

Synthesis of monoterpene hydrocarbons from [1-3H]linalyl pyrophosphate by carbocyclase from *Citrus limonum*

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A partially purified enzyme preparation from the flavedo of *Citrus limonum* utilized [1-3H]linalyl pyrophosphate as a substrate for cyclic terpene hydrocarbon formation more efficiently than the pyrophosphates of nerol and geraniol. The products formed from all three substrates are α -pinene, β -pinene, limonene, and β -terpinene. Nerol and geranyl pyrophosphate inhibit the formation of these products from linalyl pyrophosphate. No free linalyl pyrophosphate could be detected during the enzymatic formation of cyclic terpene hydrocarbons from geranyl pyrophosphate. Mn^{2+} catalyzes the nonenzymatic solvolysis of linalyl pyrophosphate, forming myrcene and ocymenes and no bicyclic hydrocarbons. Linalyl pyrophosphate is a sterically plausible precursor of cyclic hydrocarbons, but the present data support only its role as an alternative substrate and not as an obligatory free intermediate in terpene biosynthesis. © 1982.