calcium in the body and excreta of rachitic and vitamin D-treated rats.

The fecal excretion of the orally administered calcium confirms the theory that the administration of vitamin D promotes the absorption of calcium from the intestines. However, the fecal excretion of the injected calcium shows that there also seems to be a fairly constant transfer of calcium to the feces. The experiments with the injected calcium show clearly that the vitamin D has a marked direct effect on the ~~deposition of calcium. Thus, vitamin D has at least~~ two favorable effects—first, the promotion of calcium absorption, and second, the promotion of calcium deposition.

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Acid Sodium Stearates[*]

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Introduction

OUR interest in acid soaps developed out of the necessity of obtaining records of their X-ray diffraction patterns so that the latter might not be confused with the patterns of several neutral soap phases recognized for the first time in this laboratory (1). For this purpose the following series of crystallizations from 95% alcohol at 65 and 90°F. were designed to deposit all the crystalline products intermediate between neutral sodium stearate and free stearic acid.

Experimental

Solutions in 250 c.c. volumes of No. 3-A alcohol of constant weights of anhydrous sodium stearate (prepared from stearic acid fractionated to a purity of at least 95%) plus increasing weights of stearic acid, in small increments, were obtained by refluxing. The constant weight of neutral soap was selected for each crystallizing temperature to yield a concentration just under the gel point, a condition found desirable for the growth of satisfactory neutral soap crystals (2). After partial cooling under a condenser each stoppered flask was kept overnight at the crystallizing temperature of 65 or 90° F. in a thermostated room. Each crop of crystals was then suction-filtered and air-dried before examination. Thus, the sole variable in each series was the weight of stearic acid (or ratio of stearic acid to soap) present in the original solution.

Examination consisted of low-power microscopic inspection, titration of the excess stearic acid content in alcohol with N/10 sodium hydroxide and the preparation of X-ray diffraction patterns.[**]

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[*] Presented in part at the fall meeting of the American Oil Chemists' Society in Chicago, Nov. 7-9, 1945.

[**] The diffraction patterns were prepared by Miss G. E. Cook under the direction of M. J. Buerger of the Massachusetts Institute of Technology who has already published (5, 6) crystallographic data for several of the neutral and acid soap crystals and is preparing a paper on the diffraction data of the remaining acid soap crystals encountered in this work.

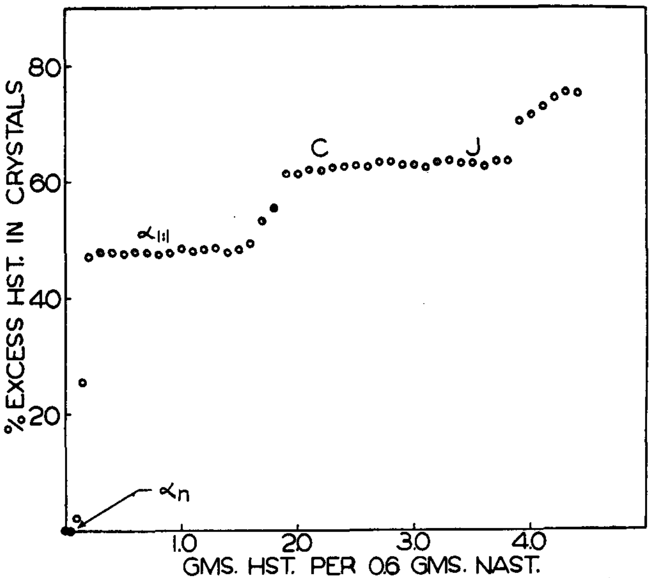


FIG. 1. Crystallizations of acid sodium stearates at 65° F. from 250 c.c. volumes of alcohol.

