An Appraisal of the
Stereochemistry of Sylveterpins and 1:18-Terpins

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ABSTRACT

The two sylveterpins, (i) trans (α) C\textsubscript{10}H\textsubscript{18}(OH)\textsubscript{2} (I, x = \textit{OH}, m.p. 137-138°) and (ii) the cis (β) isomer (m.p. 70-75°) have been prepared\textsuperscript{1-3} from d-sylvestrene dihydrochloride (I, x = \textit{Cl}) and sylveterpineol (II and III). The above cis and trans assignments are based only on their melting points. In Part I of the thesis we present chemical and spectroscopic data which conclusively prove that these structures are untenable and higher melting sylveterpin has the cis and low melting r the trans configurations.

Following the procedure of Perkin et al\textsuperscript{2} two sylvesterpins were prepared in their pure forms (TLC) (A); m.p. 138°,

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1. Wallach, O., Annalen, 1907, 357, 73.
Dehydration of Sylvesterpins to m-Cineole
The bulky hydroxyisopropyl group will adapt an equatorial position in both the isomers. Based on the above IR and Rf data\(^5\) sylvesterin (A) should then have the cis configuration (IV) in which the hydroxyl group is equatorially oriented and sylvesterin (B) the trans configuration (V) with the hydroxyl group axially oriented.

In confirmation with these assignments, on acid catalysed dehydration, the cis-isomer yielded 55% and the trans-isomer only 29% of m-cineole; a mechanism has been proposed to account for the variable yields of the ether from the cis and trans-isomers.

The PMR spectra of the cis-isomer displayed methyl signals at \(\delta 1.15\) (s, 6H) and at \(1.27\) (s, 3H) whereas the trans-isomer (V) showed three singlets (3H each) at \(\delta 1.12, 1.18\) and \(1.25\). These differences in the chemical shift are


probably due to anisotropic effect of the oxygen of the axial hydroxyl.

Inactive sylvetepins (carveertpins) are also known, the trans, m.p. 127°, originating by the action of dl-sylvestrene (carvestrene) dihydrobromide (I, x = Br) with silver acetate,\(^7\),\(^8\) and the cis, m.p. 94°, by stirring dihydrocarvestrene (II) with dilute sulphuric acid.\(^8\),\(^9\)

dl-Sylvetepins were also prepared, the isomer (C) m.p. 127° (lit.\(^7\),\(^9\) 127°) and the isomer (D) m.p. 94° (lit.\(^7\),\(^9\) 94°). Rf values and IR spectra of sylvetepins (C and A) and (B and D) were identical and, therefore, the earlier stereochemical assignments for these inactive glycols should also be reversed.

It may be added that for screening the homogeneity of the sylvetepins, a TLC technique was developed involving

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the use of the solvent system: ethyl acetate/n-hexane/n-butanol (1:2:1) and spraying agent: 1% vanillin in concd. sulphuric acid.

\( \text{\textit{m}} \)-Cineole (GIC: single peak) has been prepared from sylweterpineol and its structure established from IR and NMR data.

Parallel investigations of the stereochemistry of \( 1:8 \)-terpins constitute Part II of the thesis. Originally the two isomeric glycols m.p. 117° and 158° have been assigned respectively the cis (VI) and trans (VII) configurations though the only valid experimental evidence being the ease of formation of the monohydrate from the cis isomer.

Data backing the above configurations squeezed out from proton catalysed dehydration study on the terpins to \( 1:8 \)-cineole, do not seem to be foolproof and more so in the light of the recent observation that such a reaction favours the conversion to \( 1:4 \)-cineole than \( 1:8 \)-cineole. Further, the stereochemistry of these terpins has been questioned by Barnes

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whose arguments require a reversal of the structures of the cis-trans modifications. These considerations therefore demand a re-investigation of the stereochemistry of 1:8-terpins.

The main contributions are:

Anhydrous cis-1:8-terpin, m.p. 104 °C (TLC: single spot), Rf 0.76, \(\sqrt[\text{KBr max}} 900 \text{ cm}^{-1}\) (axial C-O) and trans-1:8-terpin, m.p. 157.5 °C (TLC: single spot), Rf 0.66, \(\sqrt[\text{KBr max}} 1115 \text{ cm}^{-1}\) (equatorial C-O), were prepared.

The Rf values and IR bands are in harmony with the accepted cis-trans structures, but the NMR chemical shifts have no discriminating value.

From 4-terpinenol, 1:4-cineole (GLC: single peak) has been prepared and its structure established from IR and NMR data.

Of the ethers, the exclusive formation of 1:8-cineole from the terpins, as cited in literature, is shown to be in error.

For the first time, chemical evidence is presented to substantiate the stereochemical assignments of the 1:8-terpins. Dehydration of the trans-1:8-terpin with 1% sulphuric
acid yielded almost double the quantity of \(-\)terpineol than that available from the cis-isomer.

Both 1:8- and 1:4-cineoles were released in the dehydration reactions and the amount of either of the ethers obtained thereby was almost equal and hence has no diagnostic significance.

To round up, the TLC, IR and dehydration studies have firmly established the accepted cis-trans assignments of 1:8-terpins.