SHORT COMMUNICATIONS

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The size and shape of micelles of some synthetic phospholipids in aqueous dispersions

In a paper by BIRD *et al.*¹ the authors have suggested that the difference in the rates of hydrolysis by phospholipase A (EC 3.1.1.4), of two isomeric mixed acid lecithins, is probably due to differences in the micellar properties of their aqueous sols. An examination of the micelles in dispersions of these compounds, prepared by ultrasonic irradiation, is reported in this paper. The results show that there are differences in the asymmetry of the micelles formed by the two isomers which can account for the observed differences in hydrolysis rates.

The four synthetic L- α -lecithins examined had the following fatty acid compositions: A, dibutyl; B, dioleyl; C, γ -butyryl- β -oleyl; D, γ -oleyl- β -butyryl; they were prepared as previously described¹.

Clear sols of all these lecithins were obtained by ultrasonic irradiation of 2 % (w/w) dispersions prepared by the method used for natural lecithins². The irradiation was continued for 2 h, a period which has been found to give homogeneous sols with natural lecithins. The irradiated sols of A and B were mobile, C was somewhat more viscous, D was highly viscous.

The size and shape of the dispersed aggregates or micelles, were studied by measurements of light scattering using an apparatus described in a previous communication², by measurements of viscosity at different concentrations and by sedimentation equilibrium studies in a Beckman ultracentrifuge.

The results of the measurements are summarised in Table I.

TABLE I

MICELLAR PROPERTIES OF SOME SYNTHETIC LECITHINS AND THEIR SUSCEPTIBILITY TO PHOSPHOLIPASE A

Fatty acid composition of the L- α -lecithin	Light scattering		Mol. wt. by sedimentation	Viscosity		Per cent hydrolysis by phospholipase A in 1 h
	Micellar weight	Radius of gyration (nm)		Viscosity increment $\left(\frac{\eta_{sp.}}{(\Phi)}\right)_{\Phi \rightarrow 0}^*$	Axial ratio for prolate ellipsoids assuming no hydration	
A. di-butyl	$> 10^4$	—	$5.8 \cdot 10^3$ (1)	2.5	spheroidal	5
B. di-oleyl	$3.2 \cdot 10^6$	16	$3 \cdot 10^6$ (2)	2.6	spheroidal	37
C. γ -butyryl- β -oleyl	$2 \cdot 10^6$	60	—	6.6	8	62
D. γ -oleyl- β -butyryl	$3.4 \cdot 10^6$	90	$3.1 \cdot 10^6$ (1)	48	70	complete in 5 min

* Φ is the volume fraction of solute.

(1), value obtained by velocity measurements.

(2), value obtained by equilibrium measurements.

The micelles of both dibutyl and dioleoyl lecithin are spheroidal and these compounds are hydrolysed by phospholipase A more slowly than the mixed acid lecithins. Compound C has micelles which are more asymmetrical than A or B and this asymmetry is coupled with an increase in the rate of hydrolysis. Compound D forms highly asymmetric micelles which are very rapidly hydrolysed by the enzyme.

The order of asymmetry of the micelles is shown by the increasing radius of gyration from B to C to D, this radius obtained from light-scattering measurements is, however, sensitive to polydispersity in the sols. A better indicator of asymmetry is the viscosity increment which shows a very large difference between C and D, similar to the large difference in rates of hydrolysis between these two compounds. The axial ratios from viscosity measurements given in Table I are not too certain because the more asymmetrical micelles of C and D may be hydrated, although the negligible slope of the Zimm-plot lines representing light scattering against concentration, suggests that there is little solute-solvent interaction. The low viscosity numbers for A and B indicate that the micelles are spheroidal and this shape appears to stabilise them against the enzyme. The light-scattering results indicate that the micelles of C and D are elongated structures and these shapes facilitate enzyme attack.

The dispersions of D resembled mixed lecithin-lysolecithin sols³ in having very high viscosities. Above a concentration of 0.25 % (w/w) the sols of Compound D had non-Newtonian flow properties.

In the light of these results it is interesting to speculate on the possibility that in a living system lysolecithin may act as an auto-catalyst in the hydrolysis of lecithin by phospholipase A. For example, the first action of this enzyme, contained in snake venom, on serum lecithin would be to produce traces of lysolecithin which would couple with further lecithin to give a viscous dispersion containing open, asymmetrical micelles which would then be subject to more rapid attack by the enzyme.

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A simple spectro-refractometer

The optical rotatory power of a substance in solution is dependant, amongst other things, on the refractive index of the solution. In order to compare results

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