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YOMOGI ALCOHOL A, A NEW MONOTERPENE ALCOHOL FROM ARTEMISIA FEDDEI LÉV. ET VAN.

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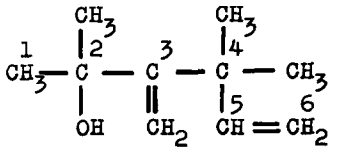
A new monoterpene alcohol was isolated from the essential oil of Artemisia feddei Lév. et Van. (Himeyomogi in Japanese), and its structure was determined as formula I, which revealed a new skeletal type of naturally occurring monoterpene. We propose the name Yomogi alcohol A for this alcohol, and here present the evidences for the proposed structure.



I

Artemisia feddei Lév. et Van. used in the present investigation was collected at the suburbs of Hiroshima city. The essential oil obtained by steam-distillation of the stalks and leaves of the plant was eluted through a silica gel column with a mixed solvent of n-hexane (85 vol.) and ethyl acetate (15 vol.), and Yomogi alcohol A was isolated in gas-chromatographically pure state. This alcohol, n_D^{25} 1.4570, d_4^{25} 0.8751, $[\alpha]_D^{25}$ 0°, showing no absorption maximum in the UV spectrum, had absorption bands at ν_{OH} 3350 and ν_{C-O} 1140 cm^{-1}, and exhibited a proton signal (1H, S) to be exchangeable with D_2O at 1.58 ppm (Fig. 1), but this alcohol had no proton

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signal due to hydrogens located on the carbon atom carrying a primary and secondary hydroxyl group. These spectrometric evidences indicate the hydroxyl group to be a tertiary one. In the higher side of the mass spectrum merely three abundant ions are recognized at m/e = 139, 136 and 121. A peak (60 %) of m/e = 139 is too strong as a parent peak of tertiary alcohol, and a medium peak (40 %) of 136 is difficult to be explained by thinking 139 as the parent peak. These three peaks are now well explained as (M - CH_3)$^+$, (M - H_2O)$^+$ and (139 - H_2O)$^+$ + (136 - CH_3)$^+$ ions respectively and also the values of the elementary analysis satisfy $C_{10}H_{18}O$ (molecular weight 154).

This alcohol having absorption bands of $\nu_{=CH_2}$ 3070 and $\nu_{C=C}$ 1630 cm^{-1}

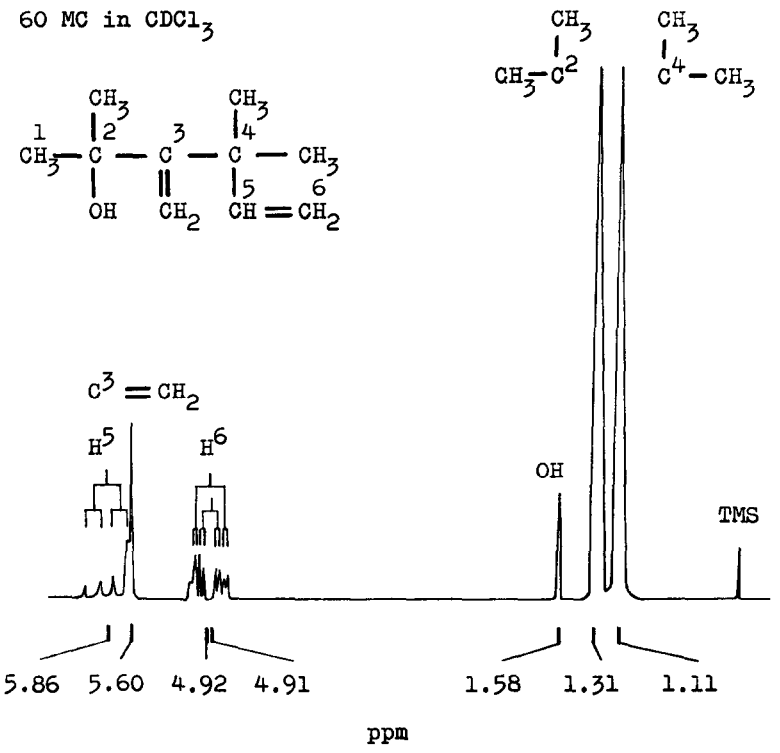
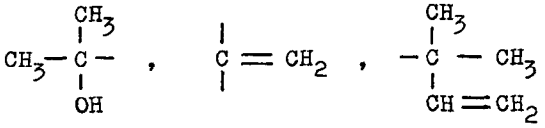


Fig. 1 NMR spectrum of Yomogi alcohol A

consumed two molar equivalent of hydrogen in catalytic hydrogenation with Adams platinum oxide in acetic acid. Besides, the olefinic region (5H) of the NMR spectrum can be reasonably explained as the overlap of a methylene singlet of a vinylidene group (5.60 ppm, 2H) and proton signals of an ABX-type vinyl group (τ_A 4.91, τ_B 4.92 and τ_X 5.86 ppm, respectively 1H, J_{AB} = 1.5, J_{AX} = 10.0 and J_{BX} = 18.0 cps), and further the quartet pattern of H_X indicates that a carbon atom adjacent to the vinyl group is quaternary.

The methyl region of the NMR spectrum indicates the existence of two geminal dimethyl groups ; one singlet at 1.31 ppm (6H) can be assigned to a dimethyl group of an isopropanol group, the presence of which is also supported by the appearance of an abundant peak of m/e = 59, and the other singlet at 1.11 ppm (6H) to the geminal dimethyl group on the above-mentioned quaternary carbon atom adjacent to the vinyl group.

We now have the following three partial structures.



Thus the structure of Yomogi alcohol A was determined as formula I, that is, 2,4,4-trimethyl-3-methylene-5-hexene-2-ol.

When the alcohol was dehydrated with thionyl chloride in pyridine, only one product whose UV spectrum (λ_{max}^{EtOH} 229 mμ, ε 25,000) corresponded to a dialkylsubstituted butadiene (calc. 227 mμ) was obtained. The production of such an olefin and no optical rotation of the alcohol also fit well in the above structure.

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