This article was downloaded by:

On: 29 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

Polyprenyl Phosphates: Do they Form Vesicles, Like Natural Phospholipids?

Y. Nakatani^a; N. Plobeck^a; S. Eifler^a; A. Brisson^{ab}; G. Ourisson^a

^a Laboratoire de Chimie Organique des Substances Naturelles, CNRS, Strasbourg, France ^b Laboratoire de Génétique Moléculaire des Eucaryotes, CNRS, Strasbourg, France

To cite this Article Nakatani, Y., Plobeck, N., Eifler, S., Brisson, A. and Ourisson, G.(1993) 'Polyprenyl Phosphates: Do they Form Vesicles, Like Natural Phospholipids?', Phosphorus, Sulfur, and Silicon and the Related Elements, 77: 1, 125—128

To link to this Article: DOI: 10.1080/10426509308045635 URL: http://dx.doi.org/10.1080/10426509308045635

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POLYPRENYL PHOSPHATES: DO THEY FORM VESICLES, LIKE NATURAL PHOSPHOLIPIDS?

YOICHI NAKATANI, NIKLAS PLOBECK, STEPHANE EIFLER, ALAIN BRISSON+ and GUY OURISSON

Laboratoire de Chimie Organique des Substances Naturelles, CNRS, and +Laboratoire de Génétique Moléculaire des Eucaryotes, CNRS, Strasbourg, France.

<u>Abstract</u> By sonication of sodium di-polyprenyl phosphates, spherical selforganized structures have been obtained. They are plausible models of primitive biomembranes.

INTRODUCTION

Discussions of molecular aspects of prebiotic chemistry tend to be focussed mostly on the origin of proteins and nucleic acids. They are remarkably superficial, or even totally silent, on the prebiotic origin of membranes.

One of us¹ and Wächtershäuser² have independently proposed a theory concerning prebiotic steps in biomembrane formation: the prenyl phosphate - prenyl phosphate condensation (isoprenyl unit elongation) might occur on the surface of a clay or other minerals and thus di-polyprenyl phosphates might form spontaneously and self-organize into vesicles.

SYNTHESIS

We have synthesized di-monoprenyl (n=0) or di-polyprenyl (n=1, 2, 3) phosphates from their phosphites with iodine as oxidant, according to Eq.(1).

$$n = 0, 1, 2, 3$$

$$\frac{3)_{12}/pyr/H_2O}{4) NaOH}$$

$$\frac{1) PCl_3/pyr}{2) H_2O}$$

$$\frac{3)_{12}/pyr/H_2O}{ONa}$$

$$(1)$$

Total yield is 50 -70 % (except for DDMAPNa: 10%). The free acid is not stable. Its sodium salt was prepared and found quite stable, as such or in water solution. The structures of five di-isoprenyl phosphates (DIPPNa: sodium di-isopentenyl phosphate, DDMAPNa: sodium di-dimethylallyl phosphate, $\mathbf{1}$, $\mathbf{n} = 0$, DGPNa: sodium di-geranyl phosphate, $\mathbf{1}$, $\mathbf{n} = 1$, DFPNa: sodium di-farnesyl phosphate, $\mathbf{1}$, $\mathbf{n} = 2$, DGGPNa: sodium di-geranylgeranyl phosphate, $\mathbf{1}$, $\mathbf{n} = 3$) were confirmed by ¹H-NMR, FAB-MS, ³¹P-NMR and microanalysis (Ca salt).

PHYSICAL PROPERTIES

Differential scanning calorimetry showed no endothermic phase transitions (5-70°C) for these phosphates. Isothermal compression study of monolayer films obtained on a water surface from the compounds (n = 2 and 3) showed no fluid-condensed transition. The ¹H-NMR spectra of aqueous suspensions of the phosphates presented fairly sharp peaks. These facts show that their assemblies are fluid. The C_5 phosphates give optically homogeneous solution. The other ones gives milky suspensions.

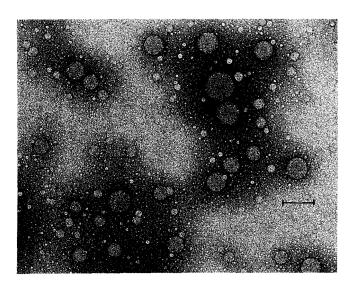
FORMATION OF SELF-ORGANIZED STRUCTURES

We have sonicated an aqueous suspension of each phosphate (Ar, 1 h). After centrifugation and extrusion through polycarbonate filters, the sample was subjected to the observation by electron microscope after staining with uranyl acetate or phosphotungstic acid. Sodium di-geranyl phosphate (C_{10}), di-farnesyl phosphate (C_{15}) and di-geranyl phosphate (C_{20}) gave almost exclusively spherical vesicular type structures with the average diameter is about 200 nm, which was confirmed by dynamic light scattering measurements.

The presence of closed vesicular systems was also demonstrated by a trapped water soluble fluorescence probe, 5-carboxyfluorescein.

Di-dimethylallyl phosphate (C₅) and di-isopentenylphosphate (C₅) are soluble in water: their lipophilic chains are too short to self-organize.

The formation of organized systems already with C_{10} chains (bilayer thickness: about 16\AA) was unexpected.



Electron micrograph of the sonicated sample of sodium di-geranylgeranyl phosphate, stained by uranyl acetate. Scale: 250 nm.

128/[680] Y.NAKATANI, N.PLOBECK, S.EIFLER, A.BRISSON and G.OURISSON

REFERENCES

- G. Ourisson, <u>Pure Appl.Chem.</u>, <u>62</u>, 1401-1404 (1990).
 G. Wächtershäuser, <u>Microbiol. Rev.</u>, <u>52</u>, 452-484.(1988).