Communications to the Editor

[Chem. Pharm. Bull.]
33(6)2609—2610(1985)

THE C-24 STEREOCHEMISTRY OF CYCLOHOMONERVILOL, A NON-CONVENTIONAL
SIDE CHAIN TRITERPENE FROM *NERVILIA PURPUREA* SCHLECHTER

Tohru Kikuchi,* Shigetoshi Kadota, and Takehiko Shima

Research Institute for Wakan-Yaku (Oriental Medicines), Toyama Medical
and Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan

The C-24 stereochemistry of cyclohomonervilol, isolated from *Nervilia purpurea* SCHLECHTER, was determined to be 24S by chemical comparisons with 24S-dihydrocyclofuntumienol.

KEYWORDS — cyclohomonervilol; triterpene; *Nervilia purpurea*;
reversed-phase HPLC; stereochemistry

In a previous paper,¹⁾ we reported the isolation of cyclohomonervilol, a new triterpene having a non-conventional side chain, together with 24-isopropenylcholesterol,²⁾ from *Nervilia purpurea* SCHLECHTER (Orchidaceae) and proposed the structure 1a for this compound except the stereochemistry at the C-24 position. In order to determine the stereochemistry, we examined the transformation of 1a into the 24-ethyl compound (6b) and the result is reported here.

Cyclohomonervilol benzoate (1b) (5.0 mg), mp 156–158°C, $C_{39}H_{58}O_2$, was oxidized with osmium tetroxide to give a diol (2b) (5.2 mg). Treatment of 2b with periodic acid (3 mg) in aqueous dioxane for 8 min at 20°C and subsequent reduction with sodium borohydride afforded a mixture of epimeric alcohols, which was separated by preparative layer chromatography to give 3b (1.8 mg), mp 144.5–146.5°C, MS m/z 562 (M^+ , $C_{38}H_{58}O_3$), and 4b (2.0 mg), mp 150–152°C, MS m/z 562 (M^+ , $C_{38}H_{58}O_3$).

First, an attempt at the reductive desulphurization of 3b mesylate with sodium iodide-zinc powder³⁾ did not give the desired compound, but only a mixture of elimination products. Then, 3b (1.0 mg) was converted to the phenoxythiocarbonate (5b) and the latter was reduced with tributyltin hydride⁴⁾ in toluene to give a crystalline mass, which showed four peaks in an approximate ratio of 7:8:7:78 on reversed-phase HPLC as shown in Fig. 1. Preparative HPLC of the mixture⁵⁾ led to the isolation of the major product (peak 4) (0.5 mg), mp 149–151°C, MS m/z 546 (M^+ , $C_{38}H_{58}O_2$), 1H -NMR ($CDCl_3$) δ : 0.19, 0.45 (each 1H, d, $J=4.0$ Hz, 19- H_2), 0.82, 0.84 (each 3H, d, $J=6.8$ Hz, 26- and 27- H_3), 0.86 (3H, t, $J=7.5$ Hz, 29- H_3), 0.88 (3H, d, $J=6.6$ Hz, 21- H_3), 0.91 (3H, d, $J=6.4$ Hz, 30- H_3), 0.92, 0.98 (each 3H, s, 32- and 18- H_3), 4.80 (1H, m, 3-H), 7.50, and 8.08 (5H, aromatic H), which was found to be identical with 24S-dihydrocyclofuntumienol benzoate (6b)¹⁾ by MS, 1H -NMR, and HPLC comparisons. The other alcohol 4b (1.0 mg) was also deoxygenated in the same manner to give 24S-dihydrocyclofuntumienol benzoate (6b) (0.2 mg). Thus, the side chain of cyclohomonervilol (1a) was proved to have the 24S-configuration.

It is worth noting that sterols carrying the same or analogous side chain have also been obtained from marine sponges, *Verongia cauliformis* and *Pseudaxinyssa* sp.⁶⁾

Chart 1

Fig. 1. HPLC Chromatogram of the Reductive Deoxygenation Products

Condition: column, TSK-GEL ODS-120A (25cm x 4.6mm i.d.);
solvent, CHCl₃-CH₃CN (2:8); flow rate, 0.6 ml/min;
temperature, 20°C; detector setting, UV 240 nm.

REFERENCES AND NOTES

- 1) T. Kikuchi, S. Kadota, H. Suehara, and T. Namba, *Tetrahedron Lett.*, **22**, 465 (1981); T. Kikuchi, S. Kadota, H. Suehara, and T. Shima, *Chem. Pharm. Bull.*, in press.
- 2) T. Kikuchi, S. Kadota, H. Suehara, and T. Namba, *Chem. Pharm. Bull.*, **30**, 370 (1982); *idem.*, *ibid.*, in press; T. Kikuchi, S. Kadota, and T. Shima, *Tetrahedron Lett.*, in press.
- 3) F. Fujimoto and T. Tatsuno, *Tetrahedron Lett.*, **17**, 3325 (1976).
- 4) W. Hartwing, *Tetrahedron*, **39**, 2609 (1983); M.J. Robins, J.S. Wilson, and F. Hasske *J. Am. Chem. Soc.*, **105**, 4059 (1983).
- 5) The other products (peak 1-3) were isolated by repeated preparative HPLC. The third peak was assigned to cyclofuntumienol benzoate (7b) by MS and HPLC analyses.
- 6) W. C. M. C. Kokke, C. S. Pak, W. Fenical, and C. Djerassi, *Helv. Chim. Acta*, **62**, 1310 (1979); W. Hofheinz and G. Oesterhelt, *Helv. Chim. Acta*, **62**, 1307 (1979).

(Received April 22, 1985)