[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

A Comparison of the Long Spacings of Some Soap Hemihydrates

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Values for the cell dimensions of "alpha" sodium palmitate hemihydrate[1] and "alpha" sodium stearate hemihydrate have been published by Buerger.[2] These published values gave an increase in d_{001} value between the palmitate and stearate which was larger than would have been expected. It was therefore thought to be of interest to check the values obtained for the palmitate and stearate, and to extend the series to include sodium myristate and sodium arachidate hemihydrates. An attempt was also made to grow crystals of sodium laurate hemihydrate, but to date no suitable crystals of this substance have been obtained.

Experimental

The authors are indebted to M. J. Buerger for crystals of sodium arachidate hemihydrate obtained from him. Suggestions for growing crystals of the other hemihydrates were obtained from a publication[3] by de Brettville and Ryer.

The crystals obtained in this Laboratory were grown from sodium soaps produced by titrating the corresponding Eastman Kodak Co. fatty acid dissolved in alcohol with equimolar proportions of alcoholic sodium hydroxide, using phenolphthalein as an outside indicator. The resulting sodium soaps were recrystallized from alcohol before use. A series of analytical tests were run on the Eastman acids used, to determine their freedom from esters, unsaturation, and fatty acids of other molecular weights. Data on the methyl arachidate and arachidic acid from which the sodium arachidate was prepared have been furnished by Dr. F. V. Ryer of the Lever Bros. Company.

TABLE I

ANALYTICAL DATA

Substance	Equiv. wt.	Dev., %	Sapon. value	Dev., %	Iodine no.	Temp., °C. Setting point	Temp., °C. Setting point (Francis and Piper)[5]
Myristic acid	228.4	0.0	245.7	1.0	0.1	52.92	53.65
Palmitic acid	256.6	.1	224.7	2.7	0.1	61.54	62.60
Stearic acid	285.8	.5	204.8	3.9	1.2	68.42	69.39
Arachidic acid			172.3(ester)	0.3	0.2(ester)	74.3(m. p.)	75.35(m. p.)

The equivalent weights were calculated from acid values run according to Scott's "Standard Methods of Analysis." Saponification values were also run according to Scott's "Standard Methods of Analysis." Iodine numbers required a more specialized technique because of the low percentage of unsaturation present in the fatty acids. Accordingly these determinations were run by M. Yasuda's method[4] using pyridine sulfate dibromide as the halogenating agent.

In the first attempt to grow crystals of NaL and NaMy, approximately 0.6% solutions of the compounds in 95% ethyl alcohol were made up, a few grains of sodium chloride were added, and the solutions were placed in a thermostat at 20°. A few tiny crystals of NaMy were obtained, and later proven to be "alpha" form, but no usable crystals of NaL appeared. Approximately 0.2% solutions of NaP, NaSt, and NaL were then made up in 95% ethyl alcohol, a few grains of sodium chloride added to the NaP and NaL solutions, and the solutions were allowed to evaporate slowly at room temperature. The NaL solution produced no single crystals. The NaSt solution produced a large number of single crystals of the "alpha" form. The NaP solution produced a few crystals of a rod shape which were shown by X-ray studies to be different from the "alpha" form. Immediately after these crystals appeared, another crystalline form began to grow, which proved to be "alpha" NaP.

The habit of the NaSt and NaAr crystals corresponds to that described by Buerger[6] for NaSt.

The habit of the NaP crystals corresponds to Buerger's description[6] except that the form (10 *l*) is present to about the same degree as the (11 *l*), making the crystal appearance hexagonal rather than diamond shape. The crystals have good (010) cleavage.

The few NaMy crystals obtained were not sufficiently well developed to obtain crystallographic characteristics.

Data on cell constants were obtained from oscillation photographs for a_0 and b_0 values, and from equi-inclination Weissenberg photographs for c_0 values. CuK radiation with nickel filter was used for all photographs. (Camera diameter = 56.85 mm., obtained by calibration with NaCl, $a_0 = 5.6394$ Å., $CuK\alpha\lambda = 1.5418$ Å.) Constants of the unit cells appear in Table II.

TABLE II

CONSTANTS OF THE UNIT CELL

Substance	a_0, Å.	b_0, Å.	c_0, Å.	β
$NaMy\cdot{}^1/_2H_2O$	9.32	8.00	82.63	$93^3/_4°$
$NaP\cdot{}^1/_2H_2O$	9.23	8.01	92.94	$94°^a$
$NaSt\cdot{}^1/_2H_2O$	9.23	8.02	103.13	$93^3/_4°$
$NaAr\cdot{}^1/_2H_2O$	9.21	8.03	113.45	$93^1/_2°$

[a] This β value was not redetermined, but was taken from values published by Buerger.[2]

Discussion

The published values[2] for the cell constants of $NaP\cdot{}^1/_2H_2O$ and $NaSt\cdot{}^1/_2H_2O$ show an increase in d_{001} between the two of 11.02 Å.[7] Since the unit

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[1] The following abbreviations are used in this paper for organic radicals:

Composition	Name	Abbreviation
$C_{12}H_{23}O_2$	Laurate	L
$C_{14}H_{27}O_2$	Myristate	My
$C_{16}H_{31}O_2$	Palmitate	P
$C_{18}H_{35}O_2$	Stearate	St
$C_{20}H_{39}O_2$	Arachidate	Ar

[2] Buerger, *Am. Mineral.*, **30**, 551 (1945).

