crop of crystals frequently appears. Second, the saturation of a suspension of triethyl lead chloride in ether with hydrogen chloride induces some of the triethyl lead chloride to dissolve. This latter phenomenon appears to be unusual with organolead halides.

Summary

Diethyl lead dichloride and triethyl lead chloride can be very conveniently prepared in essentially quantitative yields by the reaction between tetraethyl lead and hydrogen chloride.

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SOME PHYSICAL CONSTANTS OF MONACETIN, MONOPROPIN AND MONO-NORMAL-BUTYRIN[1]

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The discovery of the nature of fatty oils by Chevreul over a century ago gave a marked impetus to the synthesis of simple and mixed glycerides. The monoglyceryl esters of the acids of low molecular weight have not, however, shared the same degree of interest. Published information thereon is apparently non-existent for one of the esters pertinent to this communication; the reported physical constants of another are obviously in need of correction; and such data as are available have been determined at temperatures for which there is no uniformity.

In view of this situation there is an evident need for new data and for a revision of some of that now extant. These ends have been accomplished by the synthesis of the glycerides in question and the determination of their vapor pressures, densities, refractive indices and surface tensions. The method of preparation which was followed led to the formation of racemic compounds which probably possess, as might be expected, different constants than the corresponding naturally occurring glycerides, none of which, however, seems to have been isolated.

Monacetin has been made by Berthelot,[2] who heated a mixture of glycerol and acetic acid under pressure; by Geitel,[3] who isolated it from the reaction product resulting from heating a mixture of glycerol and acetic acid at atmospheric pressure; by Averill, Roche and King,[4] who synthesized α-monoglycerin by a method developed by Fischer[5] and his

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[1] Constructed from a thesis submitted by John T. Hale to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science, June, 1928.

[2] Berthelot, *Ann. chim. phys.*, [3] **41**, 216 (1854).

[3] Geitel, *J. prakt. Chem.*, **163**, 417 (1897).

[4] Averill, Roche and King, THIS JOURNAL, **51**, 866 (1929).

[5] Fischer, Bergwin and Barwind, *Ber.*, **53**, 1589 (1920).

collaborators; and by one of us,[6] who improved upon Geitel's technique by introducing a suitable catalyst into the reaction mixture. Butyrin was made by Berthelot by a method already indicated;[2] by Guth[7] from sodium butyrate and α-monochlorohydrin; and by Hanriot, it is reported,[8] who used a biological method of synthesis in that he caused lipase to act upon a mixture of glycerol and butyric acid.

Experimental

A uniform method of procedure was followed in the synthesis of the monoglycerides pertinent to this communication. Its salient features consist of the use of phosphoric acid as catalyst; an esterification temperature whose order of magnitude is lower than that of the boiling point of the acid in question; and the removal of by-product water as fast as it is formed. The last two conditions were met by dispersing the reactants in carbon tetrachloride and carrying out the operation with the aid of a continuous separator.[9]

Because of the similarity in method the synthesis of but one glyceride is described as illustrative of a typical case. In each instance equivalent quantities of glycerol and fatty acid necessary to produce the monoglyceride in question were taken.

That a monoglyceride had actually been synthesized was deduced from the satisfactory degree of agreement between the molecular refractivity (Gladstone and Dale formula) and the sum of the atomic refractivities of the compound in question. Although it is true that no claim for great delicacy can be made for this method of identification, yet it would seem that, in this instance, the assumption is valid in view of the close concordance between observed and theoretical saponification equivalents.

Monopropin.—A mixture consisting of 150 g. of glycerol (1 mol), 118 g. of propionic acid (1 mol) (b. p. 140–141°), 10 g. of phosphoric acid (85%) and 200 cc. of carbon tetrachloride was heated under a reflux for approximately four hours, during which time an amount of water was recovered which was slightly in excess of the theoretical. Ten g. of sodium propionate was then added to the reaction mixture, and the whole concentrated by distillation at a temperature below 130°. The insoluble phosphate was then removed by filtration, whereupon the filtrate was distilled at a pressure of 3 mm., the fraction boiling between 132–134°, indicative of a 58% yield, being saved for further purification.

The following constants were noted: d_4^{20} 1.1537, n_{20} 1.4503; saponification equivalent, 148.2, calcd. for monopropin, 148.1; molecular refraction, 57.81, calcd. for monopropin, 57.18; γ_{20} 40.3 dynes/cm.

Monacetin.—The fraction boiling between 129–131° (3 mm.) on purification yielded the following constants: d_4^{20}, 1.2060; n_{20} 1.4517; saponification equivalent, 134.1,

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[6] Schuette and Sah, THIS JOURNAL, **48**, 3161 (1926).

[7] Guth, *Z. Biol.*, **44**, 78 (1903).

