The Assignment of the Methyl Proton Signals in the NMR Spectrum of Hibaene[*1)]

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Hibaene, a diterpene isolated from the essential oil in the leaves of *Thujopsis dolabrata* Sieb. et Zucc., has been shown[1)] to have structure I.

In order to assign the methyl proton signals in the NMR spectrum of hibaene, the chemical shifts have been compared with those of dihydrohibaene (II), isophyllocladene (III), and phyllocladane (IV).

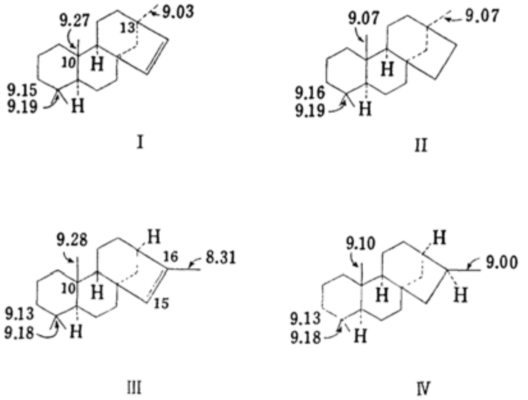

Fig. 1. Chemical shifts of methyl protons.

Hibaene shows four methyl proton signals;[*2] on the other hand, in dihydrohibaene[1)] (II), the positions of some of the methyl group signals are displaced in comparison with those of hibaene. This is considered to be due to some of the methyl groups in hibaene being influenced by the anisotropy effect of the double bond. Such effects have been observed, for example, in Δ^7-steroids.[2)]

The signals at τ, 8.31 ($J=2$ c. p. s.) of isophyllocladene[3)] (III) and at τ, 9.00 ($J=6$ c. p. s.) of phyllocladane[4)] (IV) appear as doublets; they are, therefore, to be assigned to the C_{16}-methyl group, which is coupled with the C_{15}-proton in III and with the C_{16}-proton in IV. Because there is no change in the chemical shifts of the peaks at τ, 9.13 and 9.18 of III compared to the corresponding peaks of IV, it is deduced that these signals are due to the *gem*-dimethyl group. The remaining methyl signal at τ, 9.28 in III corresponds, therefore, to the C_{10}-angular methyl group; the corresponding signal in IV appears at a lower field (τ, 9.10). The C_{10}-angular methyl group in III is recognized to be shielded by the anisotropy of the double bond.

By applying the results of the above assignments to the spectra of I and II, the methyl proton signals were assigned as follows: (a) the signals at τ, 9.15 and 9.19 of I and at τ, 9.16 and 9.19 of II originate from their respective *gem*-dimethyl groups; (b) the signal at τ, 9.07 of II is due to the C_{10}-angular methyl-group; this is shielded in the the case of I and appears at a high field (τ, 9.27); (c) consequently, the signal at τ, 9.07 of II is assigned to the C_{13}-methyl group in II; this signal appears at a low field (τ, 9.03) in the case of I because of deshielding.

The results of these assignments are depicted in Fig. 1. The C_{10}-angular methyl and the C_{13}-methyl group in I are subject to bond anisotropy effects of the opposite sign, a finding which is in agreement with what would be expected from an inspection of the molecular models.

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1) Y. Kitahara and A. Yoshikoshi, to be published.

[*2] Measurements were made on a Varian A60 NMR spectrometer using CCl_4 solutions.

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3) P. K. Grant and R. Hodges, *Tetrahedron*, **8**, 261 (1960).

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