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Variation of Unit-Cell Dimensions of a Crystal Form of Long Normal Chain Carboxylic Acids

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The unit cells of form *C* of long normal chain carboxylic acids with 12, 14, 18, 22 and 26 carbon atoms are determined, using powder methods. All dimensions in the monoclinic cell are found to be dependent of the number of carbon atoms in the chain. The *a* and *b* axes and the angle β decrease asymptotically with increasing chain length. The *c* axes and long spacings, *d*(001), obey linear laws.

Introduction

This work was carried out in connexion with crystal-structure investigations of long normal chain carboxylic acids.

Vand, Aitken & Campbell (1949) found that all the unit-cell dimensions of silver soaps changed with chain length. In order to find the behaviour of the unit-cell dimensions of a crystal form of long normal chain carboxylic acids the unit cells of form *C* of several acids with an even number of carbon atoms were determined, using powder methods. The crystal structure of form *C* of lauric acid has been determined by Vand, Morley & Lomer (1951). The unit cell is monoclinic with four molecules in the cell. The hydrocarbon chains have the orthorhombic packing determined by Bunn (1939) and Vainshtein & Pinsker (1950). Unit-cell determinations of this form have been made by Thibaud & Dupré la Tour (1932) (palmitic acid) and by Trillat & v. Hirsch (1932) (stearic acid).

Preparation of specimens

Very pure acids with 12, 14, 18, 22 and 26 carbon atoms were obtained from Prof. E. Stenhagen and his collaborators. The melting points are: 44·5–44·8, 54·2–54·5, 69·6, 79·6–79·8 and 87·6–87·7° C.

According to Stenhagen & von Sydow (1953), form *C* of even acids is obtained from the melt and from polar solvents.

Specimens were crystallized from the melt and from ethanol by precipitation with water. Form *C* of myristic acid (C_{14}) was also obtained in large crystals from slowly evaporating light petroleum.

Scotch tape was used as support for the plane powder samples. From the melt the acids were crystallized directly on the tape to avoid mechanical deformation. The dried powder obtained from ethanol was cautiously pressed on the tape. The crystals of myristic acid (C_{14}) were cut with a razor to a fine powder.

X-ray work

The powder photographs were taken in a Guinier camera using Cu $K\alpha$ radiation. In order to avoid errors due to film-shrinkage a method described by Hägg (1947) was used. The camera was calibrated five times with NaCl.

Unit-cell determination

Lauric acid was indexed first, using the single crystal data of Vand, Morley & Lomer (1951). From these data it can be seen that reflexions having $|l| = 14$ are generally strong. This is due to the periodicity in the hydrocarbon chains. The other acids were supposed to have analogous strong reflexions with $|l| = n+2$, which proved to be true. With this indexing the cell dimensions of all investigated acids could be determined. The data are found in Table 1 and Fig. 1, together with earlier published values.

Results

The cell dimensions are independent of the mode of preparation within experimental error, but all dimensions change continuously with chain length. The *a*

Table 1. *Unit-cell dimensions*

n	*a* (Å) (±0·020 Å)	*b* (Å) (±0·004 Å)	*c* (Å) (±0·08 Å)	*d*(001) (Å) (±0·04 Å)	β (±6′)
12	9·634	4·966	35·58	27·43	129° 35′
14	9·509	4·968	40·71	31·58	129° 7′
18	9·357	4·956	50·76	39·87	128° 14′
22	9·292	4·953	60·87	48·22	127° 37′
26	9·249	4·954	71·18	56·63	127° 19′
∞	9·21	4·95	—	—	127° 17′

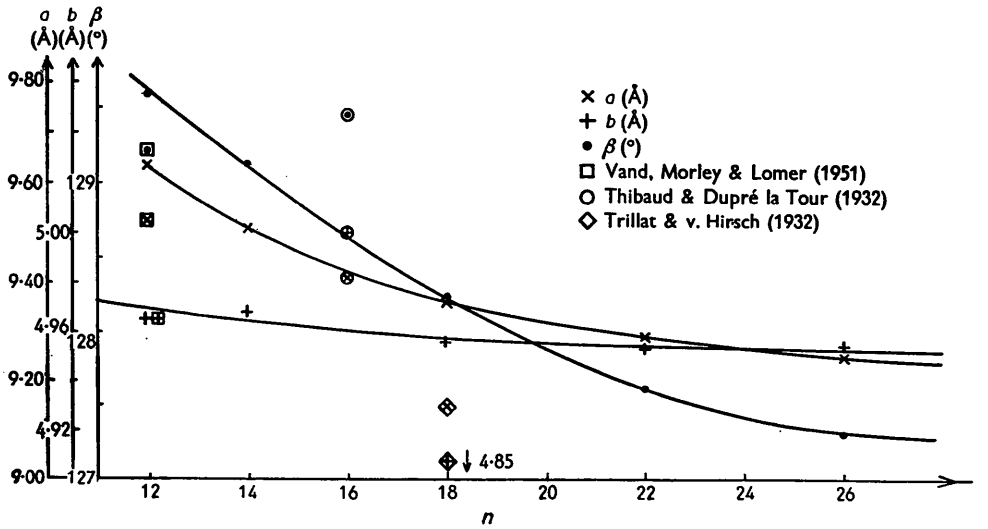

Fig. 1. Unit-cell dimensions of form C of normal fatty acids.

and b axes are found to decrease, having asymptotic values of 9·21 Å and 4·95 Å respectively. The monoclinic angle β decreases towards 127° 17′. The c axes and long spacings, $d(001)$, are linear functions of the carbon content within experimental error:

$c = pn+q$, $\quad d(001) = Pn+Q$,
$p = 2{\cdot}5378\pm0{\cdot}0042$ Å, $\quad P = 2{\cdot}0850\pm0{\cdot}0024$ Å,
$q = 5{\cdot}124\pm0{\cdot}080$ Å, $\quad Q = 2{\cdot}383\pm0{\cdot}044$ Å.

The constants are determined by the method of least squares.

Vand, Aitken & Campbell (1949) pointed out that long-chain compounds are only 'approximately homologous', and this is obviously the case with this form and likely also with the other crystal forms of normal fatty acids.

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Short Communications

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Electron diffraction by electropolished surfaces and mean inner potentials of silver and copper.

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Electropolished surfaces of metal single crystals are almost flat, and only slightly undulating. An undulating surface is composed of minute facets which form small angles with the macroscopic surface. From electron-diffraction data, Kranert, Leise & Raether (1944) estimated the angle to be 1–2° for an electropolished copper single crystal. However, they had to assume a certain value for the mean inner potential of the copper crystal.