## Confirmation of the Structure of a New Diterpene Trachyloban-19-ol, by Tris(dipivaloylomethanato)europium-shifted Nuclear Magnetic Resonance Spectroscopy

By O. ACHMATOWICZ, JUN., A. EJCHART, J. JURCZAK, L. KOZERSKI, and J. ST. PYREK\* (Instytut Chemii Organicznej Polskiej Akademii Nauk, Warszawa, ul. Kasprzaka 44/52, Poland)

Summary The Eu(dpm)<sub>3</sub>-shifted n.m.r. spectrum of a new diterpene has provided independent evidence for the location of the functional group.

WE have used tris(dipivaloylomethanato)europium, Eu-(dpm) $_{3}^{1,2}$  to obtain independent proof of the structure of a new pentacyclic diterpene, trachyloban-19-oic acid (Ia), recently isolated from sunflower flowers (*Helianthus annus* L). Its structure was established by degradation to



trachylobane and by spectral comparison with the known kaur-16-en-oic acid (IIa) which is also present in the same plant.<sup>3</sup>



FIGURE.  $Eu(dpm)_3$  shifted 100MHz n.m.r. spectrum of trachyloban-19-ol (Ib) in CCl<sub>4</sub>;  $[Eu(dpm)_3]$ : [(Ib)] = 0.90. Signals of protons of CH<sub>2</sub>OH group are strongly shifted downfield.

The application of  $Eu(dpm)_3$  enabled us to compare nearly all the corresponding ring-A and -B proton signals of the primary alcohols (Ib) and (IIb), lithium aluminium hydride reduction products of the respective acids' methyl esters. In the case of the "normal" spectrum it was only possible to compare the signal due to the methylene group attached to the hydroxy-group.<sup>3</sup>

It is known that  $Eu(dpm)_3$  deshields protons close to a hydroxy-group and spatial and bond distance dependance have been considered.<sup>2†</sup> Comparing the spectra of (Ib) and

Interpretation of Eu(dpm)<sub>3</sub>-shifted spectrum of trachyloban-19-ol (Ib) and kaur-16-en-19-ol (IIb)

| Proton<br>assignment | $\delta$ value:<br>extrapolated<br>or measured <sup>a</sup> | $rac{(\delta_{obs} - \delta) \times [Alcohol]}{[Eu(dpm)_3]}$ |
|----------------------|---|---|
| (Ib)                 |   |   |
| 1 a,e                | 1.55  | 2.50  |
| 2 a                  | 1.6-2.0   | ca. 5•6   |
| 2 e                  | 1.75  | 3.12  |
| 3 a                  | 1.6-2.0   | ca. 5•6   |
| 3 e                  | 1.9   | 12.5  |
| 5 a                  | 1.05  | 4.65  |
| 6 a                  | 1.40  | 5.3   |
| 6 e                  | 1.6-2.0   | ca. 5.6   |
| 7 a                  | ca. 1.5   | ca. 2·2   |
| 7 e                  | ca. 1.75  | ca. 1•4   |
| 9 a                  | ca. 1·3   | ca. 2·2   |
| 11 a,e               | ca. 1.5   | ca. 1.6   |
| 12, 13               | 0.67ª   | 0.55  |
| 14 exo               | 1.10  | 0.85  |
| 14 endo              | $2 \cdot 04^{a}$  | 1.28  |
| $16-H_2$             | 1.30  | 1.13  |
| 17-H <sub>3</sub>    | 1·13ª   | 0-47  |
| 18-H <sub>3</sub>    | 0.90a   | 10.0  |
| 19-H <sub>2</sub>    | 3.20ª   | 21.0  |
| $20-H_3$             | 0.93ª   | 3.50  |
| (IIb)                |   |   |
| 2 e                  | 1.8 - 1.9   | ca. 3.0   |
| 3 e                  | ca. 1.80  | ca. 14.5  |
| 5 a                  | ca. 1.0   | ca. 4·7   |
| 6 a                  | ca. 1.5   | ca. 5.2   |
| 18-H.                | 0-88ª   | 10.7  |
| 19-H,                | 3.40ª   | 21.0  |
| 20-H.                | 0.98a   | 3.45  |
| J                    | -   |   |

(IIb) we found that the corresponding protons surrounding the hydroxy-group are shifted to the same extent (see Table), which indicates that the hydroxy-group is at the same position in the kaurene and trachylobane systems.

The high separation of the signals appearing in a spectrum recorded using a concentration ratio of  $Eu(dpm)_3$  to trachylobanol of 1.0—1.5, as compared with the "normal" spectrum, made it possible to assign all 32 protons of this alcohol after additional decoupling experiments (see Table and Figure).

 $\dagger$  We found that the shift caused by Eu(dpm)<sub>s</sub> is linearly dependent upon the complex-to-substance ratio; this makes it possible to calculate chemical-to-shift values for protons which are normally unresolved. Chemical shifts change markedly with size and structure of the alcohol, but the concentration dependence for the same concentration ratio is small.

The coupled signals of the axial 5-H and 6-H protons were crucial for the interpretation. Decoupling experi-

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ments were successful for all geminal and axial-axial

couplings, as shown in the Figure.

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