## Letters to the Editor.

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## X-ray Crystal Analysis as an Auxiliary in Organic Chèmical Research.

At the suggestion of Prof. W. L.-Bragg, I recently sent to Dr. G. Shearer, of the Davy Faraday Research Laboratory, a series of four keto-acids which had been synthesised by my wife. Dr. Shearer was not aware of the identity of the substances, which were, however, stated to belong to the series

 $CH_3(CH_2)_m \cdot CO \cdot (CH_2)_n \cdot CO_2H.$ 

No case so complex had been tried in the aliphatic series previously, and yet, from the X-ray examination of a minute amount of these compounds, Dr. Shearer was able to deduce that (A), (B), (C), and (D) have chains containing 22, 18, 16, and 19 carbon atoms respectively. Furthermore, it was possible to assign positions to the carbonyl groups in (A), (B), (C), and (D) from a consideration of the distribution of intensity among the various orders of reflection from the principal planes, and it was found that the carbonyl group is 0.52, 0.67, 0.55, and 0.50 respectively, of the whole length of the molecule from the end terminating in a methyl group. The corresponding theoretical values are 0.54, 0.65, 0.50, and 0.48, which means a maximum error of one carbon atom in placing the oxygen.

The outcome, considering the difficulties, is remarkable; and this is surely the most noteworthy invasion which the physicist has yet made of the domain of the purely structural organic chemist. The specimen (B), for example, is identical with an acid found by Bougault and Charaux (1911) in various species of Lactarius, and therefore called lactarinic acid. Its relation to stearic acid was quickly realised, but a determination of the situation of the carbonyl group involved a longer investigation. Should such a case arise again, we can replace the analytical research by an X-ray examination and confirm the conclusions by direct synthesis.

by direct synthesis. In view of the importance of the normal-chain unsaturated acids in biochemistry and their ready conversion into crystalline oxygenated derivatives, there can be little doubt that Dr. Shearer's work will find many applications even in this restricted field. On a broad view the possibilities are limitless, and gradually more and more groups of carbon compounds will become amenable to this kind of direct examination. Our more difficult problems, such as that presented by the determination of the molecular structure of strychnine, cannot be completely solved by X-ray analysis at the present time, yet, even here, Sir William Bragg has recently made a suggestion in regard to a possible utilisation of the method. It is to *stain* the molecule with heavy halogen atoms and locate these, at least in the crystal.

A different kind of use for the X-ray spectrograph in organic chemistry is illustrated by a further incident. Mrs. Robinson has synthesised the two keto-stearic acids,  $CH_3(CH_2)_7$ .  $CO(CH_2)_8$ .  $CO_2H$  and  $CH_3(CH_2)_8$ . CO.  $(CH_2)_7$ .  $CO_2H$ , which are the possible

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products of hydration of stearolic acid, CH<sub>3</sub>(CH<sub>2</sub>)7.C  $\equiv$ C. (CH<sub>2</sub>)<sub>7</sub>. CO<sub>2</sub>H. It is stated in the literature that the addition of the elements of water to stearolic acid gives only the first-mentioned keto-stearic acid, but both synthetical acids melt at a higher temperature than does the substance derived from stearolic acid. Possibly the latter is a mixture of the two, and in order to confirm this view we had recourse to Dr. Shearer. He found that the principal spacings in the three specimens were identical, but that the intensity distributions among the different orders of reflection from the principal planes showed marked differences in the case of the two homogeneous acids, whilst the intensity distributions were intermediate in the case of the acid derived from stearolic acid. It is almost certain, therefore, that the acetylenic linkage of stearolic acid is hydrated in each of the theoretically possible directions when the substance is treated successively with sulphuric acid and water.

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## The Structure of Stearic and Stearolic Acid.

CRVSTALS of fatty acids and similar long chain compounds are difficult to obtain in sizes large enough to give good "single crystal" X-ray photographs. Mr. W. B. Saville has succeeded in growing fairly large and thick crystals of stearic acid. They were obtained from a saturated solution of stearic acid in carbon bisulphide.

X-ray analysis shows that stearic acid crystals obtained under these conditions are monoclinic. The size of the unit cell is found to be :  $a = 5 \cdot 60$ ,  $b = 7 \cdot 38$ ,  $c = 50 \cdot 9$  Å.U., and  $\beta = 59 \cdot 7^{\circ}$ . The choice of the unit cell is to a certain extent arbitrary, these data give the lowest indices to the strongest reflecting planes. The density is slightly more than  $r \cdot o5$ ; this gives four molecules to the unit cell. Previous work on series of similar compounds led to the conclusion that the carbon atoms are arranged in long and uniform chains. The c axis in the present case has been put in a plane of highest density. The chain which coincides nearest with the c axis is found to be of the tetrahedral type if the diameter of the carbon atom is taken over from the diamond structure.

A single crystal of stearolic acid investigated by means of X-rays gave different photograms from those obtained from stearic acid. The symmetry is lower, and all the data seem to indicate that these crystals are triclinic. Stearolic acid has the same number of carbon atoms as stearic acid (18), but it has a triple bond in the middle of the chain.

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Davy Faraday Laboratory, Royal Institution, July 1.

## Solar Activity and Atmospheric Electricity.

In view of the footnote to Dr. Chree's article in NATURE of June 27, and an explanatory note received from him recently that his article was in type before he saw my article in the March issue of the journal *Terrestrial Magnetism*, it would scarcely be fair to him to make any comments. However, I shall be glad to send a reprint of my article to any one interested in becoming acquainted with all the points involved. Furthermore, since my March article, we have found Dr. Chree's recommendation made at the Madrid meeting of the Geophysical Union impracticable. Meteorologists have likewise not adopted his recommendation for their purposes.