

Geranylfarnesol, a New Acyclic C₂₅ Isoprenoid Alcohol isolated from Insect Wax

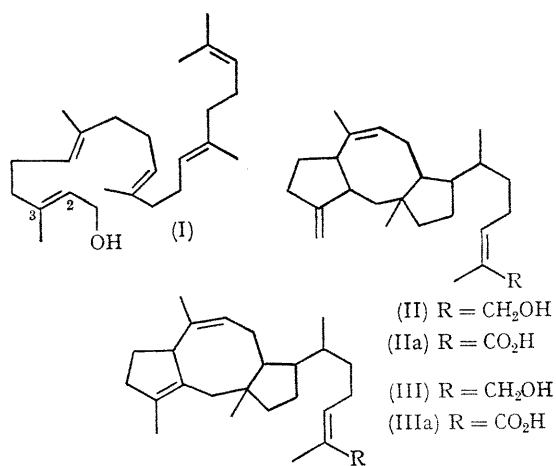
By TIRSO RÍOS* and S. PÉREZ C.

(Instituto de Química de la Universidad Nacional de México, México, 20, D.F.)

We have previously isolated ceroplastols I (II) and II¹ (III), albolic acid (IIIa), and ceroplasteric acid (IIa). The structures of albolic acid and ceroplastol II were correlated with that of ceroplastol I. The structure of the last-mentioned was determined by X-ray crystallographic analysis of its 4-*p*-bromobenzoate.²

We now report the isolation and characterization of the acyclic C₂₅ isoprenoid alcohol from the wax of *Ceroplastes albolineatus*, which we have shown to be geranylfarnesol (I).

The geranylfarnesol (I) C₂₅H₄₂O (*M*⁺ 358) showed ν_{\max} 3290, 1665, and 828 cm.⁻¹. The n.m.r. spectrum† showed signals at 1.58 (s, methyl groups *trans* to olefinic protons in the isoprene residues), and 1.65 (s, methyls *cis* to olefinic protons).³ The ratio of areas of these two peaks was 4:1;⁴ signals were also found at 1.70 (d, *J* 1 c./sec., 3-Me) and 2.0 (m, allylic methylene bearing the hydroxy-group). The signals due to the C-4 protons, partially overlapped with the



† δ Values relative to Me₄Si.

signal for the vinylic proton at C-2 (5.3, t, J 7 c./sec.), appeared together at 5.05.

Chromium trioxide-pyridine oxidation of geranylarnesol (I) afforded a conjugated aldehyde (λ_{max} 235 nm.) (M^+ 356) which showed i.r. absorption at 1668, 1625, and 830 cm^{-1} ; the n.m.r. spectrum showed signals at 1.58s and 1.65sh (vinylic methyls), 5.1 or (4 vinylic H), 5.75 (d, J 8 c./sec., C-2 vinylic H), and 9.33 (d, J 8 c./sec., CHO).

The sesterterpenes have been considered to be formed

from the hypothetical geranylarnesyl pyrophosphate (or its biochemical equivalent) which in turn might be constructed from five isoprene units linked head-to-tail in a linear fashion. A successive two-step cyclization of the geranylarnesyl pyrophosphate could give rise to the five-eight-five-membered ring system.⁵ The isolation of geranylarnesol in relatively good yield supports the first part of the hypothesis for the biogenesis of the sesterterpenes.†

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† Geranylnerolidol is the other acyclic sesterterpene, reported by Nozoe *et al.* (ref. 4).

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