

# Binary Mixtures of Fatty Acid Derivatives. I. Dihydrzides of Dicarboxylic Acids—Glutaric to Sebacic\*

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IT has been reported recently by Kyame, Fisher, and Bickford (1) that monoacyl hydrazides are satisfactory derivatives for the identification of n-aliphatic acids in their mixtures. The present work is an extension of this technic to mixtures of the dihydrazides of the dicarboxylic acids such as might be obtained from the oxidative degradation of unsaturated fatty acid derivatives in studies of molecular structure.

**Experimental.** The acids used were Eastman Kodak Company white label grade except for the suberic acid which was obtained from the Bios Laboratories. The dimethyl esters were prepared from the acids by refluxing for 2 hours in 10 volumes of absolute methanol containing approximately 2% by weight of  $H_2SO_4$ . The cooled solution was diluted with two or more times its volume of water to precipitate the esters. Any esters remaining in the water layers were extracted with four small portions of U.S.P. ether. The combined ester layer and extractions were washed free of mineral acid with two small portions of water. The ether solution was evaporated on the steam bath. The last traces of solvent and water were removed at room temperature by means of a high vacuum mechanical pump before the esters were distilled through a 6-inch Vigreux column at approximately 0.1-mm. pressure. A center cut containing 80-90% of the distillation charge was used in the preparation of the dihydrazides (Table I). Methyl stearate was purified by fractional distillation (Podbielniak column) and recrystallization from Skellysolve B and from methanol (M.P.  $39.5^\circ C.$ , cor.).

TABLE I  
Preparation of Dimethyl Esters

Acid	% Yield	$n_D^{20}$
C-10, Sebacic.....	88	1.4352
C-9, Azelaic.....	83	1.4328
C-8, Suberic.....	70	1.4306
C-7, Pimelic.....	85	1.4276
C-6, Adipic.....	66	1.4251
C-5, Glutaric.....	74	1.4210

The dihydrazides were readily prepared practically in quantitative yields by refluxing 10 ml. of absolute ethanol containing 3 g. of the dimethyl ester and 3 ml. of 100% hydrazine hydrate (Edwal Laboratories) for two hours on the steam bath. A considerable amount of the dihydrazide precipitated during reflux. The cooled, slushy mass was filtered by suction and washed three times with 3-ml. portions of absolute ethanol. The crystals were air dried overnight, and yield and melting point were determined. The crude dihydrazide was recrystallized from 70% ethanol (see Table II for volumes) at  $3^\circ C.$ , filtered, and washed once with 10 ml. of 70% ethanol. The crystals were air dried overnight and yields, melting points, and nitrogen content were determined (Table II).

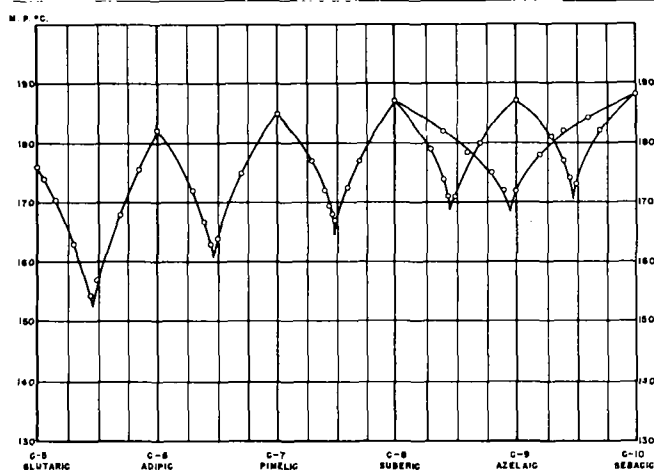


FIG. 1. Melting points of binary mixtures of dicarboxylic acid dihydrazides C-5 to C-10.

In preparing mixtures containing the lower melting component in 15, 20, 30, 50, 60, 70, or 85% by weight, the pure dihydrazides were weighed separately in 1-inch watch glasses and in amounts to give a total of 100 mg. Mixtures of intermediate composition were prepared from these primary mixtures. The weighed samples were transferred to a 3-inch Pyrex watch glass, mixed well by means of a piece of wire, and finally ground by means of a fire-polished glass rod. Capillary melting point tubes were filled to a depth of approximately 5 mm. Mixtures were then fused by dipping the capillary momentarily in a bath at approximately  $10^\circ$  above the melting point of the higher melting component. They were removed and cooled as soon as the completely liquid sample was clear of air bubbles. Melting points (disappearance of last trace of solid) were then taken on the resolidified sample in the usual manner with a temperature rise of approximately  $0.5^\circ C.$  per minute at the melting point in a Hershberg melting point apparatus (2).

