

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

Monoalkyl Phthalates from Normal Aliphatic Alcohols

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This work was undertaken because of the growing importance of the alkyl phthalates and the possibility of using them as checks for identification of alcohols, as well as to study the type of melting point curve given by these derivatives. Pickard and Kenyon¹ and others have prepared monoesters of the secondary alcohols for use in resolving their racemic mixtures, and some of the metallic salts of the monoesters have been patented for use in synthetic resins, yet very few of the normal monoesters have been described. The melting points and analyses are given in Table I and plotted in Fig. 1.

TABLE I

Ester	M. p. (corr.)	Acid number	
		Calcd.	Found
Methyl ^a	82.4-82.7	311.5	313.1
Ethyl ^b	(47-48)
Propyl	54.1-54.4	269.6	270.3
Butyl	73.1-73.5	252.6	252.8
Amyl	75.4-75.6	237.6	237.0
Hexyl	24.6-25.4	224.3	222.9
Heptyl	16.5-17.5	212.4	211.8
Octyl	21.5-22.5	201.7	202.2
Nonyl	42.4-42.6	192.0	192.6
Decyl	37.8-38.0	183.2	182.7
Undecyl	43.8-44.1	175.2	175.2
Dodecyl	50.2-50.4	167.9	168.1
Tridecyl	52.4-52.7	161.1	160.2
Tetradecyl	59.8-60.0	154.9	154.6
Pentadecyl	60.3-60.5	149.1	148.9
Hexadecyl ^c	66.7-66.9	143.7	144.0
Heptadecyl	66.6-66.8	138.8	138.4
Octadecyl	72.4-72.6	134.1	133.4
Nonadecyl	70.8-71.0
Eicosyl	77.1-77.3

^a Walker, *J. Chem. Soc.*, **61**, 717 (1892), gave m. p. 82.5°; Cohen, Woodroffe and Anderson, *ibid.*, **109**, 231 (1916); Kitamura, *J. Pharm. Soc. Japan*, **58**, 29-37 (1938), gave m. p. 82-82.5°.

^b Amann, *Monatsh.*, **36**, 505-8 (1915), gave m. p. 47-48° after keeping at low temperature for a long time for crystallization.

^c Willstätter, Mayer and Hüni, *Ann.*, **378**, 90 (1911), gave the m. p. as 61-62°.

Experimental

The method of preparation and purification of Pickard and Kenyon was followed with certain modifications. Esters from methyl through butyl were prepared by heating 4 g. of the anhydride with 1 g. of the alcohol at the

(1) Pickard and Kenyon, *J. Chem. Soc.*, **91**, 2058-2061 (1907); **99**, 58 (1911); **103**, 1937 (1913).

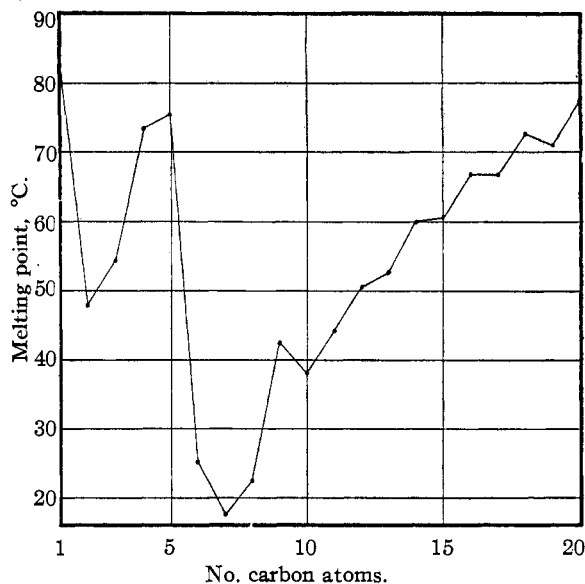


Fig. 1.—Melting points of the monoalkyl phthalates.

reflux temperature for thirty minutes. From amyl to octadecyl, 0.5 g. of alcohol was heated with twice the required amount of anhydride at 105-110° for periods varying from thirty minutes to two hours, as the molecular weight of the alcohol increased. With nonadecyl and eicosyl, only 0.25 g. of the alcohol was used.

For purification, the reaction mass from methyl to hexyl was shaken with 25 cc. of benzene, filtered from excess anhydride and neutralized by dilute sodium carbonate, leaving the mixture slightly acid. The aqueous layer was extracted three times with 50-cc. portions of benzene to remove the unreacted alcohol and possible diesters. The esters were precipitated as colorless liquids or white crystalline solids from the water solution by dilute hydrochloric acid and crystallized three times from a mixture of 90% petroleum ether and 10% benzene.

