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INTERCONVERSION OF PTEROSINS, ILLUDOID SESQUITERPENES: SYNTHESIS OF ONITIN (4-HYDROXY-PTEROSIN Z) AND (±)-PTEROSIN D

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Two pterosins, onitin (5) (4-hydroxy-pterosin Z) and (±)-pterosin D (6), were synthesized from pterosin Z (3) by chemical transformations.

We have reported[1,2] the isolation of three pterosins, H (1), I (2) and Z (3),[3] illudoid sesquiterpenes with the indanone group, and hypacrone (4), a novel seco-illudoid which is a possible precursor of pterosins, from Hypolepis punctata Mett. In a related field, more than ten pterosins and their glucosides (pterosides) have been isolated from some species of fern,[4] which are close to Hypolepis punctata taxonomically. Since pterosin Z is readily available from the plant in relatively good yield (ca. 0.1% from fresh leaves) and its structure has already been established by the unequivocal synthesis,[1] we thought that chemically transforming it into some other pterosins or other illudoids would be worthwhile. We report here the conversion of pterosin Z (3) into onitin (5) (4-hydroxy-pterosin Z), which was recently isolated from Onychium auratum as being a phenolic pterosin,[5] and (±)-pterosin D (6)[4b].

Nitration [$Cu(NO_3)_2$-Ac_2O][6] of pterosin Z, followed by acetolysis with Ac_2O-H_2SO_4[7], gave a mixture of products. Fractionation of the mixture by TLC gave three components, diacetate (7) : 10% yield, $\nu_{max}^{CHCl_3}$ 1730, 1700, 1600 cm^{-1}, $\delta_{ppm}^{CDCl_3}$ 2.03 (6H,s); nitroacetate (8), $C_{17}H_{21}O_5N$: 30% yield, mp 88-89°, $\nu_{max}^{CHCl_3}$ 1730, 1710, 1600, 1535 cm^{-1}, $\delta_{ppm}^{CDCl_3}$ 2.03 (3H,s); and nitrodiacetate (9) : 5% yield, mp 103-104°, $\nu_{max}^{CHCl_3}$ 1730, 1700, 1600, 1530 cm^{-1}, $\delta_{ppm}^{CDCl_3}$ 2.06 (6H,s). Saponification (KOH-MeOH) of the diacetate (7) gave a diol (6), mp 187-188°, ν_{max}^{KBr} 3320, 1705, 1600 cm^{-1}, $\delta_{ppm}^{CD_3OD}$ 1.07 (3H,s), 1.17 (3H,s), 2.45 (3H,s), 2.60 (3H,s), 3.00 (2H,t,J=8), 3.60 (2H,t,J=8), 4.71 (1H,s), 7.22 (1H,s). These spectral data of the diol were identical with those of natural pterosin D.

The nitroacetate (8) was hydrogenated ($PtO_2/AcOH/H_2$) to quantitatively form an aminoacetate (10), $C_{17}H_{23}O_3N$: mp 111-112°, $\nu_{max}^{CHCl_3}$ 3440, 3380, 1730, 1695, 1625, 1590 cm^{-1}. The compound (10) was treated at 0°C with sodium nitrite in 10%-hydrochloric acid and the resulting solution was heated at 80°C for 1hr, after addition of 20%-sulfuric acid (final concentration of sulfuric acid was ca.15%). A diol (5), $C_{15}H_{20}O_3$:mp 213-214°, ν_{max}^{KBr} 3360, 3280, 1685, 1595, 1590 cm^{-1}, $\delta_{ppm}^{CD_3OD}$ 1.17 (6H,s), 2.30 (3H,s), 2.53 (3H,s), 2.77 (2H,s), 3.06 (2H,t,J=8), 3.60 (2H,t,J=8), λ_{max}^{EtOH} 216.5 (ε:21200), 230.5 (21800), 269 (11200), 325 nm (3000), m/e 248 (M^+), 233 (M^+-CH_3), 217 (M^+-CH_2OH), was separated by extraction from the reaction mixture and purified by preparative TLC (or more effectively by preparative HLC : Porasil T/n-hexane:i-PrOH:THF=100:3:2). The diol (5) gave a diacetate (11) (Ac_2O-Pyr) : $\nu_{max}^{CHCl_3}$ 1750, 1730, 1700, 1605 cm^{-1}, $\delta_{ppm}^{CDCl_3}$ 1.17 (6H,s), 2.03 (3H,s), 2.23 (3H,s), 2.33 (3H,s), 2.67 (5H,s), 3.03 (2H,t,J=8), 4.12 (2H,t, J=8). The compounds, (5) and (11), were identified as onitin and its diacetate, respectively, by direct comparisons.

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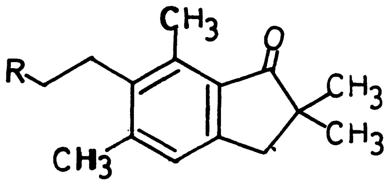
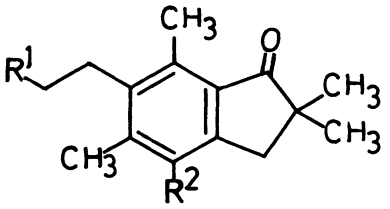
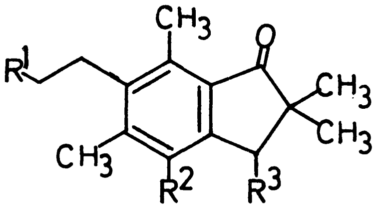


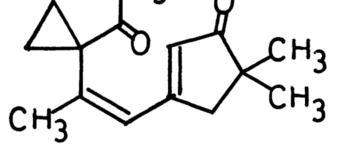
(1) R=Cl
(2) R=OMe
(3) R=OH



(5) R^1=OH, R^2=OH
(8) R^1=OAc, R^2=NO_2
(10) R^1=OAc, R^2=NH_2
(11) R^1=OAc, R^2=OAc



(6) R^1=OH, R^2=H, R^3=OH
(7) R^1=OAc, R^2=H, R^3=OAc
(9) R^1=OAc, R^2=NO_2, R^3=OAc



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