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IDENTIFICATION OF BRANCHED-CHAIN FATTY-ACIDS BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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AF MATERIALS LABORATORY
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project 7360, Task 736005

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2. Carboxylic Acids
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FOREWORD

This report was prepared by the Analytical Branch, Materials Physics Division. The work was initiated under Project 7360, "Materials Analysis and Evaluation Techniques," Task No. 736005, "Compositional, Atomic and Molecular Analysis." The work was administered under the direction of the AF Materials Laboratory, Deputy Commander/ Research and Engineering, Aeronautical Systems Division, for which 2nd Lt Robert L. Buchenauer was project engineer.

This report summarizes work conducted from August 1962 to February 1963.

This work was performed at the suggestion of Mr. William L. Baun. The author wishes to thank Prof. Stephen E. Wiberley of Rensselaer Polytechnic Institute for supplying some of the compounds used in this study and Miss Mary T. Ryan for helpful discussions during the course of this work.

ABSTRACT

The Nuclear Magnetic Resonance Spectra of twenty branched-chain fatty acids were studied in order to identify the structure of isomeric aliphatic carboxylic acids of low molecular weight. The effect of chemical shift of methyl protons as a function of distance from the carboxyl group is discussed.

This technical documentary report has been reviewed and is approved.

FREEMAN F. BENTLEY
Chief, Analytical Branch
Materials Physics Div
AF Materials Laboratory

INTRODUCTION

In 1956, Guertin, Wiberley and Bauer (ref 1) of Rensselaer Polytechnic Institute published the results of a study of the infrared absorption spectra of branched-chain fatty acids. These authors were able to identify several structural isomers by means of their infrared absorption in the carbon-hydrogen stretching region.

Since nuclear magnetic resonance spectra are sensitive to changes in molecular structure, we decided to investigate the spectra of these compounds to determine whether they could be easily distinguished from their proton-magnetic resonance spectra.

EQUIPMENT AND COMPOUNDS

The acids were obtained from Prof. Stephen E. Wiberley of Rensselaer Polytechnic Institute and from commercial sources. An A-60 Nuclear Magnetic Resonance Spectrometer was used to record the spectra. The spectra of the acids were obtained as dilute solutions in deuterated chloroform with tetramethylsilane as an internal standard. The chemical shifts are reported in parts per million from tetramethylsilane.

The acids were used as obtained without further purification. The NMR spectra of 3-methylbutanoic acid and 3,3-dimethylbutanoic acid indicated the presence of isomeric impurities but these were readily recognizable. The spectra of the other acids showed that they were of high purity.

ASSIGNMENTS

An examination of the NMR spectra of these compounds shows that the structures of the acids can be distinguished by means of the chemical shift and splitting of the methyl protons and the protons on the carbon atom alpha to the carboxylic acid group. These assignments are discussed below.

Due to branching and to the very electronegative carboxyl group, the methylene protons of most of the acids appear as an unresolved multiplet in the range 1.0 - 2.0 ppm. With the exception of the alpha hydrogens (ca. 2.4 ppm), assignments were not made to specific methylene protons. The acid proton, which occurs at a chemical shift of 11.0 to 12.0 ppm and shifts appreciably with concentration, was not studied.

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Most of the acids in this study contain chemically different methyl groups which can be detected and assigned. The methyl protons have been broken down into two types: alpha methyl (1.2 ppm) and terminal methyl (0.9 ppm). The alpha methyl protons appear as a very intense singlet or doublet and can easily be identified even though they overlap in the methylene proton region. Methyl groups other than alpha methyl usually occur as a multiplet (0.9 ppm). However, in running a series of similar compounds such as we did in this study, the methyl multiplet could be resolved enough to distinguish between chemically different methyl protons. In all but two cases (4-methylhexanoic and 5-methylheptanoic) the multiplet was resolved enough to allow assignment of chemically different methyl groups.

Another chemical shift which is easily recognized is caused by the acidic protons on the alpha carbon. These protons are less shielded than the other methylene protons and occur in the region 2.26 - 2.63 ppm. In acids where branching occurs beyond the beta carbon atom, the alpha protons result in the expected three peaks. However, the peak down field is characteristically split.

Substitution on the beta carbon causes a multiplicity of splitting of the alpha methylene proton absorption. The methylene group is adjacent to an asymmetric carbon atom and interactions during rotation about the carbon-carbon single bond causes the alpha methylene protons to be magnetically non-equivalent. This is most noticeable with methyl branching on the beta carbon.

In alpha branching the alpha hydrogen occurs as a resolved multiplet and is easily distinguished from the other types of branching.

The ease of distinguishing the methyl protons permits a study of the chemical shift of these protons as a function of distance from the carboxyl group. Table 2 shows the change in chemical shift as the methyl group is moved away from the carboxyl group for three substituted hexanoic acids.

Table 3 shows a comparison of four alpha methyl carboxylic acids. A progressive decrease in chemical shift of the terminal methyl proton is noted as the number of carbon atoms on the parent chain is increased. As the carbon chain of a compound is lengthened beyond the beta carbon, there appears to be some linear relationship in similar acids between the chemical shift of the methyl protons and the number of carbon atoms between the methyl and carboxyl group.

A correlation of the chemical shift of the methyl protons with respect to the number of carbon atoms between the methyl and the carboxyl group is found in table 4. With a few exceptions, the chemical shifts of the methyl protons appear to be dependent on the distance of the methyl group from the carboxyl group.

As may be expected, the alpha methyl shift occurs at much higher chemical shifts than the other methyl groups. It is interesting to note that the chemical shift of the methyl protons increases when a second chemically equivalent methyl group is added to the molecule. A third methyl group increases the shift still further (table 4).

