Tetrahedron Letters No. 14, pp 1267 - 1268, 1975. Pergamon Press. Printed in Great Britain.

METABOLIC PRODUCTS OF CLITOCYBE ILLUDENS XI.[1] THE STRUCTURE OF NEOILLUDOL.

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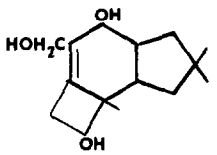
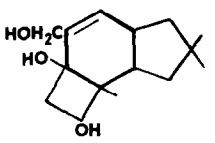
(Received in USA 19 December 1974; received in UK for publication 3 March 1975)

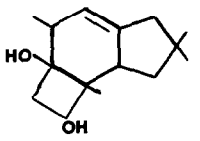
The structure of a sesquiterpenoid, "illudol" (I) isolated from culture liquids of the basidiomycete Clitocybe illudens, was reported several years ago.[2] On the basis of the data presented here we propose the structure II for neoilludol, a closely related metabolite of the same fungus.



I



II



III

Neoilludol, mp 152-3° (EtOAc) analyzes for $C_{15}H_{24}O_3$. It has no uv absorption above 200 nm. Its ir spectrum shows strong hydroxyl absorption at 3500-3150 cm^{-1}. Its nmr spectrum[3] shows two singlets at 1.00 ($2CH_3$) and 1.15 ($1CH_3$). In the low field it shows a symmetrical triplet (J=7 Hz) at 3.65 (1H), a singlet at 4.1 (2H), and a broad signal at 5.5 (1H). Neoilludol forms a diacetate, mp 83°, which still has a sharp hydroxyl peak in the ir at 3500 cm^{-1}, indicating a third hydroxyl in the parent compound. In the diacetate, the nmr signals at 3.65 and 4.1 are shifted to 4.6 and 4.71, respectively. Thus, neoilludol has one primary (possibly allylic), one secondary, and one tertiary hydroxyl group. The signal at 5.5 assigned to the vinyl proton is broadened by coupling with the angular proton. The data indicate that neoilludol is tricyclic and has one double bond.

Neoilludol does not dehydrate under mild conditions. But on refluxing in a solution of 1% sulfuric in 90% formic acid, it gives a mixture of an oil and a gum, in which 2,2,4,5,6-pentamethyl indane was identified by GLC retention time, and uv spectrum (λ max 271, 276, 281 nm). The difficulty of dehydration suggests that the tertiary hydroxyl is angular to the cyclobutane rather than to the cyclopentane ring. The formation of the indane, which fixes the skeleton, also indicates this position for the tertiary hydroxyl. In further confirmation, the proton α to the secondary hydroxyl of the cyclobutane ring appears as a triplet, with no indication of diagonal splitting.

The ms of neoilludol shows no M^+ peak but shows ions at mass 234 (M - H_2O), 216 (M - $2H_2O$, base peak), 208 (M - 44, 70%), and 190 (M - H_2O - 44, 70%). The ms of the acetate shows peaks at

336 (M^+), 318 (M - H_2O), 276 (M - CH_3COOH), 250 (M - 86) and 190 (M - CH_3COOH-86, base peak). The abundance of the species resulting from the loss of 44 (CH_2CHOH) and 86(CH_2CHOAc) indicates the presence of a cyclobutanol moiety. The position of the hydroxyl in the cyclobutane ring is assigned on the basis of the similarity of the ms fragmentation pattern to that of dihydro-illudol and its derivatives.[2] The assignment is compatible with the fact that the compound does not form an acetonide, although this in itself would not preclude the presence of a trans vicinal diol.

On hydrogenation (5% Pd on charcoal in EtOAc) neoilludol takes up about 1 mole of hydrogen in 8 min. The main product is III, mp 193-4°, formed by hydrogenolysis of the primary alcohol and migration of the double bond. The nmr spectrum of III shows 3 singlets at 0.98, 1.00 and 1.08 for the 3 tertiary methyl groups, a doublet around 1.15 (J=7 Hz), for the secondary methyl group, a triplet at 3.78 (1H) for the proton α to the OH, and a broad signal at 5.21 for the vinyl proton. These data can be explained only on the basis of the assigned positions for the double bond in II and III. The ms of III has the base peak 192 (M - H_2O-44).

Acknowledgement: This work was supported by a grant (E-226) from the National Institute of Allergy and Infectious Diseases, National Institutes of Health.

[1] Part X, M. S. R. Nair, and M. Anchel, Lloydia 36, 106 (1973)

[2] T. C. McMorris, M. S. R. Nair and M. Anchel, J. Am. Chem. Soc. 89, 4562 (1967)

[3] Values are in δ (ppm). II was in CD_3OD. II acetate and III were in $CDCl_3$.