

P9. CONFIGURATION ASSIGNMENT OF INTERNAL DOUBLE BONDS WITH ALMOST ISOCHRONOUS PROTONS VIA CYCLOPROPANATION AND NMR

Milena Z. Živković, Niko S. Radulović, Milan B. Stojković

Department of Chemistry, Faculty of Sciences and Mathematics, University
of Niš, Višegradska 33, RS-18000 Niš, Serbia

E-mail: mika.zivkovic1987@gmail.com, nikoradulovic@yahoo.com

Determination of stereochemical features of organic molecules is one of the important aims in analysis of natural products since in many cases the stereochemistry plays a crucial role in the onset of their biological activity. NMR spectroscopy is one of the reliable tools of an organic chemist in the determination of the relative or absolute configurations, but differentiation of stereochemical isomers can become difficult due to accidentally isochronous proton and non-resolved $J_{H,H}$ -coupling.

A series of long-chained internal alken-1-ols (C_{22} - C_{32}) was detected in the flower wax of *Liriodendron tulipifera* L. by GC-MS. Mass spectra of trimethylsilyl and dimethyldisulfide derivatives provided information on the position of the alcohol groups and double bonds, respectively; however, the stereochemistry of the double bonds could not be inferred thereof due to indistinguishable MS data of the stereoisomers and the lack of any literature GC retention data. 1H NMR of a chromatographic fraction containing these internal alken-1-ols displayed a higher-order splitting pattern of the almost isochronous olefinic protons, wherefrom coupling constant values were difficult to obtain. Typically, the relative configuration of cyclopropane derivatives is easily deduced from simple NMR parameters, i.e. $J_{H,H}$ -coupling, and stereoisomers can readily be distinguished based on proton shifts alone. *Simmons-Smith* cyclopropanation stereospecifically converts olefins to the corresponding cyclopropanes, and we envisaged to solve the stereochemical ambiguities of these wax constituents by converting the NMR-problematic alkenes into NMR-straightforward cyclopropanes. We started off with subjecting model compounds, (*E*)- and (*Z*)-hexen-1-ols, to *Simmons-Smith* conditions. Protons of the methylene group of the cyclopropane ring in both isomers displayed very different chemical shifts in 1H NMR spectrum (*trans*-isomer both protons at ca. 0.23 ppm; *cis*-isomer -0.35 and 0.65 ppm) which allowed unabstracted differentiation of the stereoisomers. Consequently, a sample of the surface wax, treated with CH_2I_2 in the presence of a copper-zinc couple, gave a mixture of cyclopropanated alcohols whose 1H NMR revealed an exclusive *cis* configuration of the three-membered ring, i.e. all detected wax monoenic alcohols were (*Z*)-isomers.

