1,2-Dimethylnaphthalene styphnate crystallized from methanol in yellow–orange needles; m. p. 142–143°.

Anal. Calcd. for $C_{12}H_{12}\cdot C_6H_3O_8N_3$: N, 10.5. Found: N, 10.6.

The **1,3,5-trinitrobenzene derivative of 1,2-dimethylnaphthalene** crystallized from methanol in yellow needles; m. p. 147–148°.

Anal. Calcd. for $C_{12}H_{12}\cdot C_6H_3O_6N_3$: N, 11.4. Found: N, 11.5.

Summary

A method is described for the synthesis of 1,3- and 1,4-dimethylnaphthalene and 1,2,4-trimethylnaphthalene, starting from the readily available β-benzoylpropionic acid. A similar synthesis, starting from 1-tetralone, is described for 1,2-dimethylnaphthalene.

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[CONTRIBUTION FROM THE SCHOOL OF PHARMACY, UNIVERSITY OF PITTSBURGH]

Preparation of Fatty Acid beta-Monoglycerides

BY B. F. DAUBERT

The preparation and identification of beta-monoglycerides of aromatic acids was first accomplished by Helferich and Sieber[1] by acid hydrolysis of the ditrityl ether derivatives. These investigators prepared the beta-monobenzoate and beta-mono-(*p*-nitrobenzoate) of glycerol. Jackson and King[2] and Verkade and associates[3] found that application of this method to the preparation of aliphatic beta monoesters resulted in a shifting of the acyl group to produce the alpha ester. By catalytic hydrogenation of the esterified α,α-benzylidene glycerol, Bergmann and Carter[4] were the first to prepare a beta monoglyceride of a fatty acid. The method has been verified by a number of other investigators.

Verkade and associates[5] suggested a new method for preparing beta monoglycerides that involves the catalytic detritylation of the β-acyl-α,α′-dityrityl ether of glycerol. The purpose of this investigation, since their work has not been reported in detail, is to verify the method and report the experimental data. beta-Monobutyrin also has been prepared and identified as a new compound in the fatty acid series.

Experimental

Preparation of β-Palmityl-α,α′-ditritylglycerol.—The α,α′-dityrityl ether of glycerol was prepared according to the method of Verkade, van der Lee and Meerburg.[6] The dityrityl ether (12 g.) was dissolved in a mixture of 15 ml. of quinoline and 15 ml. of chloroform. After cooling the mixture to approximately 0° in an ice-bath, there was added slowly a solution containing 6.0 g. of palmityl chloride in 15 ml. of chloroform. The mixture was allowed to stand at room temperature for twenty-four hours and then taken up in 250 ml. of ether. The ether solution was washed successively with cold 0.5 *N* sulfuric acid, saturated sodium bicarbonate solution, and water, and finally dried over anhydrous calcium sulfate (Drierite). The ether was removed by distillation under reduced pressure and the residue dissolved in 200 ml. of dry acetone. The solution was filtered, the acetone removed by distillation under reduced pressure and the residue redissolved in a warm mixture of alcohol and acetone (25–1). On cooling to 0–5° for twenty-four hours and scratching the inside of the flask, crystallization was induced. The crystal mass was suction filtered and recrystallized from a similar mixture of alcohol and acetone; yield 13.5 g. (80%), m. p. 71° (Jackson and King,[2] 71.5°).

Preparation of beta-Monopalmitin.—Twelve grams of β-palmityl-α,α′-ditritylglycerol was suspended in 250 ml. of absolute alcohol and transferred to a hydrogenation bottle together with 1 g. of palladium black. The reduction was carried out at 45 lb. (3 atm.) pressure, 45–50°. Reduction was complete after approximately four hours. The progress of the reduction was followed easily by means of the pressure gage. The warm solution was filtered immediately to remove the catalyst and then evaporated to dryness *in vacuo*. The residue was redissolved in a mixture of alcohol and ether (1–1). After repeated fractional crystallizations from cool mixtures of alcohol and ether, 4 g. (85%) of beta-monopalmitin and 5 g. (69%) of triphenylmethane were obtained. The beta-monopalmitin on recrystallization from absolute alcohol melted at 68° and the triphenylmethane at 92.5°. The same procedure was equally successful with platinum (1 g. PtO_2) as the catalyst.

Preparation of β-Butyryl-α,α′-benzylidene Glycerol.—*n*-Butyryl chloride (11.8 g.) was added slowly to 20 g. of α,α′-benzylidene glycerol dissolved in 30 ml. of dry pyridine, with cooling in an ice-bath. The mixture was allowed to stand for four hours at room temperature. When water was added (400 ml.), the compound separated as an oil. After the excess water was poured off, the residue was taken up in ether and washed successively with 0.5 *N* sulfuric acid, saturated sodium bicarbonate solution, and

(1) Helferich and Sieber, *Z. physiol. Chem.*, **175**, 311 (1928).
(2) Jackson and King, THIS JOURNAL, **55**, 678 (1933).
(3) Verkade and Meerburg, *Rec. trav. chim.*, **54**, 716 (1935).
(4) Bergmann and Carter, *Z. physiol. Chem.*, **191**, 211 (1930).
(5) Verkade, van der Lee, de Quant and Zuydewijn, *Proc. Acad. Sci., Amsterdam*, **40**, 580 (1937).
(6) Verkade, van der Lee and Meerburg, *Rec. trav. chim.*, **56**, 619 (1937).

water, and dried over anhydrous sodium sulfate. The ether was evaporated under reduced pressure leaving the residue as a yellow, oily liquid. The liquid contained a small amount of pyridine which was distilled off at 50° under vacuum. The residue was then fractionated at 165°, 5 mm. pressure, yield 21 g. (77%).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.16; H, 7.25. Found: C, 67.01, 67.08; H, 7.12, 7.08.

