Table I

<table>
<thead>
<tr>
<th>Methyldithioiobiuret concentration—0.01 M</th>
<th>Potassium ferricyanide concentration—0.10 M</th>
<th>Overall alkali concentration—7%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyldithioiobiuret taken (ml.)</td>
<td>Ferricyanide consumed (ml)</td>
<td>Ferricyanide equivalents per mole of methyldithioiobiuret</td>
</tr>
<tr>
<td>0.5</td>
<td>0.805</td>
<td>16.10</td>
</tr>
<tr>
<td>1.0</td>
<td>1.605</td>
<td>16.05</td>
</tr>
<tr>
<td>1.5</td>
<td>2.385</td>
<td>15.90</td>
</tr>
<tr>
<td>2.0</td>
<td>3.160</td>
<td>15.95</td>
</tr>
<tr>
<td>2.5</td>
<td>4.005</td>
<td>16.02</td>
</tr>
<tr>
<td>3.0</td>
<td>4.805</td>
<td>16.02</td>
</tr>
</tbody>
</table>

Results in Table I show that 16 equivalents of ferricyanide are required for 1 mole of methyldithioiobiuret. Since the reduction of ferricyanide involves only one electron the mechanism of the total oxidation process may be represented as follows:

The two half reactions involved are:

1. \( \text{CH}_3\text{NH} - \text{C} - \text{NH} - \text{C} - \text{NH}_2 + 20 \text{OH}^- \rightarrow \text{CH}_3\text{NH} - \text{C} - \text{NH} - \text{C} - \text{NH}_2 + 2\text{SO}_4^{2-} \) O O

\( + 10 \text{H}_2\text{O} + 16\text{e} \)

2. \( 16\text{Fe (CN)}_6^{3-} + 16\text{e} \rightarrow 16\text{Fe (CN)}_6^{4-} \)

Combining (1) and (2) we get:

\( \text{CH}_3\text{NH} - \text{C} - \text{NH} - \text{C} - \text{NH}_2 + 16\text{K}_2\text{Fe (CN)}_6 \rightarrow \text{CH}_3\text{NH} - \text{C} - \text{NH} - \text{C} - \text{NH}_2 + 20\text{KOH} + 2\text{K}_2\text{SO}_4 + 16\text{K}_4\text{Fe (CN)}_6 + 10\text{H}_2\text{O} \)

This suggests that methyldithioiobiuret is quantitatively oxidised to methylbiuret and sulphate ion by potassium ferricyanide in alkaline medium. The mechanism is in accord with that proposed for the oxidation of thiourea\(^5\) and thiocyanate.\(^6\)

Sincere thanks of the authors are due to Prof. G. B. Singh for facilities and to the University Grants Commission for the award of a fellowship to one of them (R. K. N.).

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Banaras Hindu University, R. K. Nandi.
Varanasi-5, December 6, 1968.


**ON THE STRUCTURE OF m-MENTHENOLS CONSTITUTING SYLVERTERPINEOL**

From sylvestrene dihydrochloride, by the action of 2% aq. KOH, Wallach\(^1\) obtained an unsaturated, optically active, tertiary alcohol, C\(_{16}\)H\(_{25}\)OH, which was designated as sylverterpineol. Upon oxidation of this alcohol with dilute KMnO\(_4\), Haworth, Perkin and Wallach\(^2\) obtained the following products: (i) a thick syrupy glycerol, C\(_{16}\)H\(_{27}\)(OH)\(_3\), b.p. 165\(^\circ\)/11 mm., which very reluctantly crystallised to a solid, m.p. 105\(^\circ\); (ii) \( \delta \)-lactone of \( \epsilon \)-keto-\( \gamma \)-hydroxyisopropylheptolic acid and (iii) 2-acetyl-1-methyl-\( \Delta^2 \)-cyclopentene. Formation of the last two products suggested that sylverterpineol, in all probability, is a mixture of \( \Delta^6 \)-m-menthen-8-ol (I) and \( \Delta^6 \)-m-menthen-8-ol (II). These alcoholic has been synthesised\(^3\)–\(^5\) but this has not clarified our knowledge regarding their structures.

