Isolation of the 9- and 10-Isomers of Carboxystearic Acid and Their Polyamidation with Hexamethylenediamine[1]

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ABSTRACT AND SUMMARY

Physical properties of the two isomers in 9(10)-carboxystearic acid were found to be sufficiently different to permit isolation by recrystallization. Fractions containing carboxystearic acid of high isomeric purity but containing such impurities as stearic and hydroxystearic acids were purified through the nylon salts formed with hexamethylenediamine to obtain each isomer in high functional and isomeric purity. Physical properties were determined for each isomer, its nylon salt, and its polyamide. The different physical properties suggest for substituted dicarboxylic acids the alternating effect in melting points and solubilities shown by the unsubstituted α,ω-alkanedioic acids.

INTRODUCTION

Carboxystearic acid has received considerable attention from industry, and its preparation and uses were reviewed in 1972 (1,2). Its synthesis from oleic acid may be accomplished by catalytic hydroformylation with carbon monoxide and hydrogen followed by oxidation (3-5), by catalytic hydrocarboxylation with carbon monoxide and water, or by carboxylation with carbon monoxide, water, and sulfuric or hydrofluoric acid (Koch reaction). Hydroformylation with cobalt carbonyl produces a multitude of isomeric products, with the branched formyl or carboxyl group attached to any one of the 16 internal carbons (6). By synthesizing and characterizing the fragmentation patterns for the 3-, 4-, 5-, 7-, 12-, 15-, 16-, and 17-carboxystearic acids, Comeau et al. (7) were able to analyze such isomeric mixtures for each isomer by mass spectrometry. Product mixtures from the Koch reaction are further complicated by methyl branching in addition to the functional group branching (8).

In contrast, selective hydroformylation (with subsequent oxidation) by rhodium-triphenylphosphine catalysts produced only the 9- and 10-carboxystearic acids (9). An equimolar mixture of the two isomers is also formed by catalytic hydrocarboxylation with palladium chloridetriphenylphosphine (10). We wish to report the isolation and some of the properties shown by the individual isomers, their nylon salts, and their polyamides. Poly(carboxystearamides) have potential commercial value (11).

EXPERIMENTAL PROCEDURES

Materials

Carboxystearic acid (CSA) was obtained by the air (12) or permanganate (9) oxidation of formylstearic acid. Both carboxystearic acid products had isomeric compositions of about 50:50 9- and 10-carboxystearic acid (9). Hexamethylenediamine (Aldrich Chemical Co., Milwaukee, WI) had a purity of 96.7% as determined by titration with standard acid solution.

Analytical Methods

Differential thermal analysis (DTA), thermal mechanical analysis (TMA), and thermal gravimetric analysis (TGA) were carried out with the respective du Pont Models 900, 940, 950 instruments, according to procedures previously described (13). TMA was carried out with a 1-g penetration load, and TGA with a 5 C/min heating rate (14).

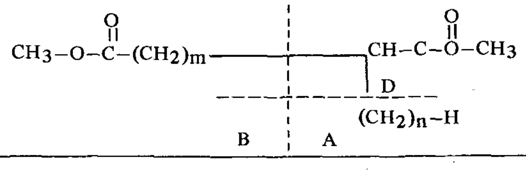
Gas liquid chromatographic analysis (GLC) was carried out on the CSA products previously converted with diazomethane to the dimethyl esters. Gas chromatographic conditions for analyses with a 3% JXR packing have been described previously (14).

Mass Spectroscopy (MS)

Isomeric distribution was determined by MS on the dimethyl esters. The fragmentation pattern is illustrated and representative analyses (for 9-CSA below) are given in Table I. The D+1 fragment was found to deviate only by

TABLE I

Mass Spectroscopie Analyses for Recrystallized 9-CSA



Branch site	A+1 fragment Mass	A+1 fragment Rel. %	D+1 fragment Mass	D+1 fragment Rel. %	(A+1)+(D+1) Average[a], %	Normalized distribution, %
7	228	0.77	202	4.92	2.85	---
8	214	2.11	216	1.78	1.95	2.08
9	200	81.21	230	85.05	83.13	88.59
10	186	7.63	244	5.94	6.78	7.22
11	172	2.53	258	1.43	1.98	2.11
12	158	5.75	272	0.88	3.31	---
		100.00		100.00		100.00

[a] Average of three runs.

