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ω - HYDROXYGERANYLFARNESOL, A NEW C_{25} ISOPRENOID ALCOHOL, ISOLATED FROM INSECT WAX †

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Further investigation of the insect wax of Ceroplastes albolineatus afforded a new sesterterpene, ω - hydroxygeranylfarnesol.

In a previous paper[1] we have described the isolation of geranylfarnesol (1), a sesterterpenic alcohol presumably being the precursor for several sesterterpenes (C_{25} isoprenoids) in the insect wax of Ceroplastes albolineatus Cockerell.[2] All compounds isolated from the wax have a primary alcohol or carboxyl group in the side chain, as ceroplastol I and II,[2a,2b] albolineol,[2c] albocerol,[2d,2e] ceralbol,[2f] ceroplasteric and albolic acids.[2g]

We now report the isolation and characterization of an acyclic C_{25} isoprenoid dialcohol from the wax of Ceroplastes albolineatus, which we have shown to be ω - hydroxygeranylfarnesol (2). The isolation of 2 suggests that this diol is an intermediate in the biosynthetic pathway of all compounds mentioned above and it explains the origin of the terminal alcohol or carboxyl group present in the side chain of the cyclic compounds.

ω - Hydroxygeranylfarnesol (2) $C_{25}H_{42}O_2$, a very viscous colorless oil, showed IR absorptions at ν_{max} (film) 3625, 3460, 1675, 1600, 900 and 860 cm^{-1} indicating the presence of OH groups and double bonds. λ_{max} (EtOH) 212 nm (ϵ, 7064). The MS exhibited an M^+ at m/e 474 and other peaks at 356 (M^+-H_2O), 338 (M^+-$2H_2O$), 43 (100%). The PMR ($CDCl_3$) spectrum showed signals at δ 1.58 (brs, 4 methyl groups "trans" to olefinic protons in the isoprene residue),[3] δ 1.70 (d, J=1 Hz, $C_{(3)}$-Me), 2.05 (m, C=C-CH_2-CH_2-C=C); 2.95 (s, OH), 3.8 and 4.0 (s, and d, J=7 Hz, allylic methylenes bearing the hydroxy groups, $C_{(20)}$ and $C_{(1)}$ respectively), 5.21 (m, C=C-H X 4), 5.32 (t, J=7 Hz, C=$C_{(2)}$-H).

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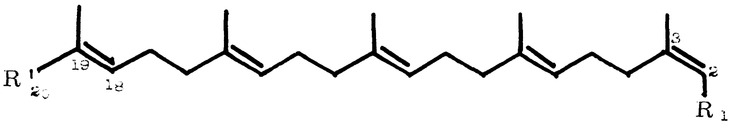
Acetylation of 2 with Ac_2O-pyridine afforded diacetate (2a) as a viscous liquid ν_{max} (film) 1730, 1670, 1600 cm^{-1}; λ_{max} (EtOH), 209 nm (ε, 8281); m/e 398 (M^+-60), 43 (100%). PMR ($CDCl_3$), δ 1.96, 1.98 (s, OAc), 4.35 (s, $C_{(19)}$-CH_2-OAc) and 4.45 (d, $C_{(2)}$-CH_2-OAc).

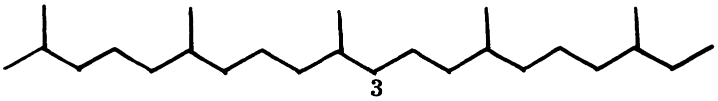
Hydrogenation of 2a in ethyl acetate using Pd/C as a catalyst gave the hydrocarbon 3, which had also been obtained from geranylfarnesyl acetate (1a) under the same conditions.

Jones oxidation of ω-hydroxygeranylfarnesol (2) afforded a conjugated dialdehyde (2b); λ_{max} (EtOH) 233 nm (ε, 19116); ν_{max} (film) 2710, 2750, 1670, 1680 cm^{-1}; (M^+ 370 $C_{25}H_{38}O_2$) PMR ($CDCl_3$), δ 1.58 (brs, C=C-Me X 3); 1.70 (d, J=1.5 Hz, C=$C_{(19)}$-Me), 2.15 (d, J=1.5 Hz, C=$C_{(3)}$-CH_3); 5.1 (m, C=CH X 3), 5.75 (brd, J=8 Hz, C=$C_{(2)}$-H), 6.33 (brt, J=7 Hz, C=$C_{(18)}$-H), 9.10 (s, C=$C_{(19)}$-CH=O), 9.42 (d, J=8 Hz, C=$C_{(2)}$-CH=O).

Ozonolysis of the 3,5-dinitrobenzoate of ω-hydroxygeranylfarnesol (2c) afforded the 3,5-dinitrobenzoate of hydroxyacetone which was compared with an authentic sample by mp and spectroscopic constants. From the above chemical and spectral data it was clear that the new compound represents an acyclic isoprenoid primary dialcohol as shown in 2 with four double bonds all "trans" and Δ^2 "cis" as in geranylfarnesol (1).[2]

1.- R=CH_2OH R'=CH_3
1a.- R=CH_2-OAc R'=CH_3
2.- R=R'=CH_2OH
2a.- R=R'=CH_2OAc
2b.- R=R'=CH=O
2c.- R=R'=CH_2O-CO-$C_6H_3(NO_2)_2$





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