More recently, the technique of extracting and purifying tertiary alcohols through p-nitrobenzoyl esters was employed by Chabudzinski\(^6\) to resolve the components of sylverterpineol. The p-nitrobenzoates obtained, m.p. 98\(^\circ\) and
66°, when saponified, were reported to yield alcohols of structures I and II respectively. In arriving at structure I, the only feeble evidence quoted is a cross melting point of the p-nitrobenzoate of m.p. 98° with that derived from naturally occurring sylvesterpineol; without any experimental backing the naturally occurring sylvesterpineol is assigned structure I. On the other hand, absolutely no proof is available for attributing structure II to the isomeric alcohol.

We are engaged in a comprehensive investigation on the chemistry of the alcohols constituting sylvesterpineol and wish to report some of the preliminary results of a new approach to the structural elucidation of one of the constituents, now shown to be Δ⁶-m-menthen-8-ol.

Reaction of sylvestrene dihydrochloride with 2%aq. KOH at 75° for 5 hr. afforded, besides hydrocarbons and sylvertins, an alcohol fraction which after a twofold distillation displayed the following characteristics: b.p. 90-92°/5 mm; (α)₂⁰°D + 46.70 (CHCl₃); d₂⁰° 0.9310, n₂⁰° 1.4782. Analysis—Calculated for C₁₉H₁₇OH: C = 77.87%; H = 11.76%; Found: C = 78.29%; H = 11.63%. Gas-liquid and thin layer chromatography of the alcohol cut disclosed that it is constituted of two components.

Following essentially the directions of Chabudzinski,6 the above oil was esterified with p-nitrobenzoil chloride in pyridine medium and the two crops of esters were repeatedly recrystallised, m.p. 66° and 98°.

The ester of m.p. 98° was examined in detail: Empirical formula C₁₇H₂₁O₄N; (α)₂⁰°D + 54.85 (CHCl₃); I.R. band in KBr at 1710 cm⁻¹ (ester > C = O). Because of long range allylic coupling, the only tentative conclusion that could be deduced from the n.m.r. spectrum of the ester is that it is likely to be derived from I. Hydrolysis of the ester adopting the procedure of Chabudzinski6 afforded a homogeneous (glc. single peak; tlc. single spot) alcohol conforming to the formula C₁₉H₁₅OH; yield, 80% theoretical; b.p. 91°/5 mm; (α)₂⁰°D + 102.80 (CHCl₃), d₂⁰° 0.9380, n₂⁰° 1.4807; I.R. bands (film): 1667 cm⁻¹ and 820 cm⁻¹ (> C = CH-), 1149 cm⁻¹ and 3671 cm⁻¹ (C-OH) and at 1379 cm⁻¹ (> C (CH₃)₃). The structure of this alcohol was established as Δ⁶-m-menthen-8-ol through n.m.r. spectrum. The irradiation of the methyl resonance in structure I gave the expected triplet with broadened lines as against a doublet with further fine splitting if alternate structure II were the case.

Additional support for the assigned structure of the alcohol resides in the n.m.r. spectrum of the triol III derived from the above alcohol. Oxidation of the alcohol with 2.5%aq. KMnO₄, furnished the desired compound as a sticky mass. This was repeatedly regenerated from a solution in ethyl acetate by addition of light petroleum (b.p. 40-60°) until homogeneous in thin layer chromatography. Formula C₁₀H₁₃(OH)₃ corroborated by analytical data; b.p. 167-169°/11 mm, (α)₂⁰° + 23.66 (CHCl₃).

According to structure III, the only proton at a carbon with a hydroxyl group is coupled to two adjacent protons; this should result in a quartet in the n.m.r. spectrum. Actually in the spectrum a quartet is seen, which is probably the X-part of an ABX system. This proves structure III for the triol and hence the sylvesterpineol which furnishes the p-nitrobenzyol derivative with m.p. 98° must possess structure I.

The full interpretation of the N.M.R. spectra referred to above requires the use of different solvents and this is in progress; the structure of the second alcoholic constituent of sylvesterpineol is also being investigated.

Our thanks are due to Dr. A. Melera and Dr. A. Dieffenbacher, Varian AG for n.m.r. analysis, Dr. S. Dev and Dr. C. N. Pillai for glc runs and Dr. D. K. Banerjee and Dr. G. S. Sidhu for i.r. spectra. This work is supported by a Junior Research Fellowship to one of us (K. G. K.) from the Council of Scientific and Industrial Research, New Delhi.

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College, Vellore, November 25, 1968.

1. Wallach, O., Annalen, 1907, 357, 73.