SHORT COMMUNICATIONS

The Formation of Lysolecithin by Reductive Cleavage of Egg Yolk Lecithin with Lithium Aluminum Hydride

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(Received February 16, 1963)

The preparation of lysolecithins by controlled chemical reactions is of interest since they are utilized as the starting material for resynthesis of "mixed acid" lecithins (two different fatty acids being esterified). Recently, Marinetti[1] has reported that the treatment of lecithin with sodium methoxide at 0°C gives a mixture of α- and β-lysolecithin in a yield of 35%. This process is, however, accompanied by the formation of glycerylphosphorylcholine. Another disadvantage is that in such a polar solvent isomerization of the β-lysolecithin to the α-form and racemization of the β-carbon of the glyceryl moiety occur, though perhaps to only a small extent under the conditions employed. The optical purity of lysolecithin in the resynthesis of lecithins is of prime importance; our method of reductive cleavage of one acyl group of lecithin with lithium aluminum hydride in anhydrous ether is considered to meet this requirement since it has already been demonstrated that the product, glycerylphosphorylcholine formed, on removal of the two acyl groups from L, α-lecithin by the reducing agent retains the configuration of the latter[2]. A further advantage of this reaction is that lysolecithin may be the sole product, provided appropriate reaction conditions are found.

Purified egg yolk lecithin prepared by Hanahan's method[3] was treated with a dilute solution of lithium aluminum hydride in anhydrous ether according to the procedure described previously[2]. The reaction mixture was separated into the ether, aqueous, and inter-phase and the aqueous phase extracted with chloroform. The ether and chloroform solutions were analyzed for inorganic and organic phosphorus and examined by paper-chromatography[4].

Some typical examples of the results obtained are shown in Table I; substantial amounts of organic phosphorus are found in both organic solutions and insignificant amounts in the aqueous phase. Table II shows the R_f values of the products formed. The compound with R_f values higher than 0.2 is considered to be the unchanged lecithin since it was observed in separate experiments that an R_f value of 0.32~0.35 for pure lecithin became smaller, 0.25, when mixed with a large amount of the reduction products (supposedly containing considerable amounts of lysolecithin). The product with an R_f

TABLE I. REACTION CONDITIONS AND RECOVERY OF PHOSPHORUS

Lecithin : $LiAlH_4 = 1 : 1.5$ (mole ratio)

Temp., °C	6	8	8	10
Time, min.	20	20	80	20
Ether phase *P*, %	76.6	67.9	41.5	83.2
Chloroform phase *P*, %	16.7	12.0	30.0	25.8
Aqueous phase *P*, %	1.1	2.7	5.5	7.7

The percentage recoveries are based on the phosphorus content of the lecithin sample employed.

TABLE II. R_f VALUES OF THE PRODUCTS PRESENT IN ETHER AND CHLOROFORM EXTRACT

	Method of detection		Compd. assumed
	P	Rhodamine-6G	
Ether phase	0.10	0.11~0.14	Lysolecithin
	0.25~0.34	0.22~0.24	Lecithin
		0.95	Fatty alcohol
Chloroform phase	0.11~0.14	0.11	Lysolecithin
	0.22~0.29	0.22~0.29	Lecithin
		0.96	Fatty alcohol

Solvent system, diisobutyl ketone : acetic acid : water, 40 : 20 : 3 (v/v/v)

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1) G. V. Marinetti, *Biochem.*, **1**, 350 (1962).

2) C. Urakami H. Okura and M. Okada, This Bulletin, 33, 144 (1960).

3) D. J. Hanahan et al., *J. Biol. Chem.*, **228**, 680 (1957).

4) G. V. Marinetti, *J. Lipid Research*, **3**, 1 (1962).

value 0.10～0.14 is therefore considered to be lysolecithin. The detection of lysolecithin in the ether phase, however, is peculiar as it is generally regarded to be insoluble in ether. This may be explained by the fact that the unchanged lecithin makes lysolecithin soluble in ether, as has been observed by Lea⁵⁾. No detectable amount of glycerylphosphorylcholine was found in the aqueous phase.

Accordingly, these results indicate that the method is promising for the preparation of optically pure lysolecithin, provided optimum reaction conditions are found. Further studies on a maximum extent of the cleavage and identification of the products are in progress.

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5) C. H. Lea et al., *Biochem. J.*, **60**, 353 (1955).