

SOME GLYCERIDES OF PHENOXYACETIC ACID¹

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Introduction

The production of 2-hydroxy-2-trichloromethyl-4-hydroxymethyl-1,3-dioxolane from glycidol and trichloroacetic acid by Hibbert and Grieg² has given new interest to the field of the glycerides of strong organic acids. For practical reasons, it is desirable to use an organic acid that is stable, that produces solid glycerides, and that has a relatively high dissociation constant. Phenoxyacetic acid was chosen as fulfilling these requirements. The dissociation constant for phenoxyacetic acid is 0.00077 at 25°C³.

Experimental

Alpha-monophenoxyacetin. Prepared by slowly adding 17 gms. of phenoxyacetyl chloride⁴ with shaking, to 13.2 gms. of acetonyl glycerol⁵ and 13 gms. of quinoline in a 250 ml. erlenmeyer flask, letting the tightly stoppered mixture stand 2 days at room temperature. The reaction mixture was extracted with 150 ml. ether and 50 ml. N/2 sulfuric acid, the ether layer was cooled to 0°C., and was shaken vigorously for 3 minutes with 75 ml. of concentrated HCl saturated with calcium chloride, to hydrolyze the acetone. In a second preparation, when an attempt was made to isolate the acetonyl-alpha-monophenoxyacetin, washing with HCl was omitted, but the initial washing with N/2 sulfuric acid evidently hydrolyzed the acetone, indicating the acetone is more readily hydrolyzed from this compound than from most acetonyl-monoglycerides. After dilution with water, the ether layer was thrice washed with 5% potassium bicarbonate and once with water. On evaporation of the ether, alpha-monophenoxyacetin separated as an oil, which was solidified with some difficulty by cooling in an ice-salt mixture. Recrystallized three times from alcohol and water, long glistening needles,

¹ Taken from the thesis presented by George F. Converse in partial fulfillment of the requirements for the degree of Master of Arts, University of South Dakota, May, 1937.

² H. Hibbert and M. E. Grieg, *Can. J. Res.*, **4**, 254-263 (1931).

³ H. Scudder, "The Electrical Conductivity and Ionization Constants of Organic Compounds." Van Nostrand, New York, (1914).

⁴ A. J. J. Vandeveldt, *Chem. Centr.*, **1**(1898), 988-999.

⁵ E. Fischer and E. Pfahler, *Ber.*, **53**, 1607 (1920).

soluble in ether, chloroform, acetone, benzene, toluene, and alcohol; insoluble in petroleum ether and water. Yield, 31%.

Saponification Number: Calculated for $C_{11}H_{14}O_5$, 248.0;
Found, 247.0, 247.5, 242.8.

Alpha-monophenoxyacetin showed the phenomenon of double melting point^{6, 7, 8} in contradiction to the conclusion of Malkin that, in the case of monoglycerides of less than 10 carbons in the fatty acid chain, the transformation from one form to the other is too rapid to be measured. The stable form of alpha-monophenoxyacetin melts at 100-100.5°C. (corr.). If the molten form is solidified by sudden cooling to 15°C., and placed in a bath at 70°C. and heated rapidly, it remelts at 79-80°C., (uncorr.). If allowed to stand, the metastable form is reconverted to the stable modification.

Alpha-chloro-alpha', beta-diphenoxyacetyl-glycerol. Prepared by slowly adding 9 gms. of phenoxyacetyl chloride to 3 gms. of alpha-monochlorohydrin⁹ dissolved in 7 gms. of quinoline. After standing 24 hours, the product was dissolved in a mixture of chloroform and ether, washed with N/2 sulphuric acid and 5% potassium bicarbonate. After evaporating the chloroform and ether, the product separated as an oil which solidified in the course of a week. Crystallized from carbon tetrachloride in small cubic crystals, m.p., 62-63°C. (uncorr.). Soluble in acetone, ethanol, methanol, benzene, carbon disulfide, and hot carbon tetrachloride; insoluble in petroleum ether and water.

Saponification Number: Calculated for $C_{19}H_{19}O_6Cl$, 444.4;
Found, 454.8.

Alpha-stearyl-alpha', beta-diphenoxyacetyl-glycerol. Prepared by slowly adding 6 gms. of phenoxyacetyl chloride to a solution of 6 gms. of alpha-monostearin¹⁰ and 5 gms. of quinoline in 20 ml. of chloroform. After standing 2 days, the product was extracted with 150 ml. ether and 50 ml. of N/2 sulphuric acid, the ether layer was washed repeatedly with N/2 sulphuric acid, 5% potassium bicarbonate, and water. The ethereal solution was dried with anhydrous sodium sulfate,

⁶ R. B. Josliker and H. E. Watson, *J. Soc. Chem. Ind.*, **47**, 365-368 (1928).

⁷ C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, **1**(1934), 666-671.

⁸ T. Malkin and M. O. Stafa Riad el Shurbogy, *J. Chem. Soc.*, **2**(1936).

⁹ *Organic Syntheses*, Vol. **2**, 33, Wiley, New York, (1922).

¹⁰ E. Fischer, M. Bergmann and H. Barwind, *Ber.*, **53**, 1589-1605 (1920).

the ether was evaporated, and the product remained as an oil which was solidified by cooling in an ice-salt mixture. The solid was recrystallized three times by dissolving in an ether alcohol mixture at room temperature and cooling slowly to -10°C., when it separated as a flocculent mass of no definite crystal form, m.p., 51-52°C. (corr.), m.p. of the metastable form, 22-24°C. It was soluble in acetone, hot alcohol; sparingly soluble in petroleum ether; insoluble in water.

Saponification Number: Calculated for $C_{37}H_{54}O_8$, 263.5;
Found, 263.3, 265.0.

Triphenoxyacetin. Prepared by slowly adding 28 gms. of phenoxyacetyl chloride to 5 gms. of glycerol and 22 gms. of quinoline dissolved in 50 ml. of chloroform. After standing for two days, the product was dissolved in 100 ml. of chloroform, washed thrice with N/2 sulphuric acid, twice with 5% potassium bicarbonate, and once with water. After drying over anhydrous sodium sulfate and evaporating the chloroform, an oil remained. On attempted crystallization from warm alcohol, the product again separated as an oil which solidified after standing for several weeks. It was recrystallized three times from warm alcohol containing a little acetone, by slowly cooling and spontaneous evaporation, as rectangular plates, soluble in acetone, chloroform, ether; sparingly soluble in warm alcohol and benzene; insoluble in petroleum ether and water. M.p., 80.0-80.5°C. (corr.), the metastable form being liquid at room temperature.

Saponification Number: Calculated for $C_{27}H_{26}O_9$, 340.4;
Found, 342.0, 340.7.

Summary

The following new compounds have been prepared:

Alpha-monophenoxyacetin

Alpha-chloro-alpha', beta-diphenoxyacetyl-glycerol

Alpha-stearyl-alpha', beta-diphenoxyacetyl-glycerol

Triphenoxyacetin

The phenomenon of double melting points has been observed for the first time for the glyceride of a strong organic acid of short chain length.