Induced Chemical Shifts in the NMR Spectrum of Methyl Petroselinate[1]

ABSTRACT

The use of a pseudo contact shift reagent, (Eu[fod]$_3$), to obtain simplified NMR spectra of a typical long chain monounsaturated fatty acid methyl ester, methyl petroselinate, is described. Spectra were obtained in which individual methylene groups are identifiable from their splitting patterns. Non-equivalent splitting patterns were observed for the methine protons with varying amounts of reagent used. The effect of concentration of the shift reagent on the chemical shift is discussed.

INTRODUCTION

The locating of the site of unsaturation in the long chain fatty acids and fatty acids derivatives has been studied by techniques and procedures too numerous to mention. All seem to encompass elaborate procedures, lack of specificity, or both. In a study of nuclear magnetic resonance (NMR) shifts of a complete series of positional isomers of octadecenoic acids, Gunstone and Ismail (1) reported that it was not possible to distinguish between the eight octadecenoic acids which have centrally located double bonds, 6-7 to 13-14. Shift reagents in NMR have been shown to allow first order spectra to be obtained for organic compounds having long methylene chains (2,3). The present report describes the use of a shift reagent in locating the olefinic group in a typical long chain fatty acid methyl ester.

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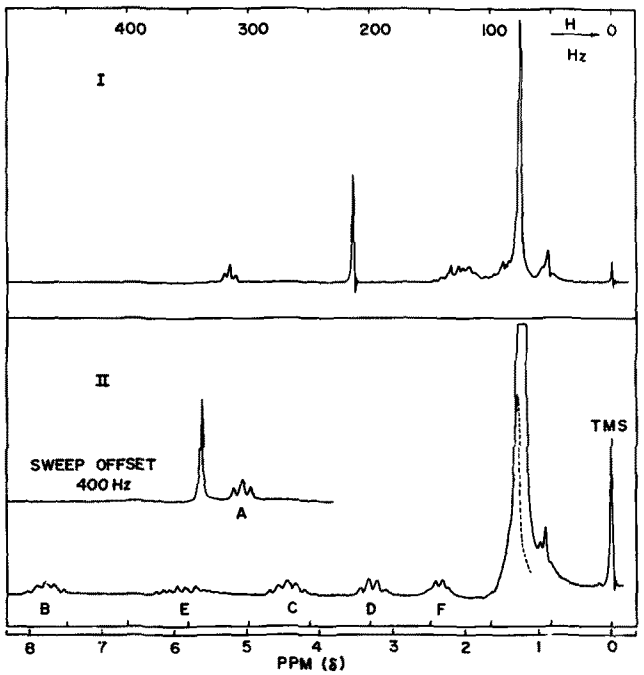

FIG. 1. Nuclear magnetic resonance spectra (60 MHz): I, methyl petroselinate; II, methyl petroselinate containing Eu(fod)$_3$. TMS = internal reference.

EXPERIMENTAL PROCEDURE

NMR spectra were measured on a Varian Associates Model A60-A spectrometer operated at 60 MHz at normal probe temperature. Chemical shifts are measured in Hz from internal reference. The NMR spectra were obtained on an approximately 0.3 g. sample in approximately 1.4 g. of CCl_4 to which was added amounts of europium (III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione), (Eu[fod]$_3$), to a molar ratio of 5.4 moles of Eu(fod)$_3$/mole of sample. The methyl petroselinate and methyl oleate were recrystallized material prepared from the pure acids. The 11-eicosenol was obtained by fractional distillation from a Jojoba oil product. The Eu(fod)$_3$ complex was purchased from the Norell Chemical Co., Inc.

RESULTS AND DISCUSSION

Figure 1-I illustrates a 60 MHz spectrum of methyl petroselinate, methyl 6-octadecenoate. There is little to distinguish the spectrum from that of any of the other

