

# HYDROLYZES OF TERPENOID DIPHOSPHATES - EFFECTS OF AZIDE ION ON PRODUCTS OF HYDROLYSIS

Por: [ALARCON, M](#) (ALARCON, M); [CORI, O](#) (CORI, O); [ROJAS, MC](#) (ROJAS, MC); [PAVEZ, H](#) (PAVEZ, H); [BACALOGLU, R](#) (BACALOGLU, R); [BUNTON, CA](#) (BUNTON, CA)

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## Abstract

Hydrolysis of geranyl diphosphate (GPP) at pH 7 in water gives largely linalool (LOH) + geraniol (GOH) in the ratio of 3:1. Added  $N_3^-$  generates mixed acyclic allylic azides and increases the LOH:GOH ratio to 15:1 in 2 M  $NaN_3$ , but does not speed up the overall reaction. Hydrolysis of neryl diphosphate (NPP) gives largely alpha-terpineol (TOH) + LOH, but their ratio is not very sensitive to  $NaN_3$  concentration although acyclic azide and small amounts of alpha-terpinyl azide ( $TN_3$ ) are formed. Hydrolysis of alpha-terpinyl diphosphate (TPP) gives large amounts of the cyclic alkenes, limonene and terpinolene. Added  $N_3^-$  does not change the amount of elimination, but increases the ratio of limonene to terpinolene, and diverts some substitution product to  $TN_3$ . Trapping of carbocationic species from GPP by  $N_3^-$  is sharply increased by addition of  $Mn^{2+}$ , which also catalyzes the overall reaction. Products of reaction of GPP are derived from acyclic intermediates and of NPP from acyclic and cyclic intermediates, and ionizations of the three substrates do not generate common carbocationic species.

## Palabras clave

**KeyWords Plus:** [REACTIVITY-SELECTIVITY RELATIONSHIP](#); [SATURATED CARBON-ATOM](#); [ALLYLIC PYROPHOSPHATE](#); [GERANYL PYROPHOSPHATE](#); [CYCLIC MONOTERPENES](#); [STEPWISE MECHANISM](#); [ALPHA-TERPINEOL](#); [BIOSYNTHESIS](#); [CYCLIZATION](#); [SOLVOLYSIS](#)

## Información del autor

### Direcciones:

- + [ 1 ] UNIV CHILE, FAC CIENCIAS, DEPT QUIM, SANTIAGO, CHILE
- + [ 2 ] UNIV CHILE, FAC CIENCIAS QUIM & FARMACEUT, DEPT QUIM, SANTIAGO, CHILE
- + [ 3 ] UNIV CALIF SANTA BARBARA, DEPT CHEM, SANTA BARBARA, CA 93106

## Editorial

JOHN WILEY & SONS LTD, BAFFINS LANE CHICHESTER, W SUSSEX, ENGLAND PO19 1UD

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