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# THE ISOLATION OF AN ACYCLIC $C_{25}$-ISOPRENOID ALCOHOL, GERANYLNEROLIDOL, AND A NEW OPHIOBOLIN

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Recently, R. Tschesche et al.(1) reported the structures of the acyclic $C_{25}$-alcohols, moenocinol and isomoenocinol, the lipid portion of the antibiotic, moenocimycin. In this communication, we wish to report the isolation and characterization of another acyclic $C_{25}$-isoprenoid alcohol, geranylnerolidol and a new ophiobolin from the phytopathogenic fungi, Cochliobolus heterostrophus, which is responsible for the leaf spot disease of maize.

Glpc analysis of the unsaponifiable portion of the extract indicated the presence of six main components in the less polar fraction. These were recognized as diterpene hydrocarbons(2), sesterterpene hydrocarbons, sesterterpene alcohols and squalene. The two sesterterpene alcohols have been isolated to the extent of ca. 0.1% of the total metabolites by silica gel chromatography and their homogeneity was confirmed by glpc and tlc as well as by nmr and mass spectroscopy.

Compound I, $C_{25}H_{42}O$ ($M^+$, 358), showed a hydroxyl absorption at 3600 $cm^{-1}$ and a terminal vinyl absorption at 925 $cm^{-1}$ in the ir spectrum. The nmr spectrum of I showed signals at $\delta$ 1.20 due to a methyl attached to a carbon bearing a hydroxyl group. The signals at 1.64 can be assigned to the protons of a methyl cis and that at 1.57 to the protons of a methyl trans to the olefinic protons in the isoprene residues(3). The ratio of areas of these two peaks was 1 : 4(4). The ABX patterns due to the vinyl group attached on a tertiary carbon are similar to those of the known tertiary isoprenoid alcohols. The signals are at 4.95

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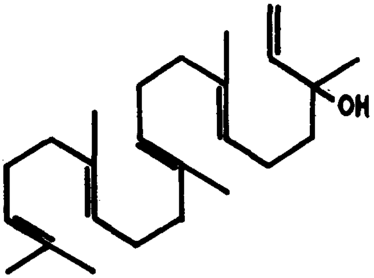

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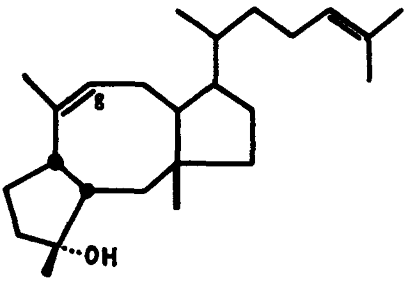

II

($H_A$), 5.12 ($H_B$) and at 5.83 ($H_X$) ($J_{AX}$=10, $J_{BX}$=17, and $J_{AB}$=1.5 cps). From these data it was clear that this compound was the all-*trans* isoprenoid alcohol, geranylnerolidol(I).

Compound II, m.p. 80-1°, $C_{25}H_{42}O$ ($M^+$, 358), $[\alpha]_D$ +23°, showed a hydroxyl absorption at 3500 $cm^{-1}$ in the ir spectrum. Since hydrogenation of II with a Pt catalyst afforded a tetrahydro derivative, $C_{25}H_{46}O$ ($M^+$, 362) and a fully saturated hydrocarbon, $C_{25}H_{46}$ ($M^+$, 346), compound II must be tricyclic. The nmr spectrum showed the presence of six methyl groups at 0.77 (d, J=6.5), 0.86, 1.22, 1.57, 1.65 and 1.74. The signals at 5.09 (1H, diffuse triplet) and at 5.52 (1H, diffuse triplet) can be assigned to the isopropylidene and $C_8$ olefinic protons. The mass spectrum of II exhibits intense peaks at m/e 343, 340, 325, 289, 247, 229 and 69. From the above mentioned data as well as from biogenetical considerations, this compound was assumed to have structure II, which we previously described as a hypothetical precursor of ophiobolin biosyntheses$^{(5)}$.

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## REFERENCES

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2) The diterpene hydrocarbons were thought to be kaurene and isokaurene.

3) R. B. Bates, D. M. Gale and B. J. Gruner, *J. Org. Chem.*, **28**, 1086 (1963).

4) The corresponding ratios for linalol, nerolidol and geranyllinalol are 1 : 1, 1 : 2 and 1 : 3 respectively.

5) S. Nozoe, M. Morisaki, K. Tsuda and S. Okuda, *Tetrahedron Letters*, 3365 (1967).