and glacial acetic acid but insoluble in ether. Although this material is probably a mixture, it was not fractionated on account of the complications arising from the ease with which it is soluble in water. The material contains 11.2% of arsenic and 4.2% of sulfur and is tolerated in doses above 1.8 g./kg.

Table III contains some observations regarding the color of these compounds; for the purpose of comparison the phthaleins used in preparing these arsenicals are included.

The expenses necessary for the pursuance of this investigation have been met in part from a fund for research in the Department of Tropical Medicine, donated by a citizen of Boston.

Summary

1. When a solution of *p*-arsonobenzene diazonium chloride is added to an alkaline solution of an equivalent quantity of a phthalein, coupling takes place, but the reaction product is a mixture of unchanged phthalein and its mono- and di-arsonobenzene-azo derivatives.
2. The mixture can be resolved by fractional precipitation from aqueous alkaline solution with alcohol.
3. *p*-Arsonobenzene-azo derivatives have been prepared from phenolphthalein, phenoltetrachlorophthalein, fluorescein, dibromo-fluorescein, and phenolsulfonephthalein.
4. The derivatives of phenolphthalein and phenoltetrachlorophthalein are more toxic than those of the other substances.
5. None of these arsenical compounds is trypanocidally active.
6. The introduction of *p*-arsonobenzene-azo groups deepens the shade but does not alter the character of the color.

BOSTON 17, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF SOUTHERN CALIFORNIA]

BUTYRIN

BY LEROY S. WEATHERBY, LILLIAN MCILVAINE AND DAVID MATLIN

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Experimental work in the preparation of butyrin led the authors to believe that the statements as to the properties of butyrin given in Beilstein and in other chemical tables, especially that giving the boiling point of tributyrin as 285°, are in error. It was believed that in the preparation of the butyrin from which these constants were determined, not sufficient care had been taken to eliminate the lower glycerides. Investigation was undertaken, therefore, for the purpose of preparing and isolating the pure triglyceride, and establishing its properties more accurately.

Butyrin was prepared by the direct esterification of glycerol and butyric acid at the boiling point of the mixture. Fig. 1 shows the course of esterification in two trials in which a 10% excess of acid was used over that required for complete esterification. The reaction was followed in the customary way by titration; the ordinates in the graph represent the number of cubic centimeters of 0.1 *N* sodium hydroxide solution required to neutralize the butyric acid in 1 cc. of the reaction mixture. It may be seen from the curve that the greater part of the reaction occurs within the first five hours and that practical equilibrium is reached after about 60 hours, at which point esterification has run about half way to completion, since at this point practically one-half of the acid possible for esterification has disappeared.

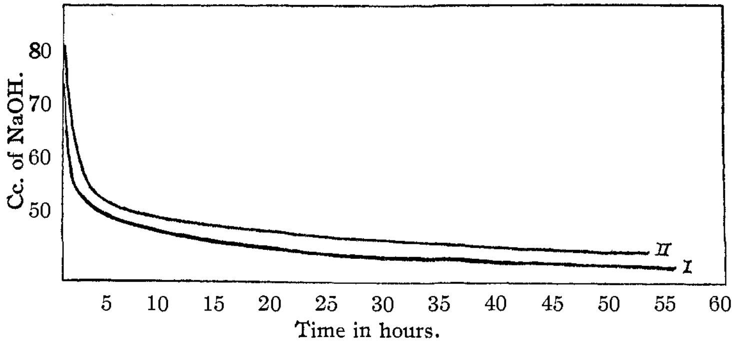

Fig. 1.—Velocity of esterification of butyric acid and glycerol.

As glycerol is a trihydric alcohol it may be expected that esterification will progress in three successive stages in which there will be formed mono-

TABLE I

COURSE OF ESTERIFICATION WITH VARIOUS QUANTITIES OF ACID

Time, hours	Volume (cc.) of 0.65 *N* NaOH for 1 cc. of mixture		
	1 mole of acid	2 moles of acid	3 moles of acid
0	11.48	12.78	14.50
0.5	7.82	11.15	12.83
1	7.64	10.92	12.62
2	6.44	9.26	12.12
4	5.20	8.25	10.20
6	4.35	7.82	9.87
8	3.92	7.27	8.95
11	2.97	6.88	8.79
13	2.15	6.46	8.43
16	1.67	6.32	8.23
18	1.29	6.26	8.11
25	0.87	6.08	7.68
42	.67	5.47	7.25
50	.63	5.35	7.20

Six moles of acid to one mole of glycerol; initial titration, 15.07 cc.; final titration, 10.30 cc. (Intermediate titrations not made.)

