SHORT COMMUNICATIONS

Nuclear Magnetic Resonance Spectra of Isopropenyl Groups

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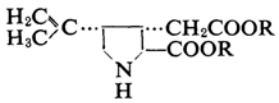
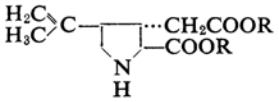
Definition of structures on α-kainic acid and α-allokainic acid as anthelmintic agent of *Digenea simplex* has been presented by Takemoto et al.[1] and by Morimoto et al.[2] In this report nuclear magnetic resonance (NMR) spectra of these compounds were observed by a Varian V-4300B NMR spectrometer at a fixed frequency 40 Mc.

Since both α-kainic acid (I) and α-allokainic acid (III) did not have a sufficient solubility in organic solvents to measure their NMR spectra at 40 Mc., their dimethyl esters, dimethyl α-kainate (II) and dimethyl α-allokainate (IV), were employed for the measurement of their spectra.



(I) R=H
(II) R=CH_3



(III) R=H
(IV) R=CH_3

The interesting patterns of olefinic protons, doublet in the case of II and singlet in IV respectively, are illustrated in Fig. 1. It is considered that there is difference in degree of receiving steric hindrance dynamically when isopropenyl group makes rotation. In other words, H_b of olefinic protons and methyl group of isopropenyl receive a steric hindrance at

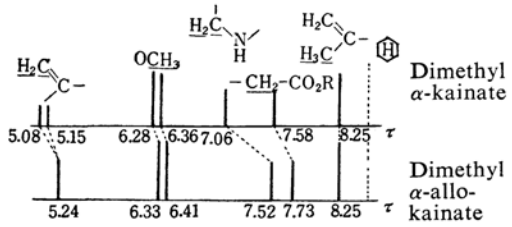


Fig. 1

TABLE I. DOUBLET IN OLEFINIC PROTONS OF ISOPROPENYL GROUP

Compound	τ
2,2,4-Trimethyl-4-pentene	
Lupeol acetate	5.17
Dimethyl cianothiate	5.4
1,5-Dimethyl-2-isopropenyl-1-cyclohexene	5.31
1,6-Dimethyl-2-isopropenyl-1-cyclohexene	5.25
1,5-Dimethyl-2-isopropenyl-1-cyclopentene	
2'-Methyl-allylidenecyclohexane	5.20

TABLE II. SINGLET IN OLEFINIC PROTONS OF ISOPROPENYL GROUP

Compound	τ
2-Methyl-1-propene	5.40
Isoprene	5.06
Limonene	5.34
Carvone	5.22
1-Acetyl-4-isopropenyl-1-cyclopentene	4.87
1-Acetoxyl-1-methyl-2-hydroxyl-4-isopropenylcyclohexane	5.37

C_5 protons when they are rotated. Further, in the case of II they also receive steric hindrance from the protons of methylene group in C_3 side chain, so that the dynamic steric hindrance is greatly increased. Therefore, H_b shifts to low field considerably. H_a also shifts very slightly. The C_5 protons and methylene of C_3 side chain in II both shift to lower field in comparison with IV. These results may be also explained as follows; when isopropenyl group is rotated, the olefinic proton H_b is locating in high probability between C_5 protons and the methylene protons of C_3 side chain which are affected by the long-range shielding of double bond of isopropenyl group.

It is of interest that olefinic protons, methylene protons of C_3 side chain and C_5 protons are all broad compared with the spectrum of

1) T. Takemoto, Z. Tei and K. Daigo, *J. Pharm. Soc. Japan* (*Yakugaku Zassi*), 76, 298 (1956).
2) H. Morimoto and R. Nakamori, *Proc. Japan Acad.*, 32, 41 (1956): *J. Pharm. Soc. Japan* (*Yakugaku Zassi*), 76, 294 (1956).

other groups and fine splittings greater than 1 c. p. s. were not observed in each of them. It is considered that the broadening are due to the asymmetry of their electron cloud caused by the dynamic steric hindrance.

Doublet patterns of NMR spectra is also observed in olefinic protons of isopropenyl group of other compounds (Table I)[3-5]. When its adjacent group is polar group or aromatic ring[3,6] its patterns shows doublet. This is thought to be caused by different degree of inductive effect or long-range shielding one. On the contrary, when the effects of polar group and of imhomogeneous magnetic field are both weak, and the effect of dynamic steric hindrance is considered small, singlet structure is observed in olefinic protons (Table II)[3,5-7].

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3) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, London, New York (1959), p. 120.
4) P. de Mayo and A. N. Starratt, *Tetrahedron Letters*, No. 7, 259 (1961).
5) Private communication from Dr. J. Wolinsky.
6) G. Van Dyke Tiers, "Characteristic Nuclear Magnetic Resonance 'Shielding Values' (Spectral Position) for Hydrogen in Organic Structures" (1958).
7) J. Wolinsky and W. Barker, *J. Am. Chem. Soc.*, **82**, 636 (1960).