As the sodium salts of the esters above octyl tend to form emulsions, the following procedure was used. The reaction mass was treated with 25 cc. of ether and filtered to remove the excess anhydride. After evaporating the ether, it was treated for forty-five minutes with 60 cc. of water, warming to 60-65° to hydrolyze any remaining anhydride. The dried residue was dissolved in 10 cc. of chloroform and filtered to remove any phthalic acid. The chloroform was evaporated under vacuum and the esters recrystallized three times from petroleum ether. It was found advantageous to use Dry-ice for cooling the solutions of the esters from hexyl through decyl, the solvent being removed by suction through a small tube tipped with porous alundum.

The melting points were taken, with mechanical stirring, in a 200-cc. bulb, fitted with a side-arm for the thermometer and melting point tube. Standard Anschütz ther-

mometers were used so the melting points may be regarded as corrected. The molecular weights were determined by titrating the esters, dissolved in 50% alcohol, with standard sodium hydroxide. The yields averaged from 35 to 50%.

Discussion

Due to the ease of hydrolysis and the time necessary at low temperature for crystallization, the ethyl ester was not isolated in pure enough form for analysis, hence Amann's value is used in the curve. The esters are white crystalline solids, having very definite melting points and soluble in organic solvents. There is sufficient variation in the melting points through dodecyl so that they could be used very satisfactorily as checks on the identification of the individual alcohols. It will be noted that up to decyl the melting points give a curious pattern and from this ester on, alter-

nation gradually increases, both the odd and even ones forming smooth curves.

This problem was suggested by Dr. E. Emmet Reid, Research Adviser, University of South Carolina, and to him the authors wish to express their appreciation for assistance, and for the higher alcohols, the odd ones from undecyl to heptadecyl being those prepared by Meyer and Reid.²

Summary

The monoalkyl phthalates of the normal alcohols from methyl to eicosyl have been prepared and their melting points determined. A melting point curve is shown; it exhibits regular alternation above the decyl ester.

(2) Meyer and Reid, *THIS JOURNAL*, **55**, 1574 (1933).

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The Sterols of Alfalfa Seed Oil. I

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1. Introduction

The fat constants and fatty acids of alfalfa seed oil have been studied by Jacobson and Holmes,¹ Schuette, Vogel and Wartinbee,² and by Schuette and Vogel.³ As far as can be determined, there has been no previous account of an investigation of the unsaponifiable material from alfalfa seed oil.

About 4% of the oil which can be extracted from alfalfa seed with ethyl ether is unsaponifiable. This unsaponifiable portion consists of a crystalline substance or substances which represent about 35% of the total unsaponifiable, and of a clear, reddish, oily liquid which makes up the remainder.

The crystalline material consists primarily of a sterol very similar to or identical with the sterol isolated by Heyl, Wise and Speer⁴ and Clenshaw and Smedley-MacLean⁵ from spinach fat and later termed α -spinasterol by Hart and Heyl.⁶ Simpson⁷ in 1937 isolated α -spinasterol from senega root. The formula first assigned to α -

spinasterol by Hart and Heyl⁶ was $C_{27}H_{46}O$. Recent work by Larsen⁸ on the completely reduced sterol, spinastanol, showed the latter to be identical with fucostanol and stigmastanol, for which the formula $C_{29}H_{52}O$ has been accepted. Since Larsen and Heyl⁹ showed α -spinasterol to be doubly unsaturated, the formula for α -spinasterol, therefore, would be $C_{29}H_{48}O$.

The reddish oily fraction gives a positive Liebermann-Burchard reaction, but colors only the sulfuric acid layer in the Salkowski reaction. The Whitby B reaction¹⁰ is positive. Further work on this material is in progress in this Laboratory.

2. Experimental

Extraction of Seed.—Ground alfalfa seed (*Medicago sativa* L.) was extracted continuously with hot diethyl ether. The extract was then filtered and the solvent distilled off in the presence of an atmosphere of carbon dioxide; yield 11.8% of a greenish oil which had an index of refraction of 1.4820 at 15°. The fat constants of this oil were in good agreement with those obtained by Jacobson and Holmes.¹

Saponification.—To 100 g. of alfalfa seed oil was added 600 ml. of ethyl alcohol and 100 ml. of 50% potassium hydroxide. This mixture was refluxed for one hour,

(1) Jacobson and Holmes, *THIS JOURNAL*, **38**, 480 (1916).

(2) Schuette, Vogel and Wartinbee, *Oil and Soap*, **15**, 35 (1938).

(3) Schuette and Vogel, *ibid.*, **16**, 16 (1939).

(4) Heyl, Wise and Speer, *J. Biol. Chem.*, **82**, 111 (1929).

(5) Clenshaw and Smedley-MacLean, *Biochem. J.*, **23**, 107 (1929).

(6) Hart and Heyl, *J. Biol. Chem.*, **95**, 311 (1932).

(7) Simpson, *J. Chem. Soc.*, 730 (1937).

(8) Larsen, *THIS JOURNAL*, **60**, 2431 (1938).

(9) Larsen and Heyl, *ibid.*, **56**, 2663 (1934).

(10) Whitby, *Biochem. J.*, **17**, 5 (1928).