Results

Figure 1, prepared from the data of Table 1, illustrates the variation in the excess stearic acid content of the crystals deposited at 65°F. with increasing weights of stearic acid added to the original solutions. The first two crystal crops showed no excess fatty acid and were identical with the neutral sodium stearate crystals first prepared by Thiessen and Stauff (3) and termed by them alpha crystals. These neutral alpha crystals have been demonstrated to be of hemi-hydrate composition (4) and complete single crystal X-ray data has been obtained for them (5, 6). Further increments of added fatty acid caused a rapid rise in the excess fatty acid content of the crystals formed on cooling. This rise leveled off at a remarkably constant value of approximately 48% over a wide range of solution composition before rising rapidly to a new, substantially flat, region of approximately 63% excess fatty acid. Beyond this level, the uncombined stearic acid content of the crystals again increased rapidly.

TABLE 1

Crystallizations at 65°F.

g. NaSt	g. HSt	Ratio $\frac{(HSt)}{(NaSt)}$	% Excess HSt in Crystals	Diffraction Patterns
.60	None	0	Nil	Neutral Alpha
.60	.05	.083	Nil	Neutral Alpha
.60	.10	.166	2.03	Neutral Alpha + Alpha 1:1
.60	.15	.250	25.49	Neutral Alpha + Alpha 1:1
.60	.20	.333	47.10	Alpha 1:1
.60	.30	.500	47.91	Alpha 1:1
.60	.40	.666	47.93	Alpha 1:1
.60	.50	.833	47.66	Alpha 1:1
.60	.60	1.00	47.98	Alpha 1:1
.60	.70	1.17	47.82	Alpha 1:1
.60	.80	1.33	47.38	Alpha 1:1
.60	.90	1.50	47.70	Alpha 1:1
.60	1.0	1.67	48.59	Alpha 1:1
.60	1.1	1.83	48.08	Alpha 1:1
.60	1.2	2.00	48.21	Alpha 1:1
.60	1.3	2.17	48.71	Alpha 1:1
.60	1.4	2.33	47.90	Alpha 1:1
.60	1.5	2.50	48.32	Alpha 1:1
.60	1.6	2.67	49.63	Alpha 1:1+"C"
.60	1.7	2.83	53.15	Alpha 1:1+"C"
.60	1.8	3.00	55.55	Alpha 1:1+"C"
.60	1.9	3.17	61.59	"C"
.60	2.0	3.33	61.36	"C"
.60	2.1	3.50	62.01	"C"
.60	2.2	3.67	61.99	"C"
.60	2.3	3.83	62.49	"C"+"J"
.60	2.4	4.00	62.65	"C"+"J"
.60	2.5	4.17	62.86	"C"+"J"
.60	2.6	4.33	62.72	"C"+"J"
.60	2.7	4.50	63.25	"J"
.60	2.8	4.67	63.22	"J"
.60	2.9	4.83	62.95	"J"
.60	3.0	5.00	62.92	"J"
.60	3.1	5.17	62.64	"J"
.60	3.2	5.33	63.26	"J"
.60	3.3	5.50	63.68	"J"
.60	3.4	5.67	63.15	"J"
.60	3.5	5.83	63.09	"J"
.60	3.6	6.00	62.89	"J"
.60	3.7	6.17	63.70	"J"
.60	3.8	6.33	63.62	"J"
.60	3.9	6.50	70.54	"J"+HSt
.60	4.0	6.67	71.60	"J"+HSt
.60	4.1	6.83	72.86	"J"+HSt
.60	4.2	7.00	74.43	"J"+HSt
.60	4.3	7.17	75.43	"J"+HSt
.60	4.4	7.33	75.02	"J"+HSt

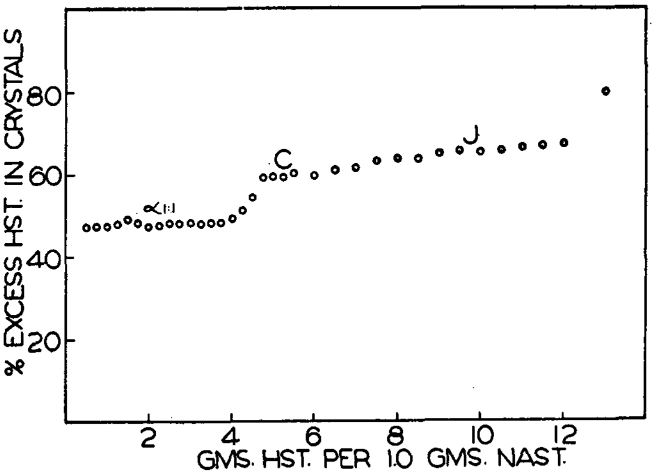


FIG. 2. Crystallizations of acid sodium stearates at 90° F. from 250 c.c. volumes of alcohol.

