Deuterium NMR studies of the interaction of cholesterol with the glycerol backbone of phosphatidyl ethanolamine

R. Ghosh, J. Seelig

Biozentrum der Universität Basel, CH-4056 Basel/Switzerland

Phosphatidyl ethanolamine specifically labelled at the various carbons of the glycerol backbone was extracted from a glycerol auxotroph of Escherichia coli.

The quadrupole splittings observed for the three positions respectively, were all of the order of 20-30 kHz and were not greatly affected by an increase of temperature of 30°C or by the presence of equimolar amounts of cholesterol. As the quadrupole splitting describes the order of the C-D segment, these data suggest that the glycerol moeity possesses a relatively stable conformation. In contrast the presence of cholesterol has been shown previously to dramatically affect the fatty acyl chains by restricting trans-gauche isomerization and also to affect the structure of the ethanolamine head-group.

The deuterium relaxation times, which reflect the motion of the C-D vector measured for all three deuterated positions are the shortest measured so far for a phospholipid molecule (4-10 ms). This suggests that the glycerol backbone is the most slowly reorienting entity of the whole molecule. The relaxation times were little affected by the presence of cholesterol or by a rise in temperature. These observations may be contrasted with fluorescence and magnetic resonance data which suggest that in the presence of cholesterol the rate of lateral diffusion of a phospholipid in the bilayer is decreased by approx. 2-5. It is therefore concluded that the deuterium relaxation times are determined by the rotational diffusion of the backbone segment which is not greatly affected by cholesterol.

Taken together, these data suggest that the glycerol backbone moiety is acting as a relatively rigid centre of rotation of the phosphatidyl ethanolamine molecule, in the liquid crystalline phase.