

dimethylcyclohexanes, concluded that the nomenclature of the 1:3-dimethylcyclohexanes should be reversed and that the higher-boiling isomer should be regarded as the *trans* isomer. This result is thus in agreement with that obtained by Mousseron and Granger (*loc. cit.*).

Only one isomer of 1:3-dimethylcyclopentane has been reported in the literature, and this has been assigned the *trans* configuration on the basis of the work of Zelinsky (*loc. cit.*). Preparations of this naphthene from 1:3:5-xylene have resulted in the production of a hydrocarbon corresponding in properties to those of the known hydrocarbon, and have not given the expected mixture of *cis* and *trans* isomers. There was some evidence from infra-red spectra that a second isomer might be present in the slightly higher-boiling tail-ends from the fractionation of the main product, but no pure compound could be isolated from the small quantities of material available.

A synthesis of *cis* 1:3-dimethylcyclopentane was therefore attempted using cyclopentane-*cis*-1:3-dicarboxylic acid as starting material. A paper describing the preparation of this acid has been accepted for publication in the *Journal of the Chemical Society*. The synthesis involved the reduction of the diethyl ester of this acid to 1:3: di(hydroxymethyl)cyclopentane, replacement of the hydroxyl groups by halogen and reduction of the dihalide to the hydrocarbon. The hydrocarbon thus obtained was identical with the known 1:3-dimethylcyclopentane. No evidence was obtained for the presence of a second isomer in this product.

Two possible explanations of this observation suggest themselves. Either isomerization to the *trans* form takes place at some stage in the above synthesis from the *cis* acid, or the hydrocarbon previously referred to as *trans* is, in fact, the *cis* isomer. The apparent closeness of the boiling points of the isomers of 1:3-dimethylcyclopentane throws some doubt on the value of Zelinsky's determination of the *trans* isomer, and in view of the work of Chiurdoglu (*loc. cit.*), the known lower-boiling isomer may be the *cis* hydrocarbon. Our observations tend to support this view.

To gain additional information on this point a synthesis of 1:3-dimethylcyclopentane from cyclopentane *trans* 1:3-dicarboxylic acid is being attempted in this laboratory. The product will be compared with the hydrocarbon obtained from the *cis* acid.

The possibility of selective adsorption of one of the optical enantiomorphs of the *trans* form of dimethylnaphthenes on an optically active adsorbent is also under investigation. The isomer which develops optical activity after such treatment must be the *trans* isomer, since the *cis* compound cannot exist in active forms.

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¹ Zelinsky, *Ber.*, **35**, 2677 (1902).

² Mousseron and Granger, *Bull. Soc. Chim. France*, **5**, 1618 (1938).

³ Chiurdoglu, *Bull. Soc. Chim. Belg.*, **53**, No. 3, 45 (1944).

⁴ Pitzer and Beckett, *J. Amer. Chem. Soc.*, **69**, 977 (1947).

Configuration and Packing of Chain Molecules of Native Starch in the B-Modification

IN a previous communication¹ I mentioned the dimensions of a unit cell of native starch in the B-modification as deduced from a fibre pattern obtained from a part of a single starch grain. It has now become evident, from consideration of the reciprocal lattice and reflexion globe, that the unexplained difference, noted in that communication, between the fibre period calculated from the pattern and the supposed true period, is a phenomenon that may be expected and that can be explained from bad parallelism between the micelles, especially from those directions of the micelle long axes which deviate from perpendicularity to the incident beam. Furthermore, a critical revision of the *d*-values derived from a powder pattern of native starch in the B-modification has shown that a fibre period of 10.5–10.6 Å. is in somewhat better agreement with these spacings than the period of 10.4 Å. previously given.

It was originally suggested¹ that the fibre period would contain two pyranose rings, as in cellulose and chitin. Further investigation has shown, however, that there are a number of arguments for rejecting this idea in favour of a chain containing three glucose units in the period, in spiral arrangement.

As distinct from the substances mentioned above and from alginic acid (see Astbury²), in which pyranose rings are united in β -1:4 linkage, the starch chain is considered to consist of glucose units in α -1:4 linkage (see, for example, K. H. Meyer³). This α -linkage gives difficulties when constructing for starch a chain configuration similar to those assumed in cellulose and alginic acid. A flat and straight, strainless chain of α -glucose units, for example, with two units per period, will, though it can be constructed in different ways, always show a much shorter period than 10.6 Å. Furthermore, the X-ray density of starch, calculated from a unit cell of the dimensions suggested¹ and filled up with chains with two glucose units per fibre period, cannot be brought into accordance with the experimental density of starch as determined under water¹, which latter should be lower than the X-ray density and not equal to it.

The proposed chain, with three glucose units per period of 10.6 Å., in three-fold screw arrangement, is strainless and continues in a constant direction. The dimensions of the projection of such a chain on the basal plane are in accordance with the dimensions and the hexagonal ratio I found for the axes in this plane¹. Assuming a rhombohedral or hexagonal unit cell in which $a = 18.1$ Å. (the double length of the shortest orthorhombic axis¹), enclosing twelve such chains (and containing thirty-six glucose units) with one water molecule per glucose unit, the X-ray density would be reconcilable with the experimental density.

Details will follow elsewhere.

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¹ Kreger, D., *Nature*, **153**, 199 (1946).

² Astbury, W. T., *Nature*, **155**, 667 (1945).

³ Meyer, K. H., "Natural and Synthetic High Polymers" (New York, 1942), 393.