[3] de Brettville and Ryer, *J. Phys. Chem.*, **48**, 154 (1944).

[4] M. Yasuda, *J. Biol. Chem.*, **94**, 404 (1931–1932).

[5] Francis and Piper, THIS JOURNAL, **61**, 577 (1939).

[6] Buerger, *Proc. Nat. Acad. Sci.*, **28**, 529 (1942).

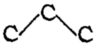
[7] This value is obtained by using a later value of c_0 for NaSt (private communication from M. J. Buerger, c_0 = 102.7 kX).

cell is four molecules long in the *c* direction, this means that an increase of 8 carbon atoms in the chain direction has caused an increase in d_{001} of 11.02 Å. In order for a change of this magnitude to occur, a change of tilt of the order of 7.5° would have to occur between the two compounds. That this difference in tilt actually exists is not probable, since Buerger[2] has shown that the symmetry properties of the two compounds are the same.

Using the cell constants determined in this Laboratory the following increases in d_{001} between the pairs of substances are noted:

Compounds	Δd_{001}, Å.
NaMy–NaP	10.26
NaP–NaSt	10.19
NaSt–NaAr	10.32

Using a least squares approximation on values for d_{001} *vs.* number of carbon atoms in the chain, the most probable value for change in d_{001} is found to be 10.25 Å.

The work of MacArthur[8] on the extension of the  link in normal long chain aliphatic compounds indicates that an addition of 8 carbon atoms to a compound of this type should give an increase in chain length of 10.16 Å. MacArthur also lists the data of a number of other workers in this field, and shows that the average of their results would lead to a value of 10.19 Å. (It is not apparent whether the figures published by MacArthur are in kX or Å. units. If the published figures are in kX units, the two results in Å. would then be 10.18 and 10.21, respectively.)

The results of this Laboratory also show a difference of 0.09 Å. between the a_0 value for NaMy and the corresponding a_0 values for NaP and NaSt. There is no apparent reason for the existence of a real difference in the values, and it is assumed that this difference arises from experimental error since the NaMy crystals obtained were poorly formed.

The agreement in d_{001} increase between pairs of compounds in this series and the agreement with the figures for other normal long chain aliphatic compounds indicates that the long axes of the chains in these compounds are very nearly normal to (001) and that there is little or no difference in tilt in the several crystals. This conclusion is also corroborated by unpublished work in this Laboratory on the hydrazides of *n*-aliphatic acids. In the hydrazides it is found that an increase of 8 carbon atoms in the chain direction leads to an increase in d_{001} of 10.19 Å.

Summary

1. The unit cell constants of the hemihydrates of NaMy and NaAr have been determined, and the values for NaP and NaSt redetermined.

2. The increase in d_{001} with increase in chain length has been found to be 1.281 Å. per carbon atom, indicating that the chains are very nearly normal to (001).

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[8] MacArthur, *Proc. Leeds Phil. Lit. Soc., Sci. Sect.*, **4**, pt. 3, 170 (1944).

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Electrophoretic Properties of Plakalbumin

BY GERTRUDE E. PERLMANN

Introduction

In a recent note, Linderstrøm-Lang and Ottesen[1] showed that ovalbumin is transformed, by the action of an enzyme from *Bacillus subtilis*, into a protein that crystallizes as rectangular plates from ammonium sulfate. They named this protein plakalbumin.[2] Since the transformation of ovalbumin to plakalbumin, A→P, occurs without serious degradation of the protein,[1] it seemed of interest to compare the electrophoretic behavior of the two materials. Consequently, the preliminary experiments[3] that indicated that plakalbumin differed electrophoretically from its parent substance, ovalbumin, have been extended and the new results are reported below.

Experimental

Plakalbumin was obtained by incubating a 6% solution of thrice recrystallized ovalbumin[4] in 0.02 ionic strength phosphate buffer at *p*H 6.8 with an enzyme preparation from *B. subtilis*, kindly supplied by Linderstrøm-Lang. After incubation for six hours at 30°, the solution was acidified with hydrochloric acid to *p*H 5.4 and the protein crystallized as rectangular plates by the addition of saturated ammonium sulfate solution.[1]

The electrophoretic experiments were carried out at 0.5° in the apparatus described by Longsworth.[5,6] Unless noted otherwise below, a protein concentration of 1% was used in the experiments and prior to electrophoresis the protein solutions were dialyzed for two to three days against liberal portions of an appropriate buffer. The mobilities were computed from the descending patterns and refer to 0°.

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[1] Linderstrøm-Lang and Ottesen, *Nature*, **159**, 807 (1947).

[2] Eeg-Larsen, Linderstrøm-Lang and Ottesen, *Arch. Biochem.*, **19** 340 (1948).

[3] Perlmann, *Nature*, **161**, 720 (1948).

[4] Sørensen and Høyrup, *Compt. rend. Lab. Carlsberg*, **12**, 12 (1917).

[5] Longsworth, *Chem. Reviews*, **30**, 323 (1942).

[6] Longsworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).