Figure 2, from the data of Table 2, illustrates the results of a similar series of crystallizations at 90°F. It may be noted that the neutral alpha crystals could not be successfully grown at this temperature. The first flat, corresponding to approximately 48% excess stearic acid in the crystals, appears as in Figure 1. The second substantially flat segment of Figure 1, however, appears subdivided in Figure 2 into two short flat segments of approximately 59.6% and 65.4% excess stearic acid content with a rising transitional range between.

The existence of these flats in the excess stearic acid content of the acid soap crystals deposited from solutions over relatively wide variations in the ratio of added fatty acid to neutral soap suggests that chemical individuals are crystallized in these regions. This conclusion was substantiated first by microscopic examinations which revealed the apparently homogeneous character of the crystals corresponding to the flats as compared with the heterogeneous nature of the crystals in the sloping transitional ranges. Visually, however, no distinction could be made between the crystals of the second and the third flat segments of Figure 2.

This limitation did not apply to the X-ray diffraction patterns, which supplied data in complete agreement with the titration values. Thus, considering Figure 1, the first two crystal crops exhibited typical neutral alpha patterns and the 48% flat an acid soap pattern labeled alpha 1:1 [for which complete single crystal X-ray data is now available (6)], the composition of which agrees well with the theoretical 48.14% excess stearic acid content of the compound 1 NaSt·1 HSt. The 63% flat of Figure 1

TABLE 2

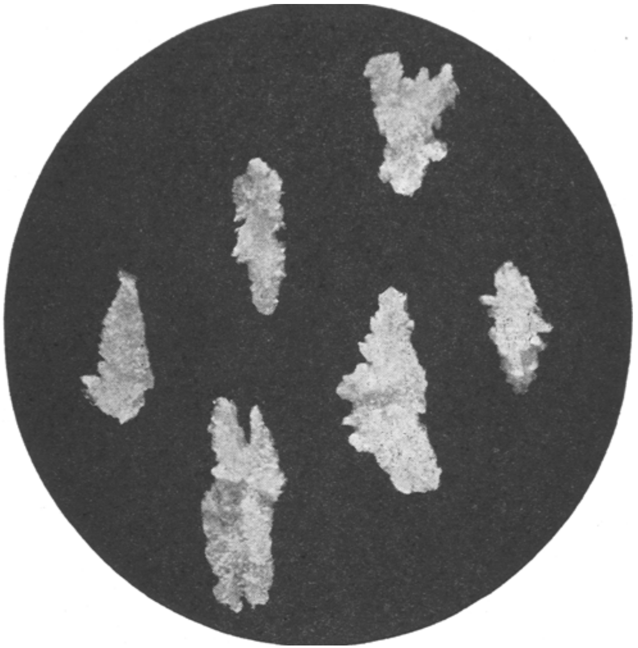
Crystallizations at 90°F.