The β-butyryl-α,α′-benzylideneglycerol crystallized to a solid mass after being placed in a refrigerator at 5° for one hour. The mass was dissolved in ethyl ether to which an equal volume of petroleum ether was added. After a short period at 5° the crystals which separated were washed with cold petroleum ether (0°) into a suction funnel, which had been previously cooled with solid carbon dioxide. The crystals were long, colorless prisms very soluble in ether and alcohol and insoluble in petroleum ether and water, m. p. 16–18° (uncor.).

The m. p. (16–18°) is consistent with the melting points of other esterified acetals prepared by other investigators. Stimmel and King[7] prepared the beta-capryl (m. p. 32.5°), beta-lauryl (m. p. 44.6°), beta-myristyl (m. p. 62°), beta-palmityl (m. p. 63.8°) and beta-stearyl (m. p. 69°) esters of α,α′-benzylideneglycerol and found that as the length of the carbon chain of the fatty acid in the beta position increased, the melting point progressively increased. Bergmann and Carter,[4] however, found that the β-acetyl-α,α′-benzylideneglycerol melted at 99–100°. This esterified acetal was also prepared by the author and the melting point reported by Bergmann and Carter was verified. The melting point of the acetyl derivative is out of line with all the analogous compounds so far prepared in the series. It is interesting to note that the mixed triglycerides containing one mole of acetic acid also exhibit relatively high melting points compared to higher members of the series.

Preparation of beta-Monobutyrin.—This beta monoglyceride was prepared from 10 g. of β-butyryl-α,α′-benzylideneglycerol by the method of Bergmann and Carter.[4] One-half gram of palladium black, as reported by Stimmel and King,[7] was found to be sufficient for the hydrogenation; yield, 5.75 g. (88%).

Anal. Calcd. for $C_7H_{14}O_4$: C, 51.49; H, 9.26. Found: C, 51.44, 51.38; H, 9.15, 9.20.

The beta-monobutyrin was a colorless liquid soluble in alcohol and ether, b. p. 140–141° (4 mm.), sap. eq. 162.10 (theory 162.18). For further identification the *beta* monobutyrin was used to prepare β-butyryl-α,α′-distearin, m. p. 51.5° (McElroy and King,[8] 51°).

Summary

Catalytic detritylation by reduction of the esterified α,α′-dityrityl ether of glycerol has been verified in the preparation of beta monopalmitin in good yield. Thus, an additional method for preparing beta monoesters of the fatty acids is available, as suggested by Verkade.

A new intermediate β-butyryl-α,α′-benzylideneglycerol, m. p. 16–18°, has been prepared and the melting point found to be consistent with other esterified acetals of the aliphatic series.

beta-Monobutyrin, a new beta monoester, has been prepared and the structure verified by making a triglyceride of known constitution.

(7) Stimmel and King, THIS JOURNAL, **56**, 1724 (1934).

(8) McElroy and King, *ibid.*, **56**, 1191 (1934).

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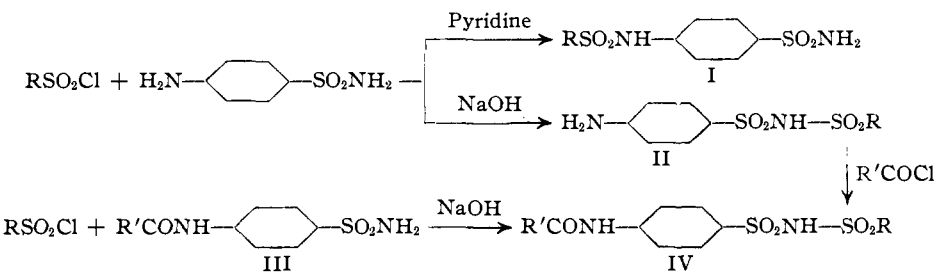
Substituted Sulfanilamides. II. N^1- and N^4-Sulfonyl Derivatives

BY JAMES M. SPRAGUE, LANE F. MCBURNEY AND L. W. KISSINGER

Certain N^4-acyl derivatives of sulfanilamide have shown good protective action against experimental streptococcal infections in mice.[1] For comparison with these acylsulfanilamides a number of sulfonyl derivatives have been prepared. N^1-*p*-Aminobenzenesulfonylsulfanilamide (disulfanilamide) and N^4-*p*-aminobenzenesulfonylsulfanilamide have been reported[2,3] recently.

The N^4-sulfonyl derivatives I were prepared by treating sulfanilamide in pyridine solution with a sulfonyl chloride.



(1) Miller, Rock and Moore, THIS JOURNAL, **61**, 1198 (1939).

(2) Crossley, Northey and Hultquist, *ibid.*, **60**, 2222 (1938).

(3) Rosenthal, *et al.*, *Pub. Health Reports*, **52**, 662 (1937); **53**, 5340 (1938); Bauer, THIS JOURNAL, **61**, 613 (1939).