[Chem. Pharm. Bull.]
28(4) 1311—1313 (1980)

Further Structural Studies of 1-Indanone Derivatives obtained from *Onychium japonicum*

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(Received August 27, 1979)

The structures of pteroside M and pterosin M isolated from the fronds of *Onychium japonicum* were reexamined by the NMR chemical shift reagent method. Furthermore, the stereostructure of pteroside M was established as 4-hydroxy-6-2'-hydroxyethyl-2(R),5,7-trimethyl-1-indanone-2'-D-glucopyranoside on the basis of the circular dichroism Cotton effect associated with the n- π^* transition of the conjugated ketones.

Keywords—pteroside M; pterosin M; absolute configuration; Cotton effect; shift reagent

Many 1-indanone derivatives have recently been isolated from ferns.²⁾ In the previous paper³⁾ the structures of new phenolic 1-indanone derivatives, named pteroside M and pterosin M, isolated from the fronds of *Onychium japonicum*, were reported. Although these two compounds have a chiral center at the 2-position, the absolute configuration has not been investigated. In this note we describe the results of further structural elucidation of these compounds by means of the nuclear magnetic resonance (NMR) chemical shift reagent method⁴⁾ and analysis of the circular dichroism Cotton effect.

Pteroside M (**1**).³⁾ C₂₀H₂₈O₈, mp 192°, (α)_D¹⁵ -27° (Me₂CO+H₂O)⁵⁾ and pterosin M (**2**).³⁾ C₁₄H₁₈O₃, mp 187°, (α)_D¹⁵ +7.9° (EtOH) were isolated from an ethyl acetate extract of the fronds of *Onychium japonicum*. As reported in the previous paper, the structures of these two phenolic compounds were unequivocally established by degradation reaction, as well as ¹³C-NMR and ¹H-NMR spectra.

Hydrolysis of **1** with β -glucosidase or acid gave one mole each of glucose and aglycone, pterosin M (**2**).³⁾ When **2** was treated with an excess of acetic anhydride in pyridine, the diacetate (**3**) mp 77—79°, *m/e* 318, was formed. The NMR spectrum of **3** in CDCl₃ showed signals at δ 1.26 (3H, d, *J*=8 Hz, >CHCH₃), 2.05 (3H, s, -COCH₃), 2.40 (3H, s, -CH₃), 2.43 (3H, s, -COCH₃), 2.70 (3H, s, -CH₃), 3.08 and 4.10 (each t, *J*=8 Hz, -CH₂CH₂-). The methyl group at δ 2.43 appeared at the usual benzylic position, whereas the methyl group at δ 2.70 appeared at low field compared with that of toluene. This showed that the latter methyl group is located near the carbonyl group of the neighboring five-membered ring. In confirmation of this, Clemmensen reduction of **2** on a water bath for 3 hr furnished a reduction product (**4**), mp 154—154.5°, in 93% yield. In compound **4** this methyl signal had moved upfield (δ 2.18), confirming that the methyl group is close to the carbonyl group. Treatment of **4** with thionyl chloride in pyridine gave (**5**), mp 108°, *m/e* 238 in 90% yield. Compound **5** was converted to the corresponding O-acetyl derivative (**6**), mp 94—95°, *m/e* 315. For reexamination

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- 5) The value of rotation given in the previous report (+129°) was in error.

hibited positive Cotton effects associated with an $n\text{-}\pi^*$ transition in the vicinity of 320 nm and bisignated CD curves in chloroform. The circular dichroism curve of pterosin M in methanol showed a positive Cotton effect due to $n\text{-}\pi^*$ transition ($O_{329} + 2720$). Therefore, the absolute configuration at C-2 of pterosin was concluded to be R. Furthermore, the contribution⁷⁾ of the glucose component to the rotation of **1** (M_D of **1**— M_D of **2** = -125.4°) suggests that the glucose belongs to the D series. Based on these results, pteroside M is concluded to be 4-hydroxy-6-2'-hydroxyethyl-2(R),5,7-trimethyl-1-indanone-2'-D-glucopyranoside.

Experimental

Acetylation of 2—Compound **2** (4.7 mg) was treated with Ac_2O (250 mg) in pyridine (1 ml) at room temperature overnight to afford a corresponding diacetate (**3**) (5.5 mg, 90% yield), mp $77\text{--}79^\circ$ (from hexane). MS m/e : 318 (M^+). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2975, 2940, 1750, 1700, 1604. NMR (in CDCl_3) δ : 1.26 (3H, d, $J=8$ Hz), 2.05 (3H, s), 2.43 (3H, s), 2.40 (3H, s), 2.70 (3H, s), 3.08 (2H, t, $J=8$ Hz), 4.17 (2H, t, $J=8$ Hz) and 2.2—3.4 (3H, m). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4$: C, 71.02; H, 7.95. Found: C, 71.00; H, 8.05.

The Clemmensen Reduction of 2—Zinc amalgam (obtained from 0.8 g of Zn and 0.9 g of HgCl_2) was added to a solution of conc HCl (30 ml), H_2O (1.5 ml) and toluene (2 ml). Compound **2** (2.7 mg) was dissolved in this, and the mixture was refluxed for 10 hr. The reaction mixture was extracted with ether and the ethereal layer was washed with water, dried, and concentrated. The residue was recrystallized from ethanol to afford **4** (2.36 mg, 93%), mp $154\text{--}155.5^\circ$. MS m/e : 220 (M^+), IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3430, 3240, 2930, 1603, 1590, 1460, 1380. NMR (in CDCl_3) δ : 0.5 (1H, s), 1.17 (3H, d, $J=7$ Hz), 2.18 (3H, s), 2.22 (3H, s), 2.25—3.20 (5H, m), 3.05 (2H, t, $J=8$ Hz), 3.22 (2H, t, $J=8$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$: C, 76.32; H, 9.15. Found: C, 76.01; H, 9.49.

Chlorination of 4—A solution of **4** (4.4 mg) in a mixture of SOCl_2 (4 ml) and pyridine (2 ml) was refluxed for 3 hr. The reaction mixture was diluted with ice-water and extracted with ether. The ethereal solution was washed with water, dried, and concentrated. The residue was recrystallized from hexane to afford crystals (4.4 mg, 87%), mp 108.9° . MS m/e : 254 (M^+), IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400, 2960, 1603, 1590, 1460. NMR (in CDCl_3) δ : 0.9 (1H, s), 1.17 (3H, d, $J=7$ Hz), 2.18 (3H, s), 2.22 (3H, s), 2.30—3.15 (5H, m), 3.01—3.20 (2H, m), 3.43—3.62 (2H, m). Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{ClO}$: C, 70.12; H, 7.98; Cl, 14.87. Found: C, 70.30; H, 8.14; Cl, 14.87.

Acetylation of 5—Compound **5** (2.9 mg) was treated with Ac_2O (300 mg) in pyridine (1 ml) at room temperature overnight to afford the corresponding acetate (**5**), in 95% yield, mp $94\text{--}95^\circ$ (from hexane). MS m/e : 280 (M^+). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 2930, 1750, 1603, 1590, 1460, 1380. NMR (in CDCl_3) δ : 1.17 (3H, d, $J=7$ Hz), 2.10 (3H, s), 2.25 (6H, s), 2.20—3.20 (5H, m), 2.96—3.16 (2H, m), 3.37—3.57 (2H, m). Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{ClO}_2$: C, 68.57; H, 7.50; Cl, 12.68. Found: C, 68.55; H, 7.90; Cl, 13.45.

Acknowledgement We wish to thank Dr. S. Natori, National Institute of Hygienic Sciences for the CD curve measurement.