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[1] Presented at the AOCS Meeting, Cincinnati, September 1975.

[2] Deceased November 20, 1975.

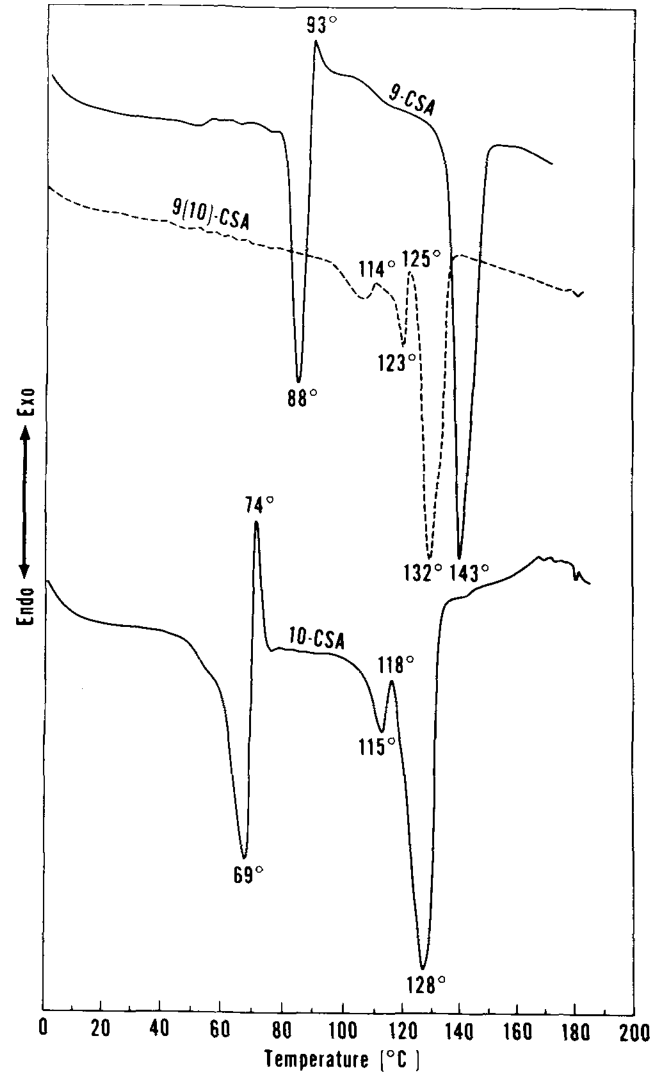

FIG. 1. Differential thermal analyses for 9-, 10-, and 9(10)-carboxystearic acid nylon salts from hexamethylenediamine.

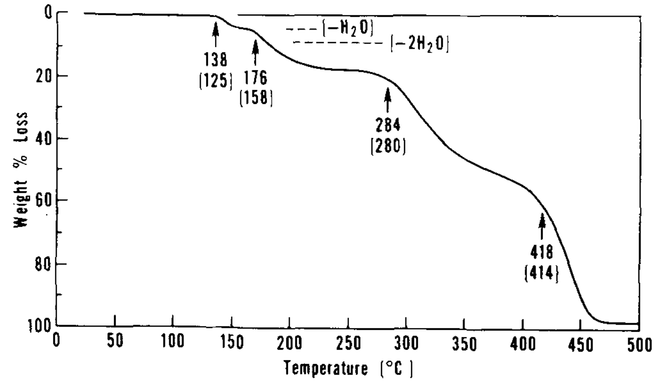

FIG. 2. Thermal gravimetric analysis for 9-carboxystearic acid, with temperatures for 10-carboxystearic acid indicated in parentheses. Dotted lines indicate points at which 1 and 2 moles of water have been evolved as the result of condensation reactions.

about 2% from the D-31 fragments described by Frankel (9), but the method is only one of estimation and probably no better than ± 10%. Since the A+1 and the D+1 percent relative intensities were abnormally high for branch sites at C-12 and at C-7 (5.75 and 4.92%, respectively) for the expected Gaussian distribution, these were discarded, and a normalized distribution was calculated.

