

Some Interesting Phenomena at the Solid-Liquid Transition of Colloidal Stearic Acid

STEARIC ACID sols (prepared by the addition of an alcoholic solution of the substance into boiling water) are found to exhibit, on standing, the phenomenon of "Schlierung" in a striking manner. In the course of an investigation it was observed (K.S.R. and K.S.G.D.) that the Schlieren effect disappeared sharply on heating and reappeared in the cold, on standing. Ultra-microscopic examination revealed that the rod-like particles of colloidal stearic acid changed to spherical ones on heating and resumed their original shape in the cold (on standing). These observations afford a most convincing line of evidence to show that the Schlierung phenomenon is caused by the non-spherical shape of the particles. Further work with purified sols [(Late) M. P. V. Iyer and K.S.G.D.] revealed the following facts:—(a) the change occurs in the neighbourhood of the melting-point of stearic acid ($66.8^{\circ}\text{C.} \pm 0.2^{\circ}\text{C.}$), (b) there is an inflection at the same temperature, in the conductivity-temperature curve of the sol and (c) there are sharp changes (as revealed by preliminary measurements) in the intensity and depolarisation of the light scattered by the particles at the same temperature. Details of these investigations as well as the subsequent work done on the subject will shortly be published elsewhere.

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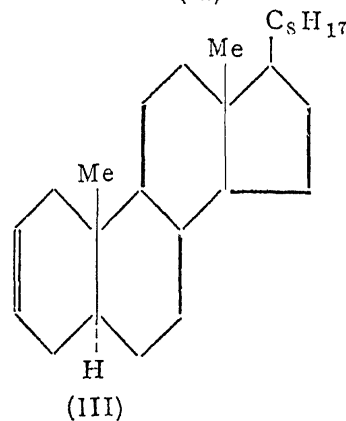
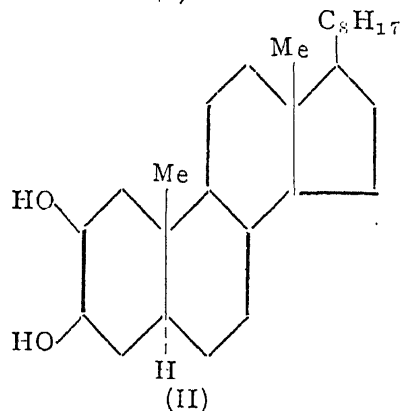
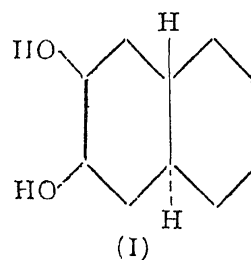
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The Configuration of the C_3 Hydroxyl Group in the Digitonin Precipitable Steroids

THERE are many indirect evidences to indicate that the C_3 hydroxyl group in the steroids which precipitate with digitonin, is *cis* to the C_{10} -methyl group.^{1,2} A direct and absolute proof for this appeared to be obtainable by extending our studies on the stereochemistry of

the 2:3-dihydroxy *trans* decalins (I)³ to the 2:3-dihydroxy cholestanes (II) which can exist in four stereoisomeric forms (the isomerism herein concerned being due only to the two hydroxyl groups attached to C_2 and C_3), of which in one the hydroxyl groups are in the *trans* and in the rest in the *cis* positions. So, starting from neocholestene (Δ^2 -cholestene III)⁴ and also 2:3-diketocholestane,⁵ by adopting the same methods as in the synthesis of the 2:3-dihydroxy *trans* decalins,³ we attempted the synthesis of the four 2:3-dihydroxy cholestanes. Recently, Marker and Plambeck⁶ have reported the synthesis of a 2:3-dihydroxycholestane (II), m.p. 201° , by the oxidation of Δ^2 -cholestene (III) with hydrogen peroxide and



similarly 2-hydroxyandrosterone and 2:3:17-trihydroxyandrostane also from Δ^2 -androstene-17 and androstenol-17 respectively, all these new hydroxyl compounds, as a class, not precipitating with digitonin. Since we are not

at present able to pursue our work, we here give our interpretation of the results of Marker and Plambeck in the light of our study of the 2:3 dihydroxy-*trans* decalins.

