

Citation:

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Chemistry. — “*On the anisotropic liquid phases of the butyric ester of dihydrocholesterol, and on the question as to the necessary presence of an ethylene double bond for the occurrence of these phenomena*”. By Dr. F. M. JAEGER. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of February 23, 1907).

§ 1. In order to explain the behaviour of substances which are wont to exhibit double-refracting liquid phases, some investigators have started the hypothesis that, in this kind of organic substances, it might be a question of systems formed of two components, and of equilibrium phenomena between tautomeric and isomeric modifications, which would be converted into each other with finite velocity.

Although it is difficult to understand how such a supposition, which is easy to propound, but very difficult to prove, could explain the numerous well ascertained facts of the *regular* optical anisotropism of these phases, it might explain, however, at least to some extent, the peculiar irreversible transitions of phases, which I found more particularly with the esters of cholesterol and α -phytosterol, and also the hindrance phenomena noticed on that occasion¹).

Such a supposition, however, is perhaps of some importance for the interpretation of the brilliant colour phenomena which accompany the phase-transitions in the cholesterol esters. For a mixture, or an emulsion of substances, whose indices of refraction differ very little, but whose dispersions differ much, might, like CHRISTIANSEN'S monochromes, cause a similar display of colours.

§ 2. There is more than one cause for tautomerism (or isomerism) in the case of these cholesterol esters, for all the esters, as well as cholesterol itself, possess an asymmetric carbon atom, and in solution they all polarise to the left.

Consequently, a racemisation during the esterification is by no means excluded, and we might, therefore, have a mixture of the optical antipodes. Cholesterol, moreover, possesses an ethylene double bond, so that we may also expect an isomerism in the sense of fumaric and maleic acids.

§ 3. As many other compounds (in fact most organic substances which are wont to exhibit these phenomena of doubly refracting

¹). F. M. JAEGER, These Proc. 1906 p. 472 and 483 (29 December).

liquid phases) possess such ethylene double bonds, one might indeed imagine that the presence thereof in the molecule is of great importance for the occurrence of the said phenomena, if not the *conditio sine qua non*, as the structure of the azoxy-compounds is not yet firmly established and because it may be assumed that they contain, perhaps, similar double bonds between *N* and *O*.

Moreover, the cholesterol esters all contain *three* liquid phases, so that this peculiar complication might perhaps also be connected with the possibility of very intricate isomerism-phenomena of those substances.

§ 4. In order to answer these questions, I asked Prof. Dr. C. NEUBERG of *Berlin* to furnish me with a specimen of his synthetic *Dihydrocholesterol*, to which request this savant most willingly acceded.

I wish to thank Prof. NEUBERG once more for his kindness.

In this *Dihydrocholesterol* the ethylene double bond has disappeared owing to the addition of two atoms of hydrogen, and the malenoid and fumaroid isomerism is therefore, *à priori* excluded.

§ 5. I have prepared from this alcohol the acetic and the normal butyric esters, by means of the pure acid-anhydrides, and have examined the same as to their phase transitions. The acetic ester will be described elsewhere later on; here the butyric ester only will be discussed.

As a highly important result I may mention that the colour phenomena on melting and the occurrence of three liquid modifications in the normal butyrate remain unaltered as before, but that the irreversibility of the phase-transitions is shown in a manner just the reverse as in the case of most of the cholesterol esters, e.g. the laurate.

Whereas of the two doubly-refracting liquid phases of the last named substance, one is always passed over *on cooling*, whilst both are found *on melting* the solid substance, this is just the reverse in the case of the dihydrocholesterol-*n*-butyrate.

6. The solid phase *S* consists of an aggregate of very thin, colourless, and clear transparent laminae in which the plane of polarisation makes an obtuse angle with the sides of demarcation and exhibit in convergent polarised light a hyperbole with very strong colour dispersion $\rho > v$.

On heating, this phase *S* passes into a doubly-refracting liquid *B*, consisting of very small, feebly doubly-refracting individuals, which in turn passes at a higher temperature into the isotropous fusion *L*.

Of colour phenomena during one of these transitions, absolutely *nothing* is noticed.

If, however, we start from the phase *L* and allow the same to cool, we first notice the doubly-refracting phase *B*, which on further cooling, amid violent sudden currents of the mass, passes into a much more strongly doubly-refracting liquid *A*, which on continued cooling crystallises suddenly, also amid very violent currents, to an aggregate of flat needles, glittering in vivid interference colours. These in turn, rapidly assume a spherulite structure so that the solid phase *S* itself appears to be also *dimorphous* and *monotropous*, as the flat needles are *not* reobtained on warming the spherulitic mass. The transformation of *A* into these needles, during cooling, is accompanied with the most vivid display of colours. Under the microscope these may be recognised by the dark-green colour of the background of the field of vision; with the naked eye, however, with incident light, that colour-display commences with a brilliant violet gradually turning into blue and finally into a radiating green when the mass crystallises. I have never noticed red or yellow colours with incident light. These phenomena return in the same order when the experiment is repeated.

