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

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

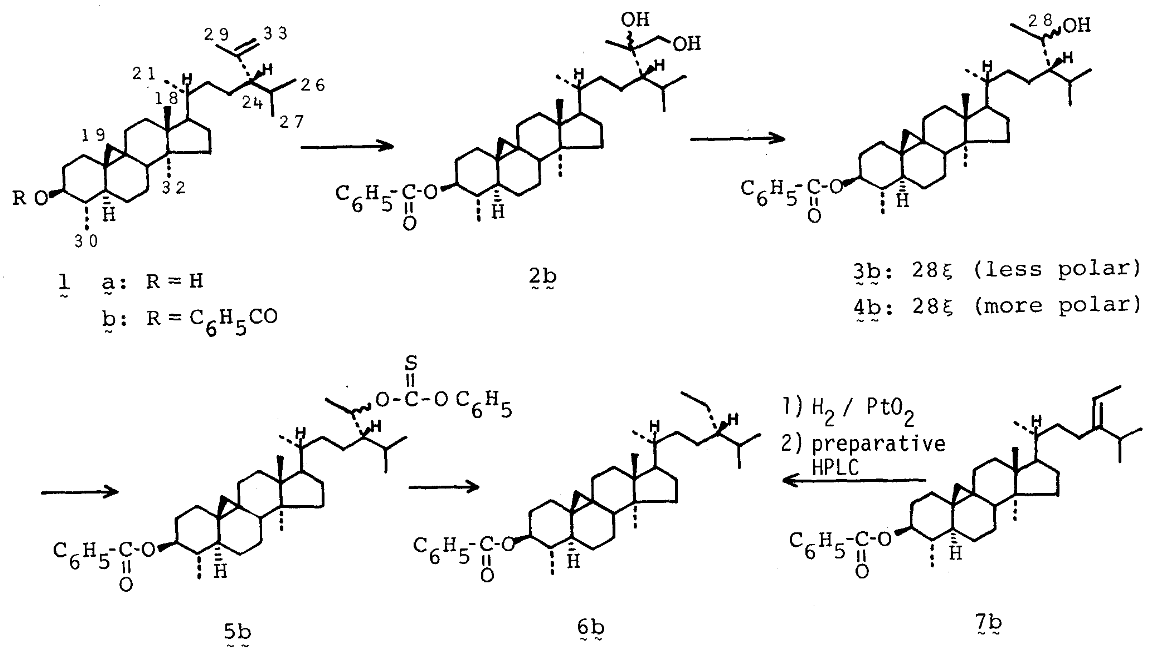
KEYWORDS —— cyclohomonervilol; triterpene; *Nervilia purpurea*; reversed-phase HPLC; stereochemistry

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^+, $C_{38}H_{58}O_2$), ^{1}H-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, ^{1}H-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)



1 a: R = H
b: R = C_6H_5CO

2b

3b: 28ξ (less polar)
4b: 28ξ (more polar)

5b

6b

7b

Chart 1

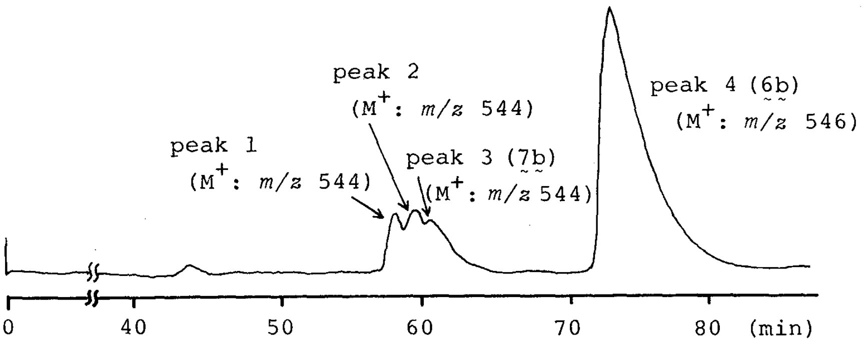


Fig. 1. HPLC Chromatogram of the Reductive Deoxygenation Products
Condition: column, TSK-GEL ODS-120A (25cm x 4.6mm i.d.); solvent, $CHCl_3$-CH_3CN (2:8); flow rate, 0.6 ml/min; temperature, 20°C; detector setting, UV 240 nm.

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