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TERPENOIDS. IX. BIOGENESIS OF SOME MONOTERPENOIDS NOT DERIVED FROM A GERANYL PRECURSOR

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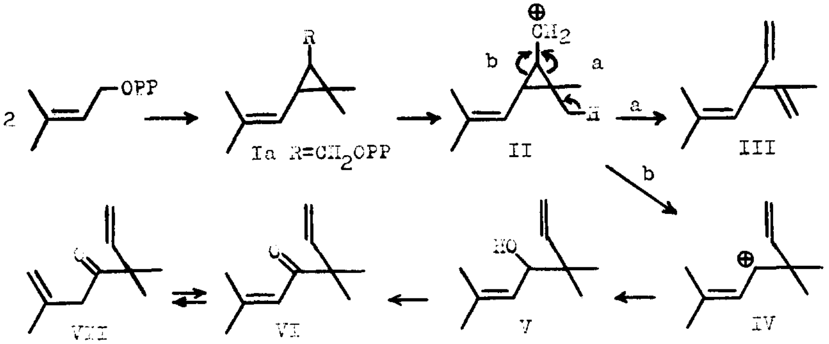
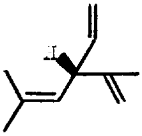
Artemisia ketone (VI) (1), isoartemisia ketone (VII) (1), and the acetate of artemisia alcohol (V) (2) are long-known representatives of the small group of monoterpenes whose carbon skeletons can not be divided into two isoprene units joined head to tail. The recent finding (3) of the hydrocarbon III from Santolina chamaecyparissus L., a plant which contains artemisia ketone (VI), appears to clarify part of the biogenetic route to V, VI, and VII, which is likely to be as shown below.



The cyclopropylcarbinyl cation II (classical ions are written instead of nonclassical alternatives for the sake of clarity), derived by ionization of the corresponding pyrophosphate (Ia), can cleave in two ways (a and b) to give homoallyl cations, with the "a" cleavage accompanied by proton loss to give III, and the "b" cleavage accompanied by formation of the alcohol V or its acetate, sometimes followed by oxidation to VI, which readily equilibrates with VII. Ia has not been found in nature, but esters of the corresponding acid Ib (R=COOH), chrysanthemic acid, occur in plants of the same subfamily (Anthemideae) as artemisia ketone (4).

The simplicity of the above scheme as compared to alternatives and the many precedents for the reactions involved argue for its correctness. We are currently trying to generate the cation II to study its solvolytic behavior. The details of the biogenesis of chrysanthemic acid (Ib,R=COOH) have not been worked out, but it has been shown to be derived from mevalonic acid (5) and a carbene-like addition mechanism has been suggested (4). We propose that the carbene-like addition leads to Ia (or the corresponding alcohol), and oxidation then leads to Ib (R=COOH). If chrysanthemic acid (Ib,R=COOH) and the hydrocarbon III are both biosynthesized from Ia (or the corresponding alcohol) by mechanisms which do not affect the configuration at the asymmetric carbon atom which they have in common, then III has the S configuration, as shown below.



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