examined did *not* contain more than one hydroxyl group each.

that calculated from DJERASSI's^{8,9} values; Δa (VI-I) = + 67. (iv) The differences Δa (IX-IV) and Δa (X-V) are for an axial methyl group in the 3-position relative to a cyclohexanone carbonyl (– 20, – 22). These values for Δa '3-axial-methyl' are similar to that found by DJERASSI, LUND, and AKHREM¹¹ for Δa '3-equatorial-methyl', viz: – 25. (v) The amplitudes of the Δ^6 -octalones (XI, XII) are *less* than those of the corresponding decalones. This is in accordance with the octant projection for the Δ^6 -octalones, in which ring B is flattened towards the horizontal symmetry plane. (vi) The negative amplitudes for the *cis*-decalones XIII, XIV, and XV show that for these compounds the 'steroidlike' conformation is preferred (DJERASSI and STAUNTON⁸). (vii) The contributions of the hydroxyl groups in the *cis*-decalone series are zero and positive as expected¹⁵.

Zusammenfassung. Die Rotationsdispersionskurven einiger optisch aktiver Dekalonderivate sind gemessen worden. Ihre Amplituden (a) und die Amplitudenbeiträge (Δa) der Substituenten werden im Rahmen der Oktantenregel diskutiert.

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Department of Chemistry, Westfield College, Hampstead, London (England), May 28, 1962.

¹¹ C. DJERASSI, E. LUND, and A. A. AKHREM, J. Amer. chem. Soc. **84**, 1249 (1962).

¹² P. BAUMANN, Promotionsarbeit ETH, Zürich (1959).

¹³ P. WALTER, Promotionsarbeit ETH, Zürich (1960).

¹⁴ B. SERDAREVIĆ, Promotionsarbeit ETH, Zürich (1961).

¹⁵ **Acknowledgment.** We are greatly indebted to Professor V. PRELOG and Dr. W. ACKLIN, ETH Zürich, for generously supplying the materials. We are grateful to the Department of Scientific and Industrial Research for a grant and to the U.S. Army Research and Development Group (Frankfurt am Main) for a contract.

Liver Catalysis in the Association of Estrogen to Protein

RIEGEL and MUELLER¹ have demonstrated the presence in rat liver of an enzyme which catalyzes the formation of a protein-bound metabolite of C¹⁴-estradiol. In a series of *in vitro* experiments SZEGO and ROBERTS² obtained results which indicated that rat liver promotes the binding of C¹⁴-estrone or its metabolites to the proteins of their serum incubation medium. On the other hand, SANDBERG et al.³ obtained evidence from a similar study which suggested that the binding of C¹⁴-estrone occurred with a serum protein or a serum soluble protein originating from the liver. This communication describes (a) the results of a comparison of the action of rat liver slices and rat liver homogenates in promoting the binding of both C¹⁴-estrone and estradiol 17 β -acetate to protein and (b) the progress made in the attempts to characterize the factors concerned with the formation of 'estroprotein' through the fractionation of rat liver homogenates.

Materials and Methods. Techniques involving the incubation of steroid and rat liver slices in serum were essentially the same as those described earlier by SZEGO⁴.

Homogenates of rat liver were prepared in 0.1 M potassium phosphate buffer (pH 7.4) according to the procedure described by BUCHER and McGARRAHAN⁵. Prior to fractionation, glutathione and Versene were introduced to give final concentrations of 0.01 M and 0.001 M, respectively. All preparative steps were carried out at 0°. The crude homogenate was first centrifuged at 5,000 $\times g$ for 10 min. The supernatant fluid, containing only microsomes and soluble cell constituents, termed 'microsol', was then fractionated as follows. The major part of the microsol fraction was centrifuged at 105,000 $\times g$ (1 h) and the supernatant fluid, S₁, decanted. The sediment was resuspended in buffer and washed once by centrifug-

¹ I. L. RIEGEL and G. C. MUELLER, J. biol. Chem. **210**, 249 (1954).

² C. M. SZEGO and S. ROBERTS, J. biol. Chem. **221**, 619 (1956), and references cited therein.

³ A. A. SANDBERG, W. R. SLAUNWHITE, and H. N. ANTONAIDES, *Recent Progress in Hormone Research* (Academic Press Inc., New York 1957), vol. 13, p. 209.

⁴ C. M. SZEGO, *Endocrinology* **52**, 669 (1953).

⁵ N. L. R. BUCHER and K. McGARRAHAN, J. biol. Chem. **222**, 1 (1956).