

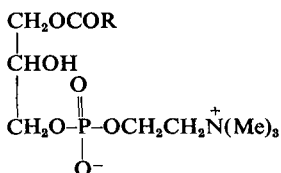
THE SURFACE ACTIVITIES OF α -AND β -(ACYL) LYSOLECITHINS

BY N. ROBINSON AND L. SAUNDERS

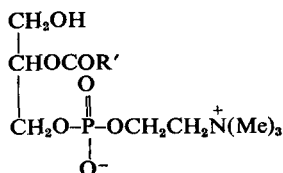
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The lysolecithins can be regarded as derivatives of monoglycerides and would be expected to possess α or β acyl linkages; the two lysolecithins examined in the present work are therefore considered to have the structures:—



α -(acyl) lysolecithin



β -(acyl) lysolecithin

R and R' are unsaturated and saturated hydrocarbon chains respectively

The sample of α -lysolecithin, obtained by acetic acid treatment of the choline plasmalogen of ox heart¹, possessed a high degree of unsaturation, whereas β -lysolecithin, obtained by the action of snake venom on lecithin isolated from egg yolk, contained a fatty acid moiety which had a very low degree of unsaturation.

The present investigation was undertaken to compare the surface activity of the two lysolecithins. Each compound possesses two distinctly different regions in the molecule, a fatty acid chain of non-polar character and another region containing the phosphate-choline group of a polar nature. The distance between these two regions in the α -lysolecithin is greater than in the β -lysolecithin and hence the amphipathic character was expected to be more pronounced in the former. On the other hand, the presence of unsaturated linkages in the fatty acid radical of the α compound gives the molecule an increased affinity for water which is likely to lessen its surface active properties.

Preparation of lysolecithins. β -(acyl) lysolecithin was prepared by treating lecithin obtained from egg yolks with Russell viper venom according to the method previously reported². The α -(acyl) lysolecithin was a gift from Dr. G. M. Gray, Lister Institute of Preventive Medicine. Analysis of the α -compound (made by the Lister Institute) and the β -compound (the authors') gave the following:—

	α	β
Nitrogen (per cent on dry wt.)	2.76	2.72
Phosphorus (per cent on dry wt.)	5.9	5.98
N:P ratio	1:0.97	1:1.02
Double bonds/mole fatty acid ester	2.22	0.12

The mean molecular weights calculated from the nitrogen and phosphorus contents were 518 and 516 respectively.

Preparation of aqueous sols. Sols of each lysolecithin were prepared by evaporating a sample of the stock solution of the compound to dryness, dissolving the known weight of material in water which had been previously distilled, passed down a small column of mixed strong ion exchange resins and then saturated with nitrogen. The sols were made up to volume and diluted when required; the α -lysolecithin sol had a pale yellow colour and the β -lysolecithin sol was colourless; both were optically clear.

Surface tension apparatus. The surface tension measurements were made at 25° and 40° using the ring (dynamic³) and Wilhelmy plate (static⁴) methods employing a chainomatic balance⁵. The Wilhelmy plate method was used for examining very dilute solutions to obtain surface areas.

Results and discussion. The effects of α - and β -lysolecithins on the surface tension of water are shown in Figure 1. At 25° and concentrations of 0.1 per cent w/v the α -compound lowered the surface tension of water to 39.0 dyne/cm., whereas the β -compound only lowered the surface tension to 41.0 dyne/cm. At 40° the α -compound again showed the greater surface activity by lowering the surface tension to 37.2 dyne/cm. compared with a lowering to 38.7 dyne/cm. obtained with the β -compound. The

