

A unique electron-accepting analog of vitamin K<sub>1</sub> found in photosystem I in several species of oxygenic photosynthetic microorganisms was confirmed to be 5'-hydroxyphylloquinone (**1**) through stereo-uncontrolled synthesis. Furthermore, the stereochemistry of **1** obtained from *Synechococcus* sp. PCC 7942 was assigned to be 5'*S* using proline-catalyzed stereocontrolled reactions.

Polar vitamin K<sub>1</sub> (**1**) was synthesized. Stereochemistry of natural **1** was determined to be (5'*S*) after a derivation, where the same derivative was also synthesized.