g. NaSt	g. HSt	Ratio $\frac{(HSt)}{(NaSt)}$	% Excess HSt in Crystals	Diffraction Patterns
1.0	None	0	No Deposit	....
1.0	.25	.25	No Deposit	....
1.0	.50	.50	47.3	Alpha 1:1
1.0	.75	.75	47.5	Alpha 1:1
1.0	1.0	1.0	47.5	Alpha 1:1
1.0	1.25	1.25	48.0	Alpha 1:1
1.0	1.5	1.5	49.1	Alpha 1:1
1.0	1.75	1.75	48.3	Alpha 1:1
1.0	2.0	2.0	47.5	Alpha 1:1
1.0	2.25	2.25	47.8	Alpha 1:1
1.0	2.5	2.5	48.1	Alpha 1:1
1.0	2.75	2.75	48.1	Alpha 1:1
1.0	3.0	3.0	48.2	Alpha 1:1
1.0	3.25	3.25	48.0	Alpha 1:1
1.0	3.5	3.5	48.4	Alpha 1:1
1.0	3.75	3.75	48.5	Alpha 1:1
1.0	4.0	4.0	49.3	Alpha 1:1
1.0	4.25	4.25	51.2	Alpha 1:1+"C"
1.0	4.5	4.5	54.5	Alpha 1:1+"C"
1.0	4.75	4.75	59.3	"C"
1.0	5.0	5.0	59.3	"C"
1.0	5.25	5.25	59.4	"C"
1.0	5.5	5.5	60.2	"C"
1.0	6.0	6.0	59.7	"C"
1.0	6.5	6.5	61.0	"C"+"J"
1.0	7.0	7.0	61.6	"C"+"J"
1.0	7.5	7.5	63.2	"C"+"J"
1.0	8.0	8.0	63.9	"C"+"J"
1.0	8.5	8.5	63.9	"C"+"J"
1.0	9.0	9.0	65.0	"J"
1.0	9.5	9.5	65.7	"J"
1.0	10.0	10.0	65.3	"J"
1.0	10.5	10.5	65.7	"J"
1.0	11.0	11.0	66.5	"J"+HSt
1.0	11.5	11.5	66.8	"J"+HSt
1.0	12.0	12.0	67.2	"J"+HSt
1.0	12.5	12.5	80.0	"J"+HSt

exhibited two acid soap patterns, one at the left hand tentatively labeled "C" and a second distinct pattern called "J," at the right hand end. The middle portion of this flat showed a gradual change from the "C" to the "J" form. In view of the relatively constant composition, it was first supposed that these two crystal forms were related polymorphically; later, however, the data contained in Figure 2 was accepted as the true state of affairs. Beyond the second flat of Figure 1 the excess fatty acid content of the crystals again increased rapidly, and the diffraction pattern of free stearic acid appeared with that of "J" crystal form. The diffraction patterns clearly indicated the mixed characters of the crystals obtained along the rising transitional segments.

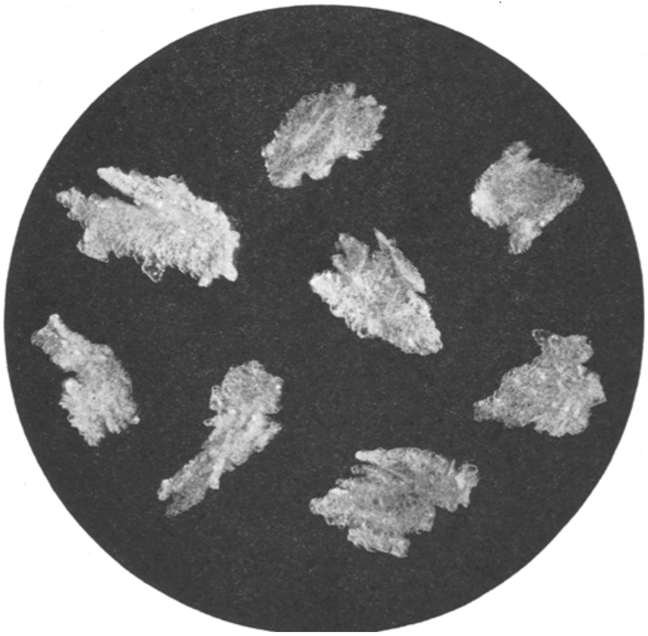
Now considering the diffraction data in conjunction with Figure 2, the first crystal deposit showed an alpha 1:1 acid soap pattern (in the absence of any neutral alpha crystallization at this temperature). This pattern persisted over the 48% excess stearic acid flat, then after a short transitional zone characterized by mixed alpha 1:1 and "C" patterns, a short flat segment averaging 59.58% excess stearic acid and characterized by a substantially pure "C" pattern was covered. After a rising transitional segment of mixed "C" and "J" patterns, the substantially pure "J" flat averaging 65.43% excess stearic acid was entered. Beyond this, the appearance of the free stearic acid pattern with "J" accounted for the rapid rise of the curve.