That the phase *A* really exhibits the behaviour of a stable phase

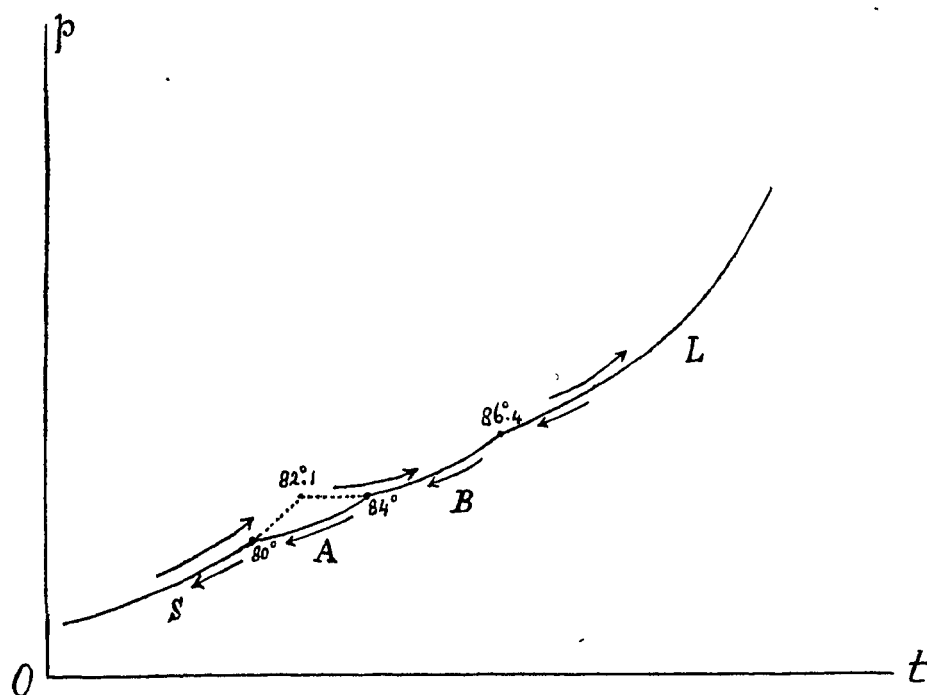


Fig. 1.

Schematic *p t*-diagram for Dihydro-cholesterol-n-butyrate

is also shown by the fact that, the colour having become blue or green on cooling, turns again violet on warming, so long as the solid phase *S* has not yet been attained. The phase is, therefore, realisable at a change of temperature in *two* directions.

§ 7. As I had but very little of the substance at my disposal, the thermometric determinations could only be studied in capillary tubes with the aid of a magnifying glass.

At 82.°1 the phase *S* melts to a doubly-refracting phase *B* which becomes clear at 86.°4 and passes into *L*. On cooling this isotropous fusion, it first passes properly into *B* at 86.°4, but at 84° into the more strongly doubly-refracting phase *A*, which may be undercooled many tens of degrees, and with retention of its violet colour, before passing into the solid phase *S*.

Want of material prevented my determining the true solidifying point of *S* by inoculation; I estimate it at about 80°.

Thus the positive proof has been given that the remarkable colour phenomena accompanying the melting the cholesterol esters *cannot* be attributed to the presence of an ethylene double bond; also that an eventual presence of funaroid and maleinoid isomers cannot be considered as the cause of the occurrence of the *three* liquids.

Zaandam, 15 Febr. 1907.

Chemistry. — “*On the action of bases, ammonia and amines on s. trinitrophenyl-methylnitramine.*” By Prof. P. VAN ROMBURGH and Dr. A. D. MAURENBRECHER.

(Communicated in the meeting of February 23, 1907).

s.-Trinitrophenyl-methylnitramine, as has been known for a long time, is decomposed at the ordinary temperature by ammonia in alcoholic solution, or on warming, by an aqueous solution of potassium hydroxide, or carbonate, in the first case with formation of picramide, in the second (with evolution of monomethylamine) of picric acid. One of us who formerly studied the reaction with bases concluded, from the occurrence of the amine and the formation of nitric acid which was also observed, that the methylnitramine which might be expected according to the equation :