[8] Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," Macmillan Co., London, **1921**, 6th ed., Vol. I, p. 8.

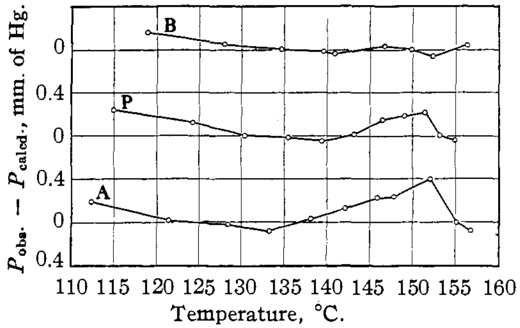
[9] Hultman, Davis and Clarke, THIS JOURNAL, **40**, 366 (1921).

calcd. for monacetin, 134.2; molecular refraction, 50.21, calcd. for monacetin, 49.53; γ_{20} 47.1 dynes/cm.; yield of crude ester, 70%.

Mono-*n*-butyrin.—The fraction boiling between 139–140° (4 mm.) on purification yielded the following constants: d_4^{20} 1.1344; n_{20} 1.4531; saponification equivalent, 162.1, calcd. for monobutyrin, 162.1; molecular refraction, 64.75, calcd. for monobutyrin 64.83; γ_{20}, 37.6 dynes/cm.; yield of crude ester, 78%.

Vapor Pressure Measurements

Measurements of the vapor pressure of the three glycerides were made by the method of Ramsay and Young[10] over a temperature range of approximately 120°, minimum and maximum being 112 and 238°, respectively. Inasmuch as decomposition probably occurred in the upper zones, the values there observed have not been recorded. Temperatures were read with a thermometer graduated to 0.2°. They were corrected for stem exposure. Pressures were read to 0.1 mm. on an ascending and a descending temperature scale. When these data were subsequently plotted it was found that the observed points fell on one curve.



A, monacetin; P, monopropin; B, mono-*n*-butyrin.

Fig. 1.—Deviation plot.

The curve for the vapor pressure of monacetin may be expressed by the empirical equation log P = 10.10518 − 3864.8/T. It holds for temperatures up to approximately 185°, and is reliable down to 112°. Similarly the equation for monopropin was found to be 10.29682 − 3961.3/T, an expression which is valid between the temperatures 115 and 183°. For mono-*n*-butyrin the curve for the vapor pressure corresponds to the equation log P = 10.78092 − 4200.8/T. It holds between the limits 119 and 176°.

Though due recognition is made of the fact that equations of this character are at best but approximate, yet the fact remains that the experimental points were found to lie on straight lines within the limits of accuracy of the experimental data. The least accurate factor probably lies in whatever limitations are inherent in the method which was employed for determining the vapor pressures.

That the differences between the experimentally determined and calculated vapor pressures might be graphically shown, there is reproduced a deviation plot (Fig. 1) for each of the glycerides pertinent to this study. Maximum and mean differences were found to be 0.40 and 0.12 mm.

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[10] Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

for monacetin. Similarly for monopropin and mono-*n*-butyrin these differences are 0.24 and 0.09, and 0.16 and 0.04, respectively.

Conclusions

The foregoing expressions of the vapor pressure–temperature relationships which obtain among the monoglycerides of low molecular weight make possible a critical inspection of such boiling points of these compounds as have found their way into some of the well-known texts and reference books. When viewed in the light of the data as herein recorded, it appears that the previously reported boiling points of monacetin of 189–191 (60 mm.)[6] and 130–132° (2–3 mm.)[8] are in substantial agreement with our observations. On the other hand, the statement[11] that monacetin boils at 158°(165 mm.) is rather difficult to explain except perhaps on the grounds of a typographical error in recording the pressure.

That monobutyrin boils at 269–271°[8] or at 271°[11] under atmospheric pressure appears to be an absurd statement because of the generally accepted view that the glycerides cannot be distilled under ordinary conditions without decomposition, and the fact that the calculated boiling point of this glyceride is approximately 535°. The assigned boiling point of 160–163° (16 mm.)[8] is in better agreement with fact.

The heat of vaporization per gram of ester when calculated with the aid of the Clausius–Clapeyron equation is for monacetin 132.4 cal., for monopropin 122.5 cal. and for mono-*n*-butyrin 118.75 cal.

Summary

The monoglycerides of acetic, propionic and *n*-butyric acids have been synthesized and their simpler physical constants determined at a uniform temperature. Of these data those for monopropin are new.

The vapor pressures of these glycerides have been determined over the temperature range in which they are stable.

The heats of vaporization have been calculated.

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[11] National Research Council, "International Critical Tables," McGraw-Hill Book Company, Inc., New York, **1926**, Vol. I, p. 193.