It is now clear that the same sequence of crystal forms is produced at either temperature. At 90°F. it appears that more favorable solubility conditions are capable of resolving the 63% flat of the 65°F. series (with its disturbing two patterns) into separate flats of 59.6% and 65.4% average excess stearic acid content.



"J" Acid Sodium Stearate

Magnification 10×



"C" Acid Sodium Stearate

Magnification 10×

A comparison of the average percentages of excess stearic acid in the crystals having single diffraction patterns, deposited along the flats, with the theoretical values for the acid soaps listed in Table 3 leaves little doubt as to the nature of the compounds formed in these experiments.

TABLE 3

Designation	Average % Excess Stearic Acid	Theo. % Excess Stearic Acid
Alpha 1:1	47.95(65°)–48.11(90°)	1 NaSt·1 HSt—48.14
"C"	59.58	2 NaSt·3 HSt—58.20
"J"	65.43	1 NaSt·2 HSt—64.99

Both the 1:1 (7) and 1:2 (8, 9) acid sodium stearates have been previously reported, but the 2:3 compound appears as a new stable form of acid soap. Moreover, no evidence for the existence of the 2:1 compound (8, 9) was obtained in these experiments.

Alpha 1:1 Acid Sodium Stearate
Magnification 10×

Neutral Alpha Sodium Stearate
Magnification 10×

This picture of long flats and abrupt transitions, as well as the dependence of the crystal form deposited on the ratio of stearic acid to soap in solution, is well illustrated by attempts to recrystallize either the "C" (2:3) or "J" (1:2) acid soap forms. When either of these acid soaps is once crystallized as indicated at 65°F., for example, and the dry crystals redissolved in a fresh volume of alcohol, neither "C" nor "J" but alpha 1:1 is deposited on cooling.

The explanation of this behavior is clear from Figure 1 which shows that a solution having a ratio of neutral soap to fatty acid found in either "C" or "J" crystals will deposit crystals of the alpha 1:1 acid soap. The latter crystals, on the other hand, can be recrystallized any number of times since their composition always supplies a ratio of fatty acid to soap in solution from which the 1:1 acid soap will again crystallize.

The effect of the crystallizing temperature on the crystal forms deposited from solutions of constant ratio is illustrated in Table 4. The crystallizations included in Figure 1 at 65°F. and containing 1.2, 3.0, and 3.6 grams of stearic acid to 0.6 gram of sodium stearate were repeated at crystallizing temperatures of 80 and 90°F. Table 4 lists the predominant diffraction patterns and the excess stearic acid content of the crystals obtained.

TABLE 4

Grams HSt per 0.6 g. NaSt	65°F.	80°F.	90°F.
1.2	Alpha 1:1 (48.21%)	Alpha 1:1 (47.64%)	Alpha 1:1 (46.93%)
3.0	"J" (62.92%)	"C" (58.29%)	Alpha 1:1 (50.80%)
3.6	"J" (62.89%)	"C" (59.16%)	"C" (57.79%)

A comparison of Figures 1 and 2 demonstrates that at either 65 or 90°F. the order of appearance of crystalline forms with increasing stearic acid to sodium stearate ratios is the same; namely, neutral alpha, alpha 1:1, "C," "J," and HSt. From Table 4 it is evident that at given ratios the effect of raising the crystallizing temperature is to displace this sequence in the neutral soap direction.

The accompanying photomicrographs illustrate the appearance of typical crystals of the neutral alpha, alpha 1:1, "C" (2:3), and "J" (1:2) forms.

Summary

The acid soaps, intermediate in composition between neutral sodium stearate and stearic acid, were crystallized at 65 and 90°F. from alcoholic solutions containing varying ratios of stearic acid to sodium stearate. Well-defined composition flats indicative of chemical individuals corresponding to the formulas 1 NaSt · 1 HSt, 2 NaSt · 3 HSt, and 1 NaSt · 2 HSt were observed. No evidence for the existence of the compound 2 NaSt · 1 HSt was obtained from these experiments.

The author wishes to express his appreciation to Prof. M. J. Buerger for the interpretation of the powder diffraction patterns.

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