TABLE I (*Concluded*)

PERCENTAGE OF ESTERIFICATION AND YIELD OF BUTYRIN

No. of moles of acid to 1 mole of glycerol	Acid esterified %	Glycerol esterified, calcd. as tributyrin %
1	95	32
2	59	39
3	50	50
6	63[a]	63

[a] Calculated on the basis of the acid possible of esterification.

butyrin, dibutyrin and tributyrin. Experimentation was conducted, therefore, to determine the effect of *mass* both on the reaction velocity and on the final stage of esterification. Table I shows the results of four esterification runs in which the quantity of acid was varied in the ratio of 1, 2, 3 and 6 moles of acid to 1 mole of glycerol, respectively.

At the end of the esterification period the excess of acid and glycerol was removed as far as practicable from the reaction mixtures by distillation. The residue was washed with cold water,t hen with cold, dil. sodium carbonate solution, and finally again with water, salt being added in each case to facilitate separation.

Those reaction mixtures in which an excess of acid was used not only yielded a greater residue on distillation (as much as 50% of product remaining undistilled at 300°); but since monobutyrin and dibutyrin are somewhat soluble in water, yielded also a disproportionately large quantity of insoluble ester. This shows, as might be expected, that an excess of acid not only causes more complete esterification, but in addition forces a greater yield of the insoluble tributyrin.

Boiling Point.—The purified product obtained as described above was dried for 24–48 hours over an excess of calcium chloride and was then distilled. In the case of those products obtained from 1 mole of acid, distillation began at about 285° and a considerable fraction distilled under 300°, indicating the presence of a considerable amount of lower glycerides. In the case of the ester obtained by the use of a large excess of acid, very little distilled under 300°, while the major portion distilled at 305° to 310°. Refractionation increased this portion.

As there appeared to be slight decomposition at the highest temperature of distillation, other esterification products were prepared in which all distillations were carried out under reduced pressure. These yielded a product which under 15 mm. pressure boiled at about 190°. This product was then distilled once under atmospheric pressure and the major portion boiled between the limits of 305° and 309°. Since it is likely that the final product still contains a trace of the lower glycerides, the fraction with higher boiling point may be taken as representing tributyrin. It is then definitely established that the boiling point of tributyrin given in chemical literature as 285° is in error due to the presence of lower glycerides. A boiling point of 305–310° is established as more nearly accurate.

The butyric acid used in these determinations was guaranteed by the maker to be normal butyric acid of the highest purity. From a 0.9kg. lot a fraction of 484 cc. was obtained having a boiling point of 162–163° (*n*-butyric acid, b. p., 162.5°). Chemically pure glycerol was used which was further dehydrated by heating under reduced pressure.

Color, Odor and Taste.—The purified tributyrin is colorless. It has a characteristic, though not unpleasant odor. It possesses a markedly bitter taste, noticeable especially in the palate area of the throat. It was thought that this taste was probably due to decomposition products, but repeated distillation under reduced pressure did not remove the substance that caused it.

Specific Gravity.—The specific gravity at 21° of the tributyrin purified by vacuum distillation was found by pycnometer measurement to be 1.027.

Freezing Point.—Freezing-point determination of the purified tributyrin was made by means of carbon dioxide snow and ether, using a standardized toluene thermometer. The butyrin began to thicken at about —35°, and at —75°, the lowest temperature obtained, it was so viscous that the thermometer could scarcely be withdrawn; yet it had not solidified. This behavior may be due in part to traces of the lower glyceride, though primarily to the nature of the substance itself.

Summary

The rate of esterification of glycerol and butyric acid was determined. The effect of mass in forcing the esterification more nearly to completion and in increasing the yield of the triglyceride was established.

Purified tributyrin was isolated and its properties established. It is a colorless liquid with characteristic odor and bitter taste; d^{21}, 1.027; b. p., about 190° (15 mm.), or 305–310° (atmos.). At lower temperatures it thickens to a viscous mass which does not solidify at —75°.

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NOTE

Rapid Preparation of Cetyl Alcohol.—No simple, rapid method of obtaining cetyl alcohol from spermaceti has been published. Beilstein[1] gives a very tedious preparation, involving saponification with potassium hydroxide in ethyl alcohol, precipitation of the cetyl alcohol and calcium palmitate with calcium chloride, filtration, drying and extraction with alcohol. Axelrad[2] gives also an unsatisfactory method with the added

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[1] Beilstein, "Handbuch der organischen Chemie," Springer, Berlin, **1918**, 4th ed., vol. I, p. 429.

[2] Axelrad, *J. Ind. Eng. Chem.*, **9**, 1123 (1917).