The non-precipitability of this 2:3-dihydroxy cholestane of Marker and Plambeck with digitonin is taken by us to be due to its C₃ hydroxyl group possessing the *epi* (α -) configuration,* a view also expressed by the American authors as a possibility. The other possibility that the presence of the adjacent C₂ hydroxyl group in the above compound may interfere with the formation of the additive compound with digitonin⁷ does not appear to be plausible because it has been found by Rosenheim⁸ and also by Marker (personal communications to the author) that the presence of the additional hydroxyl grouping at C₄ in cholesterol, cholestanol, sitosterol and stigmasterol does not influence their digitonin precipitability. It is thus to be expected that two of the 2:3-dihydroxycholestanes should precipitate with digitonin.

We assign the *trans*-configuration to the hydroxyl groups of the 2:3-dihydroxyl cholestane of Marker and Plambeck for the reasons: (i) the oxidation of the cyclic double bond with hydrogen peroxide (in the absence of osmium tetroxide) and the hydrolysis of the cyclic oxide yield the same *trans* glycol³ as for example in the preparation of 3:5:6-trihydroxy cholestane (m.p. 231°) from cholesterol¹⁰ and (ii) if the hydroxyl groups are in the alternative *cis* position (with the C₃ hydroxyl group being of the *epi* form), by analogy with the behaviour of the *cis* 2:3-dihydroxy *trans* decalin (m.p. 128), the compound should isomerise on treatment with acetic anhydride,[†] which has not been observed.

* We now consider the non-precipitability of gitogenin and digitogenin with digitonin as being due to the *epi* configuration of the C₃ hydroxyl groups.⁷ This view appears to be compatible with the concept of Lettré⁹ of the formation of additive compounds of the sterols.

† It also appears that the C₂ and C₃ hydroxyl groups in gitogenin and digitogenin are in the *trans* positions for the same reasons as in the case of 2:3 dihydroxy-cholestane now considered.

It can be seen from the space model of 2:3-dihydroxy cholestane that in the *trans* form, the C₃-hydroxyl group, now fixed to be of the *epi* configuration, is in the *trans* position to the C₁₀-methyl group. This leads to the conclusion that in the digitonin precipitable steroids, the C₃-hydroxyl group occupies the *cis* position with reference to the C₁₀ methyl group; only the two inferences drawn above by analogy have to be checked experimentally to make this proof more rigorous.

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July 29, 1939.

¹ Ruzicka, Furter and Goldberg, *Helv. Chim. Acta.* 1938, **21**, 498.

Cf. also *ibid.*, 1933, **16**, 327; 1934, **17**, 1395, 1407; 1935, **18**, 61.

Vavon and Jakubowicz, *Bull. Soc. Chim.*, 1933, **53**, 581. Lettré, *Ber.*, 1935, **68**, 766.

Miescher and Fischer, *Helv. Chim. Acta.*, 1938, **21**, 336. *Chem. & Ind.*, 1939, **58**, 113.

² *Cf.* however, Cook, *Annual Rep. Chem. Soc. London*, 1926, **33**, 341.

³ *Ber.*, 1939, **72**, 1381.

Cf. *J. Indian Chem. Soc.*, 1938, **15**, 407.

⁴ Mauthner, *Monats.*, 1909, **30**, 643.

⁵ Stiller and Rosenheim, *J. Chem. Soc.*, 1938, 353.

⁶ *J. Amer. Chem. Soc.*, 1939, **61**, 1332.

⁷ Tschesche and Hagedorn, *Ber.*, 1935, **68**, 2248.

⁸ Rosenheim and Starling, *J. Chem. Soc.*, 1937, 378.

⁹ *Annalen*, 1932, **495**, 41.

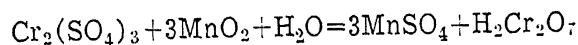
¹⁰ Westphalen, *Ber.*, 1915, **48**, 1064.

Pickard and Yates, *J. Chem. Soc.*, 1908, **93**, 1678.

Crigee, *Ber.*, 1932, **65**, 1770.

Heterogeneous Reaction between Chromic Sulphate and Manganese Dioxide

It has been found that when a solution of chromium sulphate is shaken with solid manganese dioxide, dichromate ions are formed in the solution. The reaction takes place as



The above mode of reaction has been established by estimating the amounts of dichromate ions and manganese sulphate formed and the amount of chromium sulphate used up in the reaction. It has been found that (i) the gram