time. Our present purpose is merely to indicate that the hydrochloride as obtained by us is essentially similar to that reported by others. The most significant criterion for this purpose is that of physiological activity. Representative curative tests on rats by the injection method appear in Table II.

TABLE II

CURATIVE TESTS ON POLYNEURITIC RATS

Prep. No.	Dose mg. × 10^{-3}	Result	Duration of cure, days
1920	3.75	Improved	..
	3.75	Recovered	10
	3.75	Improved	..
	5.0	Recovered	9
	5.0	Recovered	8
	5.0	Recovered	8
	7.5	Recovered	9
	10.0	Recovered	12
1944	3.75	Improved	..
	3.75	Recovered	5
	5.0	Improved	..
	5.0	Recovered	8
	5.0	Recovered	7
	7.5	Recovered	8

Additional evidence of a high level of curative effect was afforded by treatment of pigeons rendered polyneuritic by feeding on autoclaved wheat; 4 to 5 γ per os produced cures. Numerous feeding tests at various levels of dosage on both rats and pigeons will shortly be reported elsewhere. No polyneuritis has appeared in either case when the daily dose by mouth amounted to 0.005 mg.

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Summary

A method is described for securing consistent yields of antineuritic vitamin hydrochloride of approximately 5 g. per ton of rice polish. This represents a recovery of about 25% of the amount present in the rice polish, a yield several fold larger than heretofore reported. The process has been developed on a factory scale up to about a thousand fold concentration of the vitamin. Thereafter the process is well handled in laboratory glassware.

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[CONTRIBUTION NO. 279 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Synthetic Glycerides. V. Mixed Triglycerides of the Dilaurin Series[1]

BY O. E. MCELROY AND C. G. KING

The synthesis of mixed triglycerides has been undertaken primarily to provide compounds of known molecular structure analogous to the naturally occurring fats for the further study of their biological and physico-chemical relationships. Very little information is available concerning the chemical or physical properties of glycerides of known molecular structure, and much as recorded is erroneous, due to faulty methods of synthesis. The ease of migration of acyl groups from the β- to the α-position on glycerol has been responsible for many of the recorded errors.

Experimental

The acyl chlorides, used as intermediates, were prepared by the method recommended by McMaster and Ahmann,[2] from the acids (Eastman Kodak Co.) and thionyl chloride. The high molecular weight α-monoglycerides were prepared by the action of acyl chlorides on acetone-glycerol followed by hydrolytic removal of the acetone.[3] For the α-monoglycerides of acetic and butyric acids, the direct esterification method[4] was used. Fischer's method[5] for the preparation of symmetrical diglycerides was used in all cases, and followed by esterification with one mole of the second acyl chloride to furnish the symmetrical mixed triglycerides. The unsymmetrical isomers were prepared by treating the α-monoglycerides with two moles of the second acyl chloride.

Synthesis of Triglycerides

The preparation of the isomeric capryl dilaurins will serve to illustrate the general procedures followed.

α-Capryl-α′,β-dilaurin.—Lauryl chloride (3.58 g.) dissolved in chloroform was added to a mixture of α-monocaprin (2.02 g.) and 4 g. of quinoline. The mixture was allowed to stand at room temperature for five days, taken

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[1] This paper is based upon a dissertation presented by O. E. McElroy to the Graduate School in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] L. McMaster and F. E. Ahmann, THIS JOURNAL, **50**, 147 (1928).

[3] E. Fischer, M. Bergmann and K. Barwind, *Ber.*, **53**, 1589 (1920).

[4] H. A. Schuette and J. T. Hale, THIS JOURNAL, **52**, 1978 (1930).

[5] E. Fischer, *Ber.*, **53**, 1621 (1920).

up in ether and washed with half normal sulfuric acid to remove quinoline, and with 10% potassium carbonate solution to remove acids. After drying, the ether was evaporated and the product was purified by recrystallization from alcohol and a second solvent, either acetone or petroleum ether; molecular weight found 607, calculated 610.

β-Capryl-α,α′-dilaurin.—Capryl chloride (1.6 g.) dissolved in 10 cc. of chloroform was added to a mixture of 3.7 g. of dilaurin with 4 cc. of quinoline, and held at 37° for five days. It was then dissolved in ether, washed, recovered by evaporation, and purified by recrystallization; molecular weight found 598, calculated 610.

Molecular weights were determined by the ebullioscopic method of Menzies and Wright.[6] Refractive indices, melting points and solubilities were determined by methods described previously.[7,8]

The names and properties of the compounds prepared are listed in Table I.

Table I

Properties of Mixed Triglycerides

Compound	M. p., °C.	Refractive index, 70°	Solubility, g. per 100 cc. of alcohol at 23°
β-Palmityl-α,α′-dilaurin	47.8	1.43980	0.38
α-Palmityl-α′,β-dilaurin	44.8	1.43965	.54
β-Myristyl-α,α′-dilaurin	50.2	1.43907	.25
α-Myristyl-α′,β-dilaurin	42.8	1.43878	1.21
β-Capryl-α,α′-dilaurin	38.8	1.43705	3.02
α-Capryl-α′,β-dilaurin	32.6	1.43640	9.00
β-Caprylyl-α,α′-dilaurin	30.2	1.43643	14.34
α-Caprylyl-α′,β-dilaurin	28.4	1.43576	16.31
β-Acetyl-α,α′-distearin	62.0	1.43970	0.06
α-Acetyl-α′,β-distearin	55.2	1.44045	.43
β-Butyryl-α,α′-distearin	51.0		

x-Ray studies have been made of the dilaurin series and will be reported separately.

Discussion of Results

Previous work[7,8] in this Laboratory with analogous series of compounds indicated that the symmetrical isomer of a given pair would have a higher melting point, a higher refractive index and a lower solubility than the unsymmetrical compound, and that an increase in the length of the third fatty acid chain present increased the melting point and the refractive index. All of these general relations were found to hold for the dilaurin series from the C_6 to the C_{14} members. The stearyl dilaurins, described previously,[7] and the palmityl dilaurins have lower melting points, however, than the corresponding myristyl compounds. A break similar to this is indicated for the distearin series below the C_6 compounds by the high melting points of the acetyl isomers and of β-butyryl-distearin. Attempts to prepare α-butyryl-distearin were unsuccessful. The results indicated that the butyryl group had been replaced by the longer chain, which was surprising in view of the stability of the neighboring members of the series.

The authors are indebted to Dr. J. N. Roche for his counsel during the progress of the investigation.

Summary

The following triglycerides of the dilaurin series have been prepared and their melting points, refractive indices, and solubilities recorded: α- and β-palmityl dilaurin, α- and β-myristyl dilaurin, α- and β-capryl dilaurin, and α- and β-caprylyl dilaurin. The analogous acetyl-distearins and β-butyryl-distearin were also prepared and identified.

The tendency of the symmetrical isomer to have a higher melting point, a higher refractive index, and a lower solubility than the unsymmetrical isomer has been further established. Two examples of "breaks" in the relationships of melting point to chain length were found.

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[6] F. G. F. Menzies and S. L. Wright, This Journal, **43**, 2312 (1921).

[7] H. P. Averill, J. N. Roche and C. G. King, *ibid.*, **51**, 866 (1929); **52**, 365 (1930).

[8] H. E. Robinson, J. N. Roche and C. G. King, *ibid.*, **54**, 705 (1932).