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ONITIN AND ONITISIN, NEW PHENOLIC PTEROSINS FROM THE FERN ONYCHIUM AURATUM

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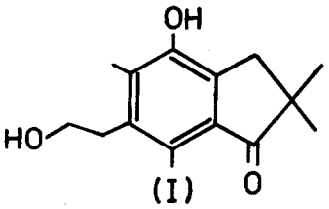
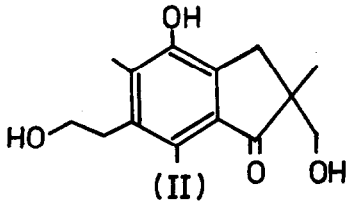
Two new phenolic sesquiterpenoids, designated ONITIN and ONITISIN have been isolated by chromatographic separation of the ether extract of Onychium auratum (Cryptogrammataceae). Characterisation of these compounds are reported in this communication.

ONITIN (I): Onitin [mp 214°; $[\alpha]_D^{25}$ 0(c, 1.0 MeOH)] has a molecular formula, $C_{15}H_{20}O_3$ (M^+ 248). Its IR spectrum (KBr) showed hydroxyl bands at 3400 and 3325 cm^{-1} and aromatic and carbonyl bands at 1595 and 1681 cm^{-1} respectively. Acetylation (Ac_2O/Pyridine, 24 hr at 25°) gave a diacetate (semi solid, TLC pure) indicating the presence of two hydroxyl groups. One of the hydroxyl groups was phenolic (I was soluble in 2 N NaOH) and was readily methylated (Me_2SO_4 - K_2CO_3/acetone, 4 hr). Absence of $AlCl_3$ shift in the UV spectrum suggested that the phenolic hydroxyl was not chelated. A strong MS peak at m/e 217 (M^+ - 31) indicated the presence of a primary alcoholic group. The UV spectrum showed the absorptions : λ_{max}^{MeOH} nm ($\log \epsilon$): 230.5 (4.3); 269 (4.1) and 325 (3.4). The UV and IR spectra indicated that I has 1-indanone skeleton. NMR data of the diacetate, $\delta(CDCl_3)$ 1.18(6H,s); 2.05 (3H,s); 2.26 (3H,s); 2.36 (3H,s); 2.70 (5H,s); 3.10 (2H, t, J = 8Hz) and 4.20 (2H, t, J = 8Hz) showed evidence that onitin contained a gem dimethyl at C-2, two aromatic methyls (one of which was deshielded and assigned the position C-7), one hydroxyethyl group attached to the aromatic ring and one isolated methylene group at C-3. Aromatic methyl and hydroxyethyl groups could be located at C-5 and C-6 respectively on biogenetic considerations since I could have originated from humulene through proto-illudane type of intermediate[1]. Consequently, phenolic hydroxyl could be placed at C-4. Onitin is, therefore, assigned structure I. Till recently, compounds derived from proto-illudane type of precursors were known only as fungal metabolites[2]. However, several 1-indanones, collectively known as "pterosins", have now been isolated from ferns[3]. A comparison of our data with those of pterosins further supports our assignments of substituents in onitin.

ONITISIN (II): Onitisin was obtained as an optically active crystalline compound mp 184°, $[\alpha]_D^{25}$ - 31.16 (c, 1.0 MeOH). It has a molecular formula $C_{15}H_{20}O_4$ (M^+ 264). IR spectrum showed bands at 3450, 3350, 1681, 1600 cm^{-1} and UV spectrum showed absorptions (λ_{max}^{MeOH} nm) at 231, 270 and 325 similar to those of I. Acetylation of II gave a triacetate indicating the presence of three hydroxyl groups. One of the hydroxyl groups was phenolic and the remaining two alcoholic, as a monomethyl ether could be obtained (Me_2SO_4-K_2CO_3, acetone 4 hr). NMR data of the triacetate δ ($CDCl_3$) 1.20 (3H,s); 1.93 (3H,s); 2.05 (3H,s); 2.27 (3H,s); 2.37 (3H,s); 2.70 (3H,s); 2.87 (2H,s); 3.10 (2H, t, J = 8Hz); 4.20 (s) merging with a (t) at 4.20 (4H) clearly indicated that II had CH_3 and CH_2-OH groups at C-2 in place of a gem dimethyl as in I. Onitisin has, therefore, been assigned the structure II.



(I)



(II)

This is the first report of the occurrence of phenolic pterosins. So far, all known pterosins have been isolated from closely related ferns and may have chemotaxonomic significance. Pharmacological study of these compounds would be of interest because of the probable radiomimetic property of pterosins[4] and antitumor activity of illudoids[5].

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