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FUNGI

MONILIALES

A NEW DEPSIDONE FROM *ASPERGILLUS UNGUIS*

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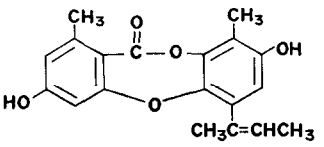
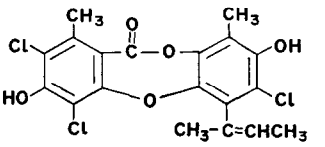
We have isolated a new C19 depsidone, which we designate as 'unguinol', from the mycelium of *Aspergillus unguis* (Emile-Weil and Gaudin) Thom and Raper[1] NRRL 5250 grown on a malt-glucose medium. Structure I appears to be a possible structure for this product, in view of its similarity to nornidulin (II), which is formed by a closely related organism.[2]



(I)



(II)

On crystallization from aqueous ethanol, unguinol gave m.p. 105–110°, shown by NMR to have ethanol of crystallization. Elementary analyses of the solvent-free product (m.p. 203–205°) are in accord with I, as are the values for the dimethyl ether, m.p. 135–137°, and the diacetate, m.p. 142–143°. Structure I is also supported by the NMR spectrum, which shows one vinyl proton and three aromatic protons, two of which are *meta* to one another. The molecular ion peak of *m/e* 326 is the expected value for $C_{19}H_{18}O_5$. The IR carbonyl band of unguinol is at 1695 cm^{-1}; this value is somewhat below the range of 1720–1750 cm^{-1} reported by Rao *et al.*[3] for depsidones, probably due to intermolecular hydrogen bonding.[4] Unguinol gives a poorly defined UV absorption curve with the absorption maximum at 266 nm ($\epsilon = 10\,900$) and a slight peak or leveling at 318 nm.[3]

In agreement with the behavior of depsidones, unguinol takes up one equivalent of alkali to a phenolphthalein end point at room temperature; acidification regenerates the starting material. *A. unguis* NRRL 5250 cannot be distinguished morphologically from *A. nidulans* NRRL 2006, the strain from which Dean *et al.*[2] obtained nornidulin; the two organisms do, however, differ somewhat in cultural behavior. The following physiological characteristics of these organisms have been observed; (a) strain 5250 grown on the chlorine-containing medium on which nornidulin is produced (by strain 2006) gave only a liquid triglyceride, but no chlorinated products; (b) strain 2006 cultivated on the malt-glucose medium used for unguinol production gave only unguinol in good yield; (c) strain 5250 grown on a malt-glucose medium containing KCl gave only unguinol.

[1] C. THOM and K. B. RAPER, *A Manual of the Aspergilli*, p. 169, Williams & Wilkins, Baltimore (1945).
[2] F. M. DEAN, D. S. DEORHA, A. D. T. ERNI, D. W. HUGHES and J. C. ROBERTS, *J. Chem. Soc.* 4829 (1960).
[3] P. S. RAO, K. G. SARMA and T. R. SESHADRI, *Proc. Indian Acad. Sci.* **66A**, 1 (1967).
[4] W. S. BENNET, G. EGLINGTON and S. KOVAC, *Nature, Lond.* **214**, 776 (1967).

EXPERIMENTAL

Production of unguinol. A malt-agar slant was inoculated with *A. unguis* (NRRL 5250 from the ARS Culture Collection here) and incubated at 25° for 4 days. An inoculum was prepared by addition of 1 ml of sterile H_2O to the slant. This spore suspension (0·1 ml) was added to 1 l. of sterilized culture liquor (1 g Difco peptone; 20 g Difco malt extract; 20 g Difco glucose; 1 l. distilled H_2O). After 1 month at 25°, the brown mycelial mat was separated by filtration, washed (H_2O), and dried. The product from 10 flasks (69·5 g) was refluxed for 2 hr with 500 ml of acetone. Filtration and concentration gave 12·51 g of oil and crystals. Extraction with hexane at room temperature left a dark gum which on trituration with Et_2O and filtration yielded 1·54 g of tan crystals of m.p. 103–108°. A second crop raised the yield to 1·82 g of alcoholate. Crystallization from aqueous alcohol gave colorless plates of m.p. 105–110°. TLC with three different solvent combinations showed only one spot.

For analysis the alcoholate had to be dried slowly to prevent the formation of gum that retained solvent tenaciously. This was done by heating the sample *in vacuo* in a rotating tube, the temperature of which was raised from 50 to 90° over 1 hr. The resulting powder, after drying for 1 hr at 120° and 1 mm, melted at 203–205°. (Found: C, 69·6; H, 5·72. $C_{19}H_{18}O_5$ required: C, 69 93; H, 5·56%); ν_{max} (KBr) 3340–3400, 1695, 1605, 1420, 1250–1260, 1142, 1100 cm^{-1}; NMR δ (acetone-d_6) at: 6·61 (d, aromatic proton), 6·52 (s, aromatic proton), 6·45 (d, aromatic proton *meta* to the proton observed at 6·61), 5·56 (qq, vinyl proton coupled to two different methyl groups), 2·39, 2·15 (s, aromatic methyls), 2·04 (m, vinyl methyl), 1·80 (dq, vinyl methyl), 9·00, 3·50 (broad absorptions attributed to hydroxyl protons).

Unguinol diacetate. Acetylation of unguinol with Ac_2O and pyridine at room temperature gave the diacetate, which crystallized from MeOH–H_2O in the form of blocks (m.p. 142–143°). (Found: C, 67·1; H, 5·73. $C_{23}H_{22}O_7$ required: C, 67·31; H, 5·40%); ν_{max} (KRS-5 plate) 1760, 1740, 1415, 1365, 1250, 1189, 1125, 1089, 1050, 1008, 895 cm^{-1}.

Dimethyl unguinol. Unguinol alcoholate in methanol was methylated with an ethereal solution of CH_2N_2. Removal of solvent left an oil that crystallized from 95% MeOH as blocks (m.p. 135–137°). (Found: C, 71·1; H, 6·43. $C_{21}H_{22}O_5$ required: C, 71·17; H, 6·26%); ν_{max} (KRS-5 plate) 1730, 1602, 1570, 1480, 1445, 1415, 1325, 1250, 1230, 1215, 1198, 1195, 1120–1130, 1090, 1070, 1050, 1005, 830–840 cm^{-1}.

Key Word Index—Aspergillus unguis; Fungi; depsidone; unguinol.

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GYMNOSPERMAE

TAXODIACEAE

TERPENES AND STEROLS OF *CUNNINGHAMIA KONISHII*

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Plant. Cunninghamia konishii Hayata. *Previous works.* Wood.[1]

The acetone extractives of the ground bark was steam distilled. The steam volatile oil was analysed by the combination of alumina column chromatography and GLC. The 11 main compounds were isolated and identified as α-cedrene (15%), β-cedrene (10%), caryophyllene (35%), β-selinene (2%), caryophyllene oxide (5%), α-terpineol (10%), 4-terpineol (0·2%), cedrol (3%), α-terpinyl acetate (1%), 1-methyl-4-(α-hydroxyisopropyl) benzene (0·2%), and α-cadinol (2%) by direct comparison of GLC, NMR and IR spectra with authentic samples. When the crude oil was placed at room temp. for several months, the

[1] T. IKEDA and Y. FUJITA, *J. Chem. Soc. Japan* **50**, 32, 66 (1929).