An Investigation of Whether Vitamin E Preferentially Interacts with Polyunsaturated Lipids

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Vitamin E (α-tocopherol) is a lipid-soluble antioxidant that has the role of protecting phospholipids from oxidation in membranes. A question that remains is how the low concentration of α-tocopherol found in whole cells can protect the relatively large concentration of polyunsaturated phospholipids found in membranes that are particularly vulnerable to oxidative attack. We hypothesize that α-tocopherol co-localizes with polyunsaturated phospholipids to optimize its role as an antioxidant. This project attempts to test this hypothesis by comparing the effect of α-tocopherol on the molecular organization of 1-palmitoyl-2-docosahexaenoyl-sn-glycerophosphatidylethanolamine (16:0-22:6PE, PDPE) and, as a monounsaturated control, 1-palmitoyl-2-oleoyl-sn-glycerophosphatidylethanolamine (16:0-18:1PE, POPE) in mixtures with sphingomyelin (SM). By solid-state ^{2}H NMR spectroscopy, we directly observe order and phase behavior of POPE-d_{31} and PDPE-d_{31} (analogs of POPE and PDPE with a perdeuterated sn-1 chain) in the mixed membranes. In complementary X-ray diffraction and differential scanning calorimetry experiments we further probe phase behavior. The spectra observed for POPE-d_{31} in POPE/SM/α-tocopherol (2:2:1 mol) reveal that a transition from gel to liquid crystalline phase is no longer apparent. At higher temperatures there is a superposition of two spectral components that we ascribe to α-tocopherol promoting a transition from lamellar to inverted hexagonal (H_{II}) phase. Analysis of depaked spectra shows that order is increased by about 8 % and that the amount of H_{II} phase increases with temperature, ranging from 7 (31 °C) to 41 % (65 °C). In mixed membranes where POPE-d_{31} is replaced by PDPE-d_{31}, we shall investigate whether there is a greater tendency for α-tocopherol to increase order and destabilize bilayer structure for the polyunsaturated phospholipid.

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