

O-Methylclausenol – a C₃₃ terpenoid from *Clausena pentaphylla*

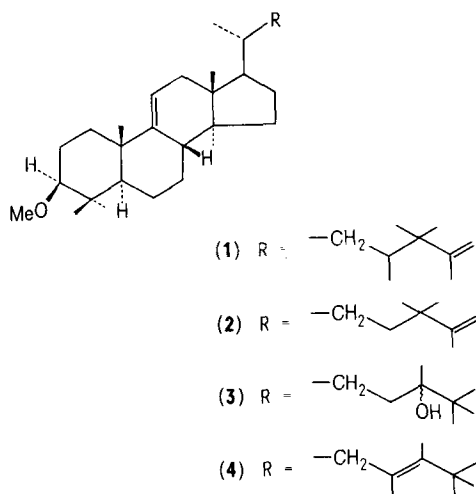
Mangala D. Manandhar, A. Shoeb, R. S. Kapil and Satya P. Popli

Medicinal Chemistry Division, Central Drug Research Institute, Chattar Manzil Palace, P. B. 173, Lucknow 226 001 (India), 1 June 1976

Summary. O-Methylclausenol (**1**), a new C₃₃ terpenoid has been isolated from the aerial parts of *Clausena pentaphylla*. Based on physico-chemical methods, its structure has been established as 3-β-methoxy-23,24,24-trimethylclausenol-9(11)-25-diene.

The petroleum ether extract of the aerial parts of *Clausena pentaphylla* (Roxb.) DC. (Rutaceae) on column chromatography over neutral alumina afforded a triterpene (Noller; tetranitromethane positive), C₃₄H₅₈O; M⁺ 482; m.p. 182–184°C (hexane); [α]_D¹⁸ + 93.7° (c, 1, CHCl₃). This communication presents evidence indicating its structure as 3-β-methoxy-23,24,24-trimethylclausenol-9(11)-25-diene (**1**).

As one methoxyl was present in its molecular make-up, this triterpene may be considered to be the methyl ether of a new alcohol, clausenol, C₃₃H₅₆O. This appears to be the second instance of the occurrence of a C₃₃ triterpene¹ in nature.



The IR spectrum of **1** revealed the presence of a vinylidene group ($\nu_{\text{max}}^{\text{KBr}}$ 1648 and 894 cm⁻¹), which was also demonstrated by a 2-proton double doublet ($J = 1.5$ Hz) centred at δ 4.74 in its NMR spectrum (60 MHz; CDCl₃). Catalytic hydrogenation (PtO₂; CHCl₃) of **1** yielded the dihydro derivative; C₃₄H₆₀O; m.p. 195°C; [α]_D¹⁹ + 86.70° (c, 1, CHCl₃); M⁺ 484 (base peak at m/e 327), in which the vinylidene protons were replaced by an isopropyl function (δ 0.74).

In addition to the nine methyl signals between δ 0.66 and 1.06, there appeared a doublet at δ 1.65 ($J = 1.5$ Hz) and a sharp 3-proton singlet at δ 3.36 showing the presence of one allylic methyl and a methoxyl group (1100 cm⁻¹) respectively. Besides, there was a 1-proton multiplet between δ 2.46 and 2.78, the shape and position of which corresponded very closely to the axial C₃-H in methyl ethers of cycloartenol, 24-methylenecycloartenol² and the C₃₂ terpenoids, **2** and **3** isolated from *Neolitsea pulchella*³. This implied that the methoxyl was equatorial. The chemical shift at δ 5.26 attributed due to the proton $\Delta^9(11)$ was substantiated by the appearance of the fragment ions²⁻⁴ at m/e 287, 273 and 261 in its mass spectrum, as

well as by its sluggish behaviour towards catalytic hydrogenation under normal conditions. Another relevant feature of the mass spectrum of **1** was the conspicuous M⁺ at m/e 482 followed by the base peak at m/e 327 which accounted for the M-side chain-2H fragment^{2,5} and suggested that the methoxyl is attached to the nucleus and the side chain has an extra carbon atom.

O-Methylclausenol, therefore, embodied all the structural features of **2** with the exception of an extra carbon atom to be placed in the side chain. In the known triterpenes, the additional carbon atoms always occupy C₂₄ position, but as this position is already substituted in **1** the extra carbon atom could only be placed at C₂₀, C₂₂ or C₂₃. **1**, on treatment with perchloric acid in benzene and acetic acid², underwent Wagner-Meerwein rearrangement giving **4**, C₃₄H₅₈O; M⁺ 482; m.p. 202–204°C. The NMR spectrum of this product showed the presence of 2 methyl groups attached to a carbon bearing a double bond (δ 1.54 and 1.65) and the absence of the vinylidene protons. This located the extra methyl at C₂₃ and, therefore, structure **1** is the complete representation of O-methylclausenol⁶.

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