

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 H₂O 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 H₂O). After 1 month at 25°, the brown mycelial mat was separated by filtration, washed (H₂O), 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 Et₂O 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. C₁₉H₁₈O₅ 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 Ac₂O and pyridine at room temperature gave the diacetate, which crystallized from MeOH–H₂O in the form of blocks (m.p. 142–143°). (Found: C, 67.1; H, 5.73. C₂₃H₂₂O₇ 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 CH₂N₂. Removal of solvent left an oil that crystallized from 95% MeOH as blocks (m.p. 135–137°). (Found: C, 71.1; H, 6.43. C₂₁H₂₂O₅ 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).

GLC showed caryophyllene oxide increased and caryophyllene decreased. It was possible that caryophyllene oxide was an artifact and produced by autoxidation of caryophyllene. The steam nonvolatile parts were chromatographed on silica gel column. Sitosterol (m.p. 134.5–136.5) was isolated and identified by IR, NMR and m.m.p. The mother liquors from sitosterol crystallization showed the presence of cholesterol and stigmasterol (GLC on SE-30 and QF-1 column).

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Key Word Index—*Cunninghamia konishii*; Taxodiaceae; monoterpenes; caryophyllene; α -cedrene; sterols.

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ANGIOSPERMAE DICOTYLEDONAE

APOCYNACEAE

ALCALOÏDES DES ÉCORCES D'*OCHROSIA OPPOSITIFOLIA**

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L'extraction des écorces d'*Ochrosia oppositifolia* a permis d'isoler huit alcaloïdes:¹ quatre d'entre eux ont déjà été isolés d'autres espèces d'*Ochrosia*: réserpine I^{2a,b} isoréserpine II,^{2a,b, 3a-f} méthoxy-10 dihydrocorynanthéol III^{3e} et ochrolifuanine A, IV.^{4a,b} Deux autres l'ont été d'autres Apocynacées: réserpine V et isoréserpine VI.⁵ Les deux derniers sont des alcaloïdes nouveaux que nous avons nommés ochropposine et ochropposinine.

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⁵ M. HESS, *Indolalkaloid in Tabellen*, Springer-Verlag, Berlin (1964 et 1968).