Confirmation of the Structure of Thujic Acid by Nuclear Magnetic Resonance

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In a previous paper\(^1\) it was pointed out that there are two likely structures for thujic acid, namely (I) and (II).

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\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_3 \\
& \quad \text{C} & \quad \text{CH} & \quad \text{CH} \\
& \quad \text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{CH}=\text{C} & \quad \text{CH} & \quad \text{CH} & \quad \text{CH} \\
\text{I & COOH} & \quad \text{II & COOH}
\end{align*}
\]

Degradation and synthesis\(^{1,2}\) were definitely in favour of (I), which has therefore been regarded as the correct structure of thujic acid.

Confirmation of this structure by some independent means, preferably by a method not involving chemical reactions appeared, however, to be very desirable. Corey et al.\(^3\) have recently solved a similar problem in the eucarvone series by the use of nuclear magnetic resonance\(^4\).

Dr. J. N. Shoolery of Varian Associates has been kind enough to measure the N M R spectrum of thujic acid methylester, which is reproduced in Fig. 1.

The shift in resonance is expressed as m gauss relative to benzene as zero standard, with an applied magnetic field of 7 050 gauss. There are three different bands of absorption. The very complex one at A is due to the ethyleneic hydrogens. The sharp peak at B is due to the ester methyl group, while the gem-dimethyl hydrogens absorb at C. There is no absorption at about 35 m gauss, where the tertiary bridge hydrogens of (II) should absorb\(^5\). Furthermore the area under A is close to that under C, but much greater than that under B, which is also in agreement with structure (I) with five ethyleneic hydrogens.

There is thus no doubt that (I) correctly represents thujic acid.

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**Fig. 1.**