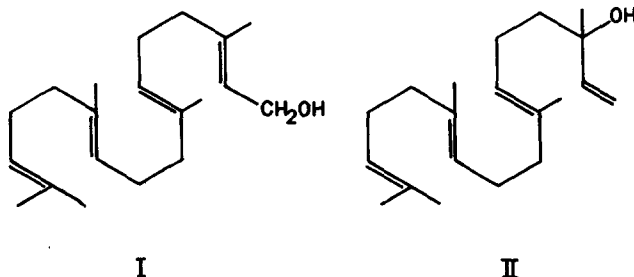


ISOLATION AND CHARACTERISATION OF GERANYLGERANIOL
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GERANYLGERANIOL (I) is considered as the immediate precursor of diterpenoids¹ and carotenoids² in nature. Though, its allylic isomer, geranyl-linalool (II) has been found³ to occur in trace quantities in the jasmin concrete, the isolation of geranylgeraniol from a natural source has not



been reported so far⁺. We now report on its isolation from the wood of Cedrela toona Roxb., wherein it occurs both as a free alcohol^{**} as well as esterified with fatty acids. It must be mentioned that geranylgeranic acid⁴ and geranyl-linalool³ have been synthesised and, the formation of

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⁺ It has been brought to our notice that geranylgeraniol has been very recently isolated from linseed oil: E. Fedeli, P. Capella, M. Cirimele and G. Jacini, J. Lipid Res. 7, 437 (1966).

^{**} The pleasant aroma of the wood is unmistakably due to this alcohol.

geranylgeraniol during biosynthetic experiments reported^{5,6}.

By systematic chromatography of the pet. ether soluble portion of acetone extract of the de-barked trunk wood, we obtained a TLC (AgNC₃-SiO₂ gel) and GLC pure, colorless liquid (b.p. 145°/0.35 mm, n_D³⁰ 1.4932, d₄³⁰ 0.9044), with a pleasant floral note, in a yield of 4% on the pet. ether extract. The compound analyses for C₂₀H₃₄O(± CH₂) and is clearly an alcohol (IR: 3200, 1000 cm⁻¹. Acetate, n_D³⁰ 1.4832; IR: 1745, 1232 cm⁻¹), oxidisable by active MnO₂ to an αβ-unsaturated aldehyde, b.p. 150°/0.5 mm, n_D³⁰ 1.4990; λ_{max}^{EtOH} 237 mμ (ε 14,360); IR: C=O 1682, C=C 1635, 1610 cm⁻¹; Semicarbazone, m.p. 118-122°, λ_{max}^{EtOH} 271 mμ (ε 31,250).

Its PMR spectrum⁷ shows signals assignable to five vinylic methyls (9H singlet at 97 c/s and, 6H singlet at 101 c/s), six vinylic methylenes (two signals, essentially singlets, located at 120 and 123 c/s and corresponding to a total of 12H), two protons linked to carbon bonded to hydroxyl (two one-H singlets at 240 and 247 c/s; these signals occur at 267 and 275 c/s respectively in the acetate and are absent in the PMR spectrum of the aldehyde) and four vinylic protons (two multiplets, essentially overlapping triplets, centred at 307 and 324 c/s. From these data it was clear that the compound is an acyclic, isoprenoid primary alcohol. As a matter of fact, its IR spectrum is quite similar to those of geraniol and trans-farnesol. The fact that the ratio of the vinylic methyl protons to those of -CH₂CH is 15:2, strongly suggested that the primary alcohol, under discussion, should be the long-sought-for geranylgeraniol (I). The PMR spectrum of the corresponding aldehyde is also in complete agreement with this conclusion. Further confirmation was obtained as follows.

Since, the vinyl proton on the olefinic linkage carrying the carbinol group is expected to be chemically shifted from other vinyl protons in the isoprenoid chain,

it was anticipated that the ratio of areas under these signals can give the number of total isoprene units in the chain. This is borne out from the data given in Fig.1, which clearly support the presence of four isoprene units in our alcohol. A better estimation is possible in the corresponding aldehyde, as the C₂-vinyl proton is now further deshielded.

Finally, its mass spectrum shows the molecular ion at m/e 290 as required. Table 1 shows the important peaks; their genesis will be discussed in the detailed communication.

Table 1 - Important peaks in the mass spectrum of geranylgeraniol.

m/e	% base peak	% Σ 50
290	2	0.3
217	7	1.0
132	77	11.5
104	100	14.7
91	70	10.4
69	36	5.0

Bates and co-workers^{8,9} have demonstrated that in acyclic isoprenoids it is possible to establish the geometry of the trisubstituted olefinic linkages by a consideration of the vinyl methyl signals in their PMR spectra. The methyl signals pattern observed for our compound requires this geranylgeraniol to have the all-trans geometry, as shown in I.

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