Melting points of the eutectics were taken as the thaw point (first trace of liquid) of samples of composition approximating that of the eutectic (e.g., 50% to 55% of the lower component) (3). Eutectic composition was determined by extrapolating to the thaw point. The melting points of the eutectics observed were  $152.5$ ,  $160.5$ ,  $164.5$ ,  $168.5$ , and  $170^\circ C.$ , respectively, for successive pairs. The  $C_8$ - $C_{10}$  eutectic melted at  $168^\circ C.$  Figure 1 shows the melting points of the various mixtures versus weight per cent composition. Most of the melting points of the dihydrazides prepared agreed well with values previously reported (4, 5, 6, 7, 8). The melting points of members of the homologous series appear to approach a limiting value below  $190^\circ C.$  Similarly, with increasing chain length, the melting points of the binary eutectics appear to level off between  $170$  and  $175^\circ C.$  A 1:1:1 mixture of the C-8, C-9, and C-10 dihydrazides was found to melt at  $162^\circ C.$  A 1:1:1:1 mixture of the C-7, C-8, C-9, and C-10 dihydrazides melted at  $155^\circ C.$

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TABLE II  
 Preparation of Hydrazides from Methyl Esters

Ester	Yield 1st Cryst.	Yield 2nd Cryst.	Vol. 70% EtOH	M.P. Found (Cor.)	M.P. Lit.	N, Calcd.	N,* Found
C-10, Subacate.....	% 91	% 85	ml. 60	188	188(4)	24.33	24.48
C-9, Azelate.....	95	89	60	187	.....	25.91	25.79
C-8, Suberate.....	85	68	50	187	187(8)	27.70	27.62
C-7, Pimelate.....	89	78	40	185	182(6)	29.77	29.67
C-6, Adipate.....	93	73	30	182	178(6)	32.16	31.90
C-5, Glutarate.....	97	68	30	176	176(5)	34.98	35.01
C-18, Stearate.....	.....	.....	.....	117	116(1)	.....	.....

\* By the Pregl Micro Dumas Method.

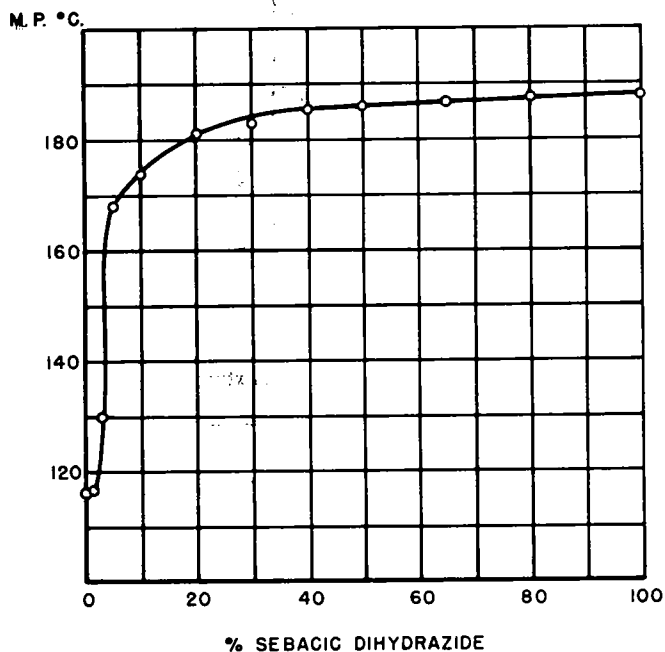


FIG. 2. Melting points of binary mixtures of stearic hydrazide and sebacic dihydrazide.

The binary mixture of stearic acid hydrazide and sebacic acid dihydrazide showed no eutectic formation by the method used. More refined methods might show a eutectic below 1-2% sebacic acid dihydrazide. The dihydrazide is very insoluble in the liquid hydrazide. Although the melting points differ by more than 70°, 50% of the stearic hydrazide lowered the

melting point of the dihydrazide by only 1.5°, 35% by only 0.5°. It is obvious therefore that melting points may be of little value in determining purity of dihydrazides if some fatty acid monohydrazides are present and that melting points should always be supported by nitrogen determinations.

### Summary

1. A simple preparation of the dihydrazides is given. The recrystallized dihydrazides of glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids melted at 176, 182, 185, 187, and 188°C., respectively.

2. The melting point curves are reported for binary mixtures of a) the dihydrazides of adjacent members of the homologous series of dicarboxylic acids from glutaric to sebacic, b) suberic and sebacic dihydrazide, and c) sebacic dihydrazide and stearic hydrazide.

3. The binary mixtures of the dihydrazides show formation of a eutectic containing 52-53 weight per cent of the lower component.

4. The binary mixture of stearic hydrazide and sebacic dihydrazide shows no eutectic by the method used.

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## Antioxidant Properties of Polyhydroxybenzoic Acids and Their Esters, and Other Nuclear Substituted Polyphenols\*

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SINCE the original work of Moureu and Dufraisse (1) in 1922, in which they found that certain phenols had antioxygenic properties, many compounds have been studied as antioxidants in fatty materials. The phenols and compounds with phenolic functional groups, however, have remained one of the most important class of compounds as antioxi-

dants for fats and oils. In 1933 Newton and Grettie obtained a United States patent (2) on the use of gum guaiac as an antioxidant. Gum guaiac is a secretion of a tropical tree, *Guaiacum officinale*, which grows in the West Indies. Its active principle is presumably guaiaretic acid, which is phenolic.

Gum guaiac was the first material to be approved for use in lard by the Meat Inspection Division of the Bureau of Animal Industry. This was in 1940. Later, nordihydroguaiaretic acid (NDGA), first re-

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