

Biosynthesis of Monoterpenes in Rose Petals

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ROSE petals assimilate and very efficiently utilize mevalonate for the synthesis of a range of acyclic monoterpene alcohols.¹ The *trans* allylic alcohol geraniol appears to be the first acyclic non-phosphorylated monoterpene formed from mevalonate in rose petals. Incorporation of mevalonate stereospecifically labelled with tritium into the flower head of the hybrid tea rose Lady Seton² demonstrated that geraniol is formed by stereospecific elimination of the 4*S* proton of mevalonate (the 2*R* proton of isopentenyl pyrophosphate) during double bond formation as might be expected by analogy with other *trans* terpenoid systems.³ The *cis* isomer nerol is formed in the same manner again by 4*S* elimination rather than by elimination of the epimeric 4*R* proton as occurs in biosynthesis of the polycis-isoprene rubber in the latex of the rubber tree *Hevea brasiliensis*.⁴ On the basis of the above findings it has been concluded that geranyl pyrophosphate (or a derivative) is converted to neryl pyrophosphate by *trans* to *cis* isomerization of the 2,3 double bond. This isomerization has not been demonstrated in terpenoid systems. Cell free extracts from rose petals of Lady Seton and Fragrant Cloud contain a dehydrogenase that reversibly oxidizes/reduces geraniol (nerol) and the aldehydes geranial (neral) in the presence of NADP/NADPH. Addition of the sulphhydryl compounds 2-mercaptoethanol or reduced glutathione to the system results in the rapid isomerization of the *trans* aldehyde geranial to an equilibrium mixture of the two isomers geranial/neral, and vice versa, the *trans* isomer predominating. The reversible dehydrogenase is capable, in the presence of NADPH, of reducing both aldehydes back to the corresponding allylic alcohols. This cycle of events results in the isomerization of the *trans*, 2,3 double bond of geraniol to the *cis* double bond of nerol, the aldehyde being the active intermediate. Thiols as well as adding to the double bond of conjugated ene-one systems are known to catalyse *trans/cis* isomerizations of the α/β double bond.⁵ Similar mechanisms have been reported for the enzymatic formation of *cis*, *trans*-farnesol in a cell free system from orange flavedo⁶ and the conversion of *trans,trans*-epoxyfarnesol to the *cis trans* isomer by the fungus *Helminthosporium sativum*.⁷

A further series of reactions occurring in rose petals and petal extracts including reductions, glycosylations, and acylations lead to the formation of dihydro alcohols,⁸ terpene glycosides and monoterpene fatty acyl esters. The overall interrelationship of these various reactions, which appear to occur mainly in the epidermal layer of cells account for the variety of monoterpene components found in the rose petal

¹ FRANCIS, M. J. O. and O'CONNELL, M. (1969) *Phytochemistry* **8**, 1705.

² FRANCIS, M. J. O., BANTHORPE, D. V. and LE PATOUREL, G. N. J. (1970) *Nature* **228**, 1005.

³ POPIAK, G. (1964) *Metabolism and Physiological Significances of Lipids* (DAWSON, R. M. C. and RHODES, D. N., eds.), p. 45, Wiley, New York.

⁴ ARCHER, B. L., BARNARD, D., COCKBAIN, E. G., CORNFORTH, J. W., CORNFORTH, R. H. and POPIAK, G. (1966) *Proc. R. Soc.* **163B**, 519.

⁵ JOCELYN, P. C. (1972) *Biochemistry of the SH Group*, Academic Press, New York.

⁶ CHAYET, L., PONT-LEZICA, R., GEORGE-NASCIMENTO, C. and CORI, O. (1973) *Phytochemistry* **12**, 95.

⁷ SUZUKI, Y. and MARUMO, S. (1972) *Tetrahedron Letters* 5101.

⁸ DUNPHY, P. J. and ALLCOCK, C. (1972) *Phytochemistry* **11**, 1887.

The Constituents of Ninde Oil

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NINDE oil (*Aeolanthus gamwelliae*; Labiatae) was first discovered in 1931 by the Misses Gamwell, who lived in what is now Zambia. The history of the development of this novel essential oil illustrates many of the problems involved in the development of such an oil, which is used as a substitute for palmarosa oil. First, problems were encountered in propagating and growing the crop; when these were overcome, there was a collapse in the market for palmarosa oil which led to the abandonment of production of ninde.

Some 14 years later when the price of palmarosa oil had recovered, further efforts were made to develop the oil both in Zambia and in Malawi, in collaboration with the Tropical Products Institute, the staff of