9-CSA

Crude CSA (173.3 g of 56.8% purity) was dissolved in hot methanol (676 g), and the solution was cooled to -18 C. The precipitated material (first crop) (42 g) was removed by filtration; it consisted mainly of ceric salts and stearic, ketostearic, and hydroxystearic acids. The filtrate was concentrated to 1/2 its original volume, cooled to -18 C, and filtered to yield 31.6 g of 9(10)-CSA (A) (second crop) and the filtrate (B). Successive recrystallization at -18 C of A from 1.7 parts heptane, then 5.7 parts methanol, yielded 16.8 g of product (C) that had a CSA purity of 72.2% but an isomeric purity of 98% 9-CSA. C (15.46 g, 0.0340 mole) and hexamethylenediamine (96.7% pure, 5.051 g, 0.0420 mole) were dissolved in hot 95% ethanol to make 91.4 g of solution. All operations were conducted under a nitrogen atmosphere. The solution was allowed to stand for 14 hr at 22 C. After filtration and drying of the filter cake, there was obtained 13.95 g of nylon salt. Results for DTA and TGA on the nylon salt are given in Figures 1 and 2, respectively. Data from the CSA regeneration described below suggest high functional purity for the nylon salt.

Analysis: Calcd. for $C_{19}H_{36}O_4 \cdot C_6H_{16}N_2$: C, 67.52; H, 11.79, N, 6.30. Found: C, 67.03; H, 11.87; N, 6.05.

CSA was regenerated from the nylon salt by dissolving the latter (11.18 g) in 75 ml of water containing 12 ml of conc. hydrochloric acid. Extraction of CSA with methylene chloride followed by removal of solvent produced 7.94 g of CSA having a GLC purity of 99.0% and an isomeric purity of 98% of 9-CSA by mass spectroscopy. Elemental analysis confirmed the functional purity. Properties of 9-CSA as well as those for 10-CSA and 9(10)-CSA are listed in Table II.

Alternatively, CSA (87.1%, 80.8 g) was dissolved in hot methanol (330 g), and crystallization was allowed to proceed at -18 C. Filtration of the first crop at -18 C yielded 6.1 g of 62.6% CSA, which was purified through the nylon salt with hexamethylenediamine to give 4.8 g of CSA having a functional purity of 99% by GLC and an isomeric purity of 89% 9-CSA by MS. This fraction contained 7% of 10-CSA with the remaining 4% consisting mainly of the 8- and 11-isomers (Table I).

10-CSA

Filtrate B was concentrated to one-fourth of its original weight, cooled to 2 C, and filtered to give 9.7 g crop of CSA having a purity of 90.3% by GLC. After successive recrystallizations from 3.7 parts methanol and 1.7 parts *n*-heptane, there was obtained 6.1 g of product (D) containing 90.7% CSA with an isomeric purity of 100% 10-CSA. D (5.594 g, 0.01543 mole) and hexamethylenediamine (96.7%, 2.0039 g, 0.01668 mole) were dissolved in 22 g of hot 95% ethanol under a nitrogen atmosphere. The solution was allowed to stand for 36 hr at 22 C. After filtration and drying of the filter cake, there were obtained 4.736 g of nylon salt. Results of DTA and TGA on the nylon salt are given in Figures 1 and 2, respectively. Regeneration was accomplished as for the 9-isomer to give 10-CSA of 99.3% functional purity. Elemental analyses confirmed the functional purities of the nylon salt and the regenerated 10-CSA.

