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SPIN-LATTICE RELAXATION TIME AS A USEFUL INDICATOR FOR THE ^{13}C-NMR ASSIGNMENT OF TERMINAL *cis*- AND *trans*-METHYLS IN 2-METHYL-1-PROPENYL MOIETY

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Abstract: T_1 gives a clue to assign cis- and trans-methyl carbons in 2-methyl-1-propenyl moiety.

2-Methyl-1-propenyl moiety shown in Fig.1 is found frequently in the terminal of naturally occuring compounds. In this communication, we describe our new finding that the ^{13}C spin-lattice relaxation time(T_1) is a useful indicator for assigning *cis*- and *trans*-methyls in 2-methyl-1-propenyl moiety.

Table I shows the T_1 values of *cis*- and *trans*-methyl carbons in the samples examined. All samples of commercial origin except (6) were purified by distillation. (6) was obtained from (5) by hydrogenation with sodium borohydride. Each sample was diluted with the same volume of $CDCl_3$ for deuterium locking of NMR. The T_1's were measured by usual 180°-τ-90° pulse sequence$^{1)}$. ^{13}C-NMR assignment of these methyls was done independently from the T_1 measurement, using mainly the γ-effect (steric shift)$^{2)}$ and other techniques, such as lanthanide induced shift(LIS), successive selective decoupling$^{3)}$ and so on. It can be seen that all the *cis*-methyl carbons shown in Table I have longer T_1 values than *trans*-methyl carbons. The *cis/trans* ratios increase as the carbon chain length of R increases, typical pattern being compared in (1), (4) and (7). In the compounds of the same carbon number, such as (1), (2) and (3), or (4), (5) and (6), the presence and polarity of the functional group will contribute to the greater extent to the absolute T_1 values and the ratios. Bromine atom in (2) reduces both *cis*- and *trans*-T_1 values to two thirds to those of (1) while the ratio increases. Among the polar groups, the hydroxyl in (6) contributes to the greater reduction of both T_1 values than the carbonyl in (5), which may be ascribed to the fact that the molecular association of (6) by hydrogen bonding reduces the molecular mobility in solution.

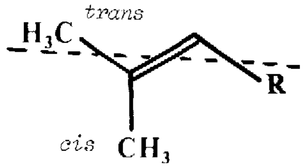

Fig. 1

The geometrical isomers, geraniol(9) and nerol(10), show the quite similar *cis*- and *trans*-T_1 values, respectively, indicating that the isomerism in the R-groups has no influence on the T_1 values of terminal methyls. Additionally, we would like to mention the T_1 difference between the inner methyls binding to C-3 carbons$^{4)}$ in (9) and (10). The geraniol inner methyl which is *cis* to the terminal CH_2OH has the T_1 value of 7.1 sec whereas the nerol inner methyl, *trans* to CH_2OH, shows the value half of the isomer, 3.4 sec. This result indicates that the relation between T_1's of the terminal *cis*- and *trans*-methyls in 2-methyl-1-propenyl moiety could be applicable to that

Table I. T_1 and δc Values of *cis*- and *trans*-Methyl Carbons in 2-Methyl-1-propenyl Moieties

		cis		*trans*		T_{1cis}/T_{1trans}
	R	T_1(sec)	δc(ppm)	T_1(sec)	δc(ppm)	
(1)	CH_3	22.5	17.1	14.5	25.5	1.6
(2)	CH_2Br	16.6	17.2	8.0	25.5	2.1
(3)	COOH⁵⁾	7.9	19.2	3.7	26.3	2.1
(4)	CH_2CH_3	23.5	17.5	12.7	25.7	1.9
(5)	$COCH_3$	21.2	20.5	8.8	27.5	2.4
(6)	$CH(OH)CH_3$	11.2	17.9	4.8	25.6	2.3
(7)	$CH_2CH_2CH_3$	17.2	17.5	8.3	25.6	2.1
(8)	$CH_2CH_2COCH_3$	12.5	16.8	5.2	24.8	2.4
(9)	$CH_2CH_2C(CH_3)=CHCH_2OH$ (*E*)	9.0	17.2	3.6	25.2	2.5
(10)	$CH_2CH_2C(CH_3)=CHCH_2OH$ (*Z*)	10.4	17.2	3.6	25.2	2.9
(11)	$CH_2CH_2C(OH)(CH_3)CH=CH_2$	10.3	17.3	3.7	25.3	2.8
(12)	$CH_2CH_2CH(CH_3)CH_2CH_2OH$	8.7	17.3	3.2	25.4	2.7
(13)	$CH_2CH_2C(CH_3)=CHCH_2CH_2C(CH_3)=CHCH_2CH_2CH=C(CH_3)CH_2CH_2CH=C(CH_3)CH_2CH_2CH=C(CH_3)_2$	7.0	17.6	2.1	25.6	3.3

of inner methyls and, therefore, the structure elucidation of their geometrical isomerism. The difference of T_1 values between *cis*- and *trans*-methyls is of particular interest since it gives the clue to elucidate the relaxation mechanism. Taking the size and polarity of R-group as well as the molecular motion in solution into account,⁶⁾ it is possible to suppose a segmental rotation axis as shown in Fig.1 as a dotted line which goes through along the sequence of *trans*-CH_3-C=C-R. Thus, we have established the empirical rule that the *trans*-methyl which is nearer the axis has always the shorter T_1 value than the *cis*-methyl. It was on the basis of this rule that we have elucidated in our previous paper⁷⁾ the stereostructure of the new aroma constituent of Turkish tobacco. Detailed discussion on the relaxation mechanism will be described elsewhere.

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