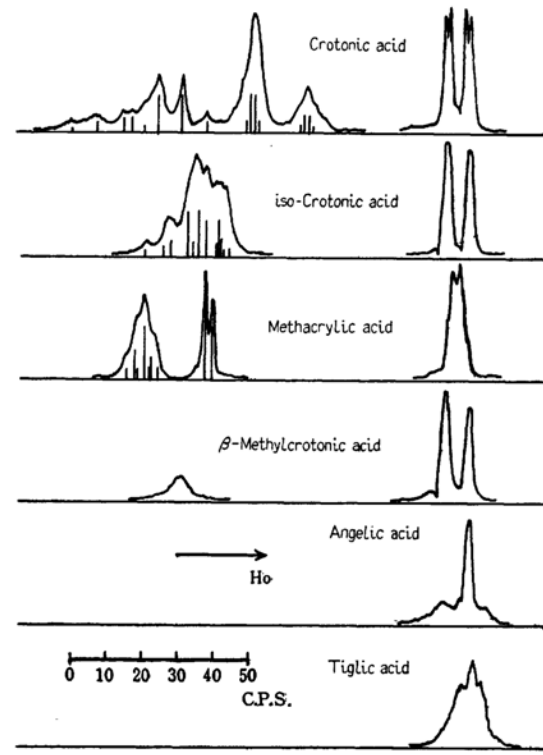

Fig. 1

NMR Study of α, β-Unsaturated Fatty Acids

By Shizuo FUJIWARA, Hiroshi SHIMIZU*, Yoji ARATA* and Sachio AKAHORI**

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The NMR spectra of six sorts of α, β-unsaturated acids were measured by the 27 Mc. high-resolution spectrometer constructed in this laboratory. The acids used in this experiment were crotonic acid (I), isocrotonic acid (II), methacrylic acid (III), β-methylcrotonic acid (IV), angelic acid (V) and tiglic acid (VI). Among these, II and III were studied in pure liquids and others as saturated solutions in carbon tetrachloride at 25°C. The observed and calculated spectra are shown in Fig. 1, and the approximate values of chemical shifts and spin coupling constants derived from observed spectra are given in Table I, where the spin coupling constants between H and H, and between H and CH_3 are about the same as in ethylenic compounds[1]. From the spectra of I and II, it will be concluded that the α-proton signal appears at the field higher than the β-proton, and that the β-proton *trans* to the carboxyl group is about 1 p.p.m. higher than the *cis* proton. The observed chemical shift between gem protons in methacrylic acid is 0.62 p.p.m., which is considerably larger than that between gem protons in the simple ethylenic compounds with the values of 0.1～0.2 p.p.m.[1] This fact seems to be consistent with the conclusion mentioned above on the chemical shifts for the β-protons of crotonic and isocrotonic acids. The magnitudes of the chemical shifts between the two methyl groups attached to the same carbon atom are not so large as the values between the gem protons.

An interesting solvent effect was observed in the system of β-methylcrotonic acid and benzene; where as the acid was diluted by benzene, the chemical shift between gem methyl groups was observed to increase, and the dilution shift at zero concentration was about 0.45 p.p.m. As reported by Shimizu[2,3] and Fujiwara[2], the active methyl group of saturated fatty

* Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Tokyo.
** Shizuoka College of Pharmacy, Koroku-cho, Shizuoka.

1) J. A. Pople, W. G. Bernstein and H. J. Schneider, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill Book Co., Inc., New York (1959), p. 242.

2) H. Shimizu and S. Fujiwara, *Chem. Pharm. Bull. (Tokyo)*, to be published.

3) H. Shimizu, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, to be published.

TABLE I. SPIN COUPLING CONSTANTS AND CHEMICAL SHIFTS OF α,β-UNSATURATED FATTY ACIDS

(3)–C=C–(2) (4)–COOH	Chemical shift p.p.m.	Spin coupling constant, c.p.s. H–H J_{23}	H–H J_{24}	H–H J_{34}	H–CH_3 J_{23}	H–CH_3 J_{24}	H–CH_3 J_{34}
CH_3, H	$\delta_{H_2}-\delta_{H_4}=1.28$		15.5		1.2		6.1
H, H; CH_3	$\delta_{H_2}-\delta_{H_3}=0.19$	9.0				$\lesssim 1.0$	7.0
H, CH_3; H	$\delta_{H_3}-\delta_{H_4}=0.62$			1.9	~ 0	1.7	
CH_3, H; CH_3	$\delta_{Me_3}-\delta_{Me_4}=0.27$				$\lesssim 1.0$	$\lesssim 1.0$	
H, CH_3; CH_3	$\delta_{Me_2}-\delta_{Me_4}=0.2$				~ 0		6.5
CH_3, CH_3; H	$\delta_{Me_2}-\delta_{Me_3}\simeq 0$					$\lesssim 1.0$	6.0

acid, such as acetic acid shows the high field shift as the result of π complex formation with benzene molecule. The *trans* methyl group which is relatively unaffected from a steric point of view will tend to form π complex more easily than the *cis* methyl group and, hence, to show the dilution shift. The fact that the CH_3–CH_3 shift was increased by the dilution will be explained if the methyl group whose signal appeared at the field higher than the other is more shifted toward a high field. Thus, it is suggested from these considerations that the signal at the higher field may be assigned to the *trans* methyl group and the one at the lower field to the *cis* group. This conclusion may seem contrary to the expectation that the active methyl usually resonates at the field lower than the inactive one owing to the less density of the electronic cloud around it. As these unsaturated molecules have planar structures, however, the magnitude of the paramagnetic effect due to the carbonyl group at the *cis* position will exceed that of the paramagnetic effect at the *trans* position whose effect is mainly caused by inductive force of the carbonyl group.

More refined values of chemical shifts and spin coupling constants will be reported in the near future[4] by H. Shimizu, Y. Arata and S. Fujiwara concerning the general discussion of the analyses of the complex NMR spectra.

University of Electro-Communications
Chofu-shi, Tokyo

4) It will appear in This Bulletin.