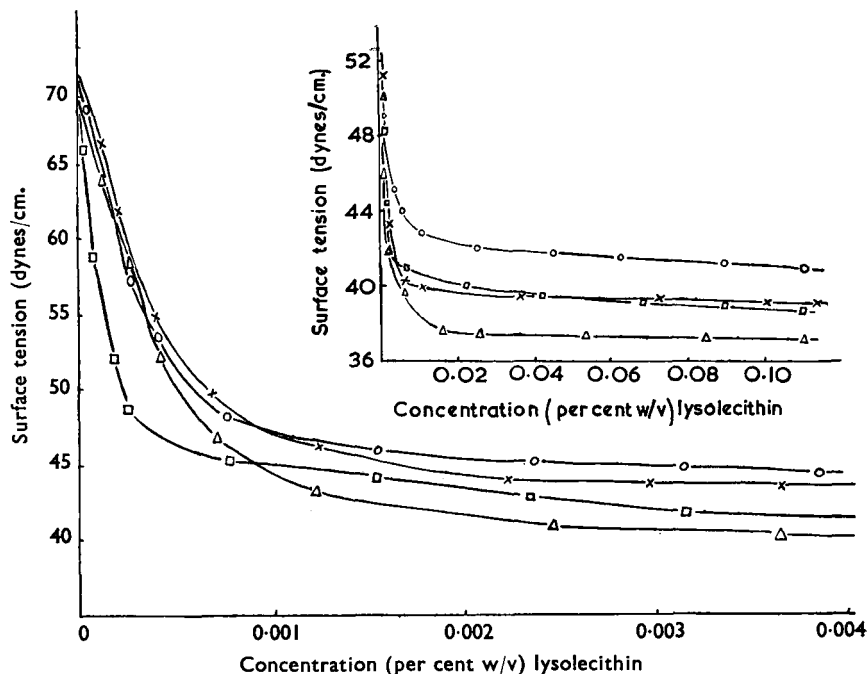


FIG. 1. Effect of α - and β -(acyl)lysolecithins on the surface tension of water. X, α -Lysolecithin at 25°; O, β -lysolecithin at 25°; Δ , α -lysolecithin at 40°; \square , β -lysolecithin at 40°.

THE SURFACE ACTIVITIES OF LYSOLECITHINS

tendency for the α -compound to show the greater effect was found throughout the range of concentrations examined except in the dilute region.

Below a concentration of 0.001 per cent w/v, at both temperatures the β -lysolecithin lowered the surface tension of water more than α -lysolecithin. It is probable that below this concentration the solutes were present as single molecules or small aggregates. In this case the greater surface activity of the β -compound can be attributed to the saturated fatty acid moiety which gives a more pronounced distinction between the lipophilic and hydrophilic regions. It is suggested that this increased amphipathic character assists molecules of the β -lysolecithin to form micelles more readily than the α -lysolecithin, so that above 0.001 per cent w/v fewer single molecules are present in equilibrium with micelles. This results in a smaller lowering of the surface tension of water with β -lysolecithin in the higher concentration range compared with that of the α -compound.

We have suggested elsewhere⁵ that the marked change in the lowering of the surface tension of water within the concentration range 1 to 2×10^{-3} per cent w/v by β -(acyl) lysolecithin at 20° is due to the formation of large micelles. The surface tension/concentration curves in Figure 1 indicate that a critical micelle concentration exists also for the α -compound in this region.

In the dilute region the areas of the α - and β -lysolecithins at the interface were calculated to be 101 and 90 Å² per molecule at zero surface pressure ($\gamma_{\text{water}} - \gamma_{\text{sol}}$) decreasing to 57 and 66 Å² per molecule respectively at a surface pressure of 12.5 dyne/cm. at 40°. These values obtained by using the approximate adsorption isotherm show that on increasing the surface pressure the area of the unsaturated α -compound is considerably reduced. This comparison between the two lysolecithins indicates that considerable solution of the α -compound is probably taking place away from the surface film.

REFERENCES

1. Gray, *Biochem. J.*, to be published.
2. Saunders, *J. Pharm. Pharmacol.*, 1957, **9**, 834.
3. Harkins and Jordan, *J. Amer. chem. Soc.*, 1930, **52**, 1751.
4. Harkins and Anderson, *ibid.*, 1937, **59**, 2189.
5. Robinson and Saunders, *J. Pharm. Pharmacol.*, 1958, **10**, 384.

DISCUSSION

This short communication was presented by MR. N. ROBINSON.

THE CHAIRMAN. What was the evidence that the acyl groups were in the α or β positions? Had the preparations been examined by polarised light? It was well known that the acyl group could wander from the β to the α position. Had the possibility been considered?

MR. A. R. ROGERS (Brighton). Was there any information available whether the two double bonds in the α -compound were conjugated or not? He suggested it might be possible to hydrogenate this unsaturated compound if the double bonds were conjugated without destruction of the

DISCUSSION

rest of the molecule to give a closer comparison of what happened to the fatty acid group in the α and β positions.

MR. H. D. C. RAPSON (Betchworth). It would be interesting to examine the compounds in the semi-solid state. Had the possibility of electro-chemical reduction been considered?

DR. G. B. WEST (London). He noticed that the α -lysolecithin was derived from mammalian sources whereas the β -compound was derived from avian sources. Was this a peculiarity of the type of species or did both occur in the ox and the egg?

MR. ROBINSON replied. By oxidation and examination of the resulting products Hannahan, Long and Penny had established the position of the β -group in 1954. The α -compound had been given to them, and its constitution had been proved in the work referred to in the first reference which was to be published. He agreed that migration favoured the α position. He could give no information about conjugation. They had not been able to analyse the α -compound because they had been given less than 100 mg. Their work on the α -compound had been limited to the surface on account of the small amount available. He had tried electro-chemical reduction with lecithin, but he had not had much success.

DR. SAUNDERS replied. In preliminary experiments under crossed nicols no streaming or birefringence had been observed. With the solid preparations under crossed nicols they had reported a crystalline appearance, and he had no doubt that with better technique they would be able to demonstrate streaming. It must be present in the very viscous sols. The β -compound, which they made, was not extracted directly from natural sources. The lecithin was first made from eggs, and then treated with an enzyme.