insoluble amorphous tetranuclear substance which is probably di-(di-*m*-xylorcinol) ether.

The action of bromine on *m*-xylorcinol, on monobromo-*m*-xylorcinol and on di-*m*-xylorcinol, and the oxidation of monobromo-*m*-xylorcinol by means of ferric bromide in aqueous solutions have also been investigated.

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SYNTHETIC GLYCERIDES. II. REFRACTIVE INDICES OF GLYCERIDES OF KNOWN CONSTITUTION

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In a previous paper,[1] methods for the synthesis of symmetrical and unsymmetrical triglycerides containing two fatty acids were given in detail and data for their melting points were included. It was pointed out that the melting point of the symmetrical isomer in each of the sets of isomeric triglycerides made was slightly higher than that of the unsymmetrical isomer. In continuing a study of the relation between their molecular structure and physical properties, a study of the refractive indices of these isomers has been made.

Although the refractive index is one of the most widely used physical constants for the identification of natural glycerides (oils and fats), very little is known of the relation of this property to the constitution of the component glycerides. Furthermore, as stated by Myddleton and Barry,[2] "at present it is not known whether the refractive index of a mixed triglyceride is the same as the corresponding mixture of simple glycerides." In this paper data are also given for the comparison of three sets of isomers with equivalent mixtures of the corresponding simple triglycerides.

It was expected that any differences in the refractive indices of the isomers would be small. Apparatus was, therefore, devised by means of which a constant temperature could be held for a considerable length of time and which permitted the use of an immersion refractometer.

Apparatus.—The constant temperature bath was a round three-liter flask with the original neck shortened and three other necks, each one inch in diameter. These contained, respectively, the immersion refractometer, leads for the heating element, a standardized thermometer and a Liebig condenser.

A Zeiss immersion refractometer was used, fitted with an auxiliary prism and a metal beaker. The metal beaker made the enclosed sample air and water tight. As

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[1] H. P. Averill, J. N. Roche and C. G. King, THIS JOURNAL, **51**, 866 (1929).

[2] W. W. Myddleton and T. H. Barry, "Fats, Natural and Synthetic," Ernest Benn, Ltd., London, **1924**, p. 93.

a further precaution a glass tip was placed over the end of the metal beaker and held in place by a tightly fitting rubber stopper protected with tin foil This stopper was about three-eighth of an inch thick, allowing uniform heating of the prisms and an uninterrupted transmission of heat into the metal case. Another rubber stopper in the shoulder of the flask held the refractometer in place. The lower end of the condenser was beveled so that the condensate could not form a seal and thus vary the pressure inside the flask. The whole apparatus was supported on a cork ring and held by a similar ring on top.

One degree variation in temperature would change the refractive index approximately 4 in the fourth place. By means of the vapor-bath it was possible to hold the temperature constant within $\pm 0.02°$ as long as desired. By using liquids such as acetone, methyl alcohol and ethyl alcohol, the temperature inside the bath reached a maximum within five or six minutes, and thereafter remained practically constant. Several runs were recorded in which the temperature did not vary more than 0.01° during thirty minutes. By the use of sodium light the border line was sharp and could be checked repeatedly to ± 0.02 scale divisions, which is equivalent to ± 5 in the sixth place for the index of refraction.

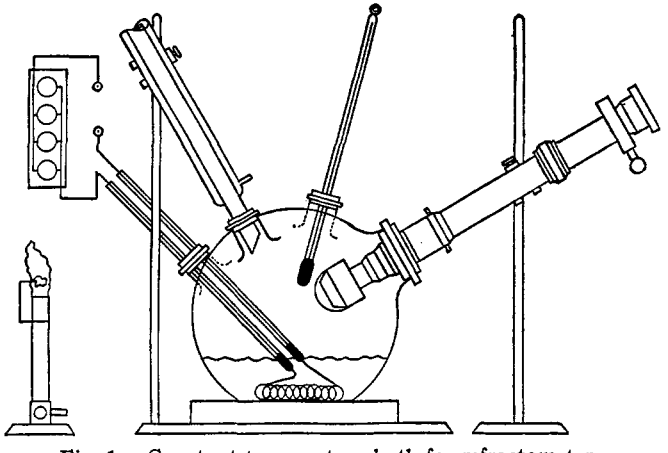

Fig. 1.—Constant temperature bath for refractometer.

Measurement of Refractive Indices.—Since there is some question as to the stability of a triglyceride when kept even at room temperature, the refractive indices were measured within a few days from the date of final crystallization. To remove any final traces of solvent, the crystalline compounds, already very dry, were placed in a vacuum desiccator at 40° and subjected to a vacuum of 8 mm. for a period of several hours. They were then carefully melted over a hot-plate and a few drops applied to the warm prisms. The metal beaker was then put in place and the refractometer inserted into the bath as shown in the accompanying diagram.

The values given in Table I for exact temperatures were obtained from readings near these points, corrected to the exact temperatures by use of the dn/dt factors obtained from a series of readings near those temperatures.

Discussion of Results.—It is evident from the data given in Table I that the symmetrical mixed triglycerides are characertized by a higher

TABLE I

REFRACTIVE INDICES

Compound	Refr. Index at 70°	Refr. index at 75°
β-Stearodilaurin	1.44031	1.43850
α-Stearodilaurin	1.43986	1.43789
Equiv. mixture of simple triglycerides	1.44036	1.43859
β-Stearodipalmitin	1.44325	1.44160
α-Stearodipalmitin	1.44289	1.44115
Equiv. mixture of simple triglycerides	1.44289	1.44112
β-Laurodimyristin	1.43901	1.43719
α-Laurodimyristin	1.43798	1.43548
Equiv. mixture of simple triglycerides	1.43847	1.43661
β-Laurodipalmitin	1.44044	1.43830
α-Laurodipalmitin	1.44016	1.43789
β-Acetodipalmitin	1.43749	1.43567
α-Acetodipalmitin	1.43709	1.43526

Average dn/dt for five symmetrical isomers, 0.00037

Average dn/dt for five unsymmetrical isomers, 0.00039

Average dn/dt for three mixtures of simple triglycerides, 0.00036

index of refraction than that of their unsymmetrical isomers (average difference for five sets of isomers, 0.00062 at 75°).

The index of refraction of equivalent mixtures of simple triglycerides may be expected to fall closely within the range covered by the respective isomers. From the constancy of readings over a period of an hour or more at 75°, it is evident that the isomeric mixed triglycerides are comparatively stable at this temperature when isolated in pure form.

Summary

Apparatus was devised for using an immersion refractometer in a constant temperature bath at a range of 65–78°. The refractive indices of five sets of isomeric mixed triglycerides (two fatty acids) have been determined at 70 and 75°. In each case the symmetrical isomer had the higher value, the average difference being 0.00062 at 75°. The average dn/dt values over this temperature range are also given. Equivalent mixtures of simple triglycerides gave values lying within the range of the corresponding isomeric triglycerides.

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