The alpha protons occur at higher chemical shifts and cover a wider range (2.28 - 2.63 ppm) than any of the other protons studied. Apparently other factors influence the chemical shift of the alpha protons.

In 1959 Webster (ref 2) completed a study on the chemical shift of R_3SiH proton with various alkyl groups attached to the silicon atom. From his results he found that the shielding of the silicon proton was influenced by the nature of the alkyl groups. By substituting different alkyl groups Webster found that the order of increased shielding of the silicon proton was

methyl < i-butyl < n-propyl = n-butyl < ethyl < i-propyl.

Table 5 shows the chemical shift of the alpha protons and the alkyl groups responsible for this shift. The order of shielding found by Webster agrees closely with the order found in this study.

SUMMARY

We used NMR in our study, which made identification of branched-chain fatty acids relatively easy. Differences in chemical shifts of methyl protons were observed as far away as five bonds from a carboxyl group. The study showed, also, that shielding of alpha protons is affected not only by the carboxyl group but also by the alkyl groups attached to the alpha carbon.

REFERENCES

1. Guertin, D. L., Wiberley, S. E., and Bauer, W. H., Journal of the American Oil Chemist's Society, Vol. XXXIII, No. 4, pp 172-174 (1956).

2. Webster, D. E., Technical Report, Contract No. Nonr-1866(13), Chemistry Branch, Office of Naval Research, August 1959.

TABLE 1

PROTON MAGNETIC RESONANCE SHIELDING IN FATTY ACIDS RELATIVE TO TETRAMETHYLSILANE

Acid Compound	Chemical shift in ppm			
	Terminal methyl	Chain methyl	Alpha methyl	Alpha protons
2-methylpropanoic	-	-	1.22	2.63
2,2-dimethylpropanoic	-	-	1.25	-
2-methylbutanoic	0.96	-	1.19	2.39
3-methylbutanoic	1.01	-	-	2.26
2,2-dimethylbutanoic	0.91	-	1.21	-
3,3-dimethylbutanoic	1.08	-	-	2.28
2-ethylbutanoic	0.96	-	-	2.29
2-methylpentanoic	0.94	-	1.20	2.48
4-methylpentanoic	0.93	-	-	2.40
2,2-dimethylpentanoic	0.93	-	1.21	-
n-hexanoic	0.92	-	-	2.39
2-methylhexanoic	0.92	-	1.19	2.45
3-methylhexanoic	0.93	0.98	-	*
4-methylhexanoic	*	*	-	2.38
5-methylhexanoic	0.91	-	-	2.37
3,5-dimethylhexanoic	0.90	0.96	-	*
2-ethylhexanoic	0.92	0.96	-	2.29
3-ethylhexanoic	0.89	0.90	-	2.29
4-ethylhexanoic	0.88	-	-	2.37
2-n-propylhexanoic	0.91	0.93	-	~ 2.38
5-methylheptanoic	*	*	-	2.36

* unresolved multiplet

TABLE 2

CHEMICAL SHIFTS OF ALPHA BRANCHED HEXANOIC ACIDS

Compound	Chemical shift (ppm)	
	Terminal methyl	Methyl on alpha chain
2-methylhexanoic	0.92	1.19
2-ethylhexanoic	0.92	0.96
2-n-propylhexanoic	0.91	0.93

TABLE 3

CHEMICAL SHIFTS OF ALPHA METHYL ACIDS

Compound	Chemical shift (ppm)	
	Terminal methyl	Alpha methyl
2-methylpropanoic	1.22	1.22
2-methylbutanoic	0.96	1.19
2-methylpentanoic	0.94	1.20
2-methylhexanoic	0.92	1.19

TABLE 4

RELATIONSHIP OF CHEMICAL SHIFT AND DISTANCE OF METHYL GROUP FROM CARBOXYL GROUP

No. of carbon atoms between methyl group and carboxyl group	1	2	3	4
	1.25**	1.08**	0.94	0.93
Chemical shift	1.22*	1.01*	0.93*	0.92
of methyl protons	1.21*	0.98	0.93	0.92
relative to	1.21*	0.96	0.93	0.92
tetramethylsilane	1.20	0.96	0.90	0.91*
in ppm	1.19	0.96		0.91
	1.19	0.91		0.90*
				0.89
				0.88*

*chemical shift of two methyl groups
**chemical shift of three methyl groups

TABLE 5

CHEMICAL SHIFT OF ALPHA PROTONS
Reference to $Si(CH_3)_4$

Compound	Alkyl groups attached to alpha carbon	Chemical shift of alpha proton (ppm)
2-methylpropanoic	Me, Me	2.63
2-methylpentanoic	Me, n-Pr	2.48
2-methylhexanoic	Me, n-Bu	2.45
4-methylpentanoic	i-Bu	2.40
2-methylbutanoic	Me, Et	2.39
n-hexanoic	n-Bu	2.39
4-methylhexanoic	C-C-C(-C)-C-	2.38
2-n-propylhexanoic	n-Pr, n-Bu	2.38
4-ethylhexanoic	C-C(-C-C-)(-C-C)	2.38
5-methylhexanoic	C(-C-C-C-)(-C)	2.37
5-methylheptanoic	C-C-C(-C)-C-C-	2.36
2-ethylbutanoic	Et, Et	2.29
2-ethylhexanoic	Et, n-Bu	2.29
3-ethylhexanoic	C-C-C(-C-)(-C-C)	2.29
3,3-dimethylbutanoic	t-Bu	2.28
3-methylbutanoic	i-Pr	2.26

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