Polyamidation

The nylon salt from 9-CSA and hexamethylenediamine (3.007 g) was placed in a 25-ml distilling flask and heated under a nitrogen atmosphere by means of a Wood's metal bath according to the following schedule: to 167 C in 1 hr, to 240 C in an additional hr, at 240 C for an additional 4-1/2 hr, and at 275 C for an additional hr. Polyamides from 10- and 9(10)-CSA were prepared similarly (Table II).

TABLE II

Properties of 9-, 10-, and 9(10)-Carboxystearic Acids (CSA) and Their Derivatives[a]

	Isomer		
Compound	9-CSA	10-CSA	9(10)-CSA
Carboxystearic acid			
Solubility, g/100 g solvent			
CH_3OH (-18 C)	26	1.6	24
CH_3OH (+2 C)	---	---	130
n-C_6H_{14} (+2 C)	---	---	40
n-C_7H_{16} (-18 C)	---	0.24	---
n-C_7H_{16} (+22 C)	---	---	15
Melting point[b], C	88	69	60,71
Hexamethylenediamine carboxystearic acid salt			
Solubility in C_2H_5OH (+22 C), g/100 g solvent	1	13	26
Main DTA endotherm, C	143	128	132
Main TGA inflection, C	284	280	288
Polyamide			
Appearance	Hazy, friable	Clear, tough	Clear, sl. tacky
TMA yield temperature, C	110	105	112
Molecular weight	1790	8060	---

[a] DTA = differential thermal analysis, TGA = thermogravimetric analysis, TMA = thermomechanical analysis.

[b] Determined by DTA.

TABLE III

Melting Points of Even- vs. Odd-Numbered Dibasic Acids

Dibasic acid	Dibasic acid type	Mp, °C	Difference in Mp, °C
	A. Isomeric carboxystearic acids		
3-Carboxystearic[a]	even	105	28
4-Carboxystearic[a]	odd	77	12
5-Carboxystearic[a]	even	89	
9-Carboxystearic[b]	even	88	19
10-Carboxystearic[b]	odd	69	
15-Carboxystearic[a]	even	73	14.5
16-Carboxystearic[a]	odd	87.5	8.0
17-Carboxystearic[a]	even	95.5	
	B. Straight chain dibasic acids		
Azelaic	odd	108	26
Sebacic	even	134	23
Undecanedioic	odd	111	18
Dodecanedioic	even	129	

[a] Mp Data from Ref. 7.

[b] Mp Data by differential thermal analysis, this paper.

RESULTS AND DISCUSSION

The isolation of individual isomers of 9(10)-carboxystearic acid was best accomplished with *n*-heptane, although a first small crop from methanol solution also effected separation. The crops having high isomeric purity also had low functional purity, which may indicate some assistance from such impurities as stearic acid in effecting the separation. Functional purity was improved through formation and crystallization of the nylon salt made with hexamethylenediamine. Ethylenediamine did not form a satisfactory nylon salt.

Examination of the structures of the two isomers suggests an explanation for the difference in their properties. Thus, 9-carboxystearic acid is a derivative of sebacic acid (2-nonyldecanedioic acid), an even-numbered acid, and 10-carboxystearic acid is a derivative of undecanedioic acid (2-octylundecanedioic acid), an odd-numbered acid. The alternating effects shown by the unsubstituted, α,ω-alkanedioic acids in both melting point (15) and solubility properties (16) are well known and have been shown to result from differences in crystal structure (17-20). Even-numbered dibasic acids have higher melting points than the odd-numbered ones (Table III).

It is perhaps surprising that the 8- or 9-carbon side chain had so little effect in diminishing the difference in melting point between the even- (9-CSA) and the odd-numbered (10-CSA) acids, i.e., a difference of 19 C for the substituted acids compared to 23 C for the unsubstituted acids (i.e., sebacic and undecanedioic acids) (Table III). Except for 15-carboxystearic acid, all of the even-numbered isomers in the series synthesized by Comeau et al. (7) also show higher melting points than the neighboring odd-numbered isomers.

ACKNOWLEDGMENTS

W.K. Rohwedder ran the mass spectroscopic analyses; C.E. Johnson ran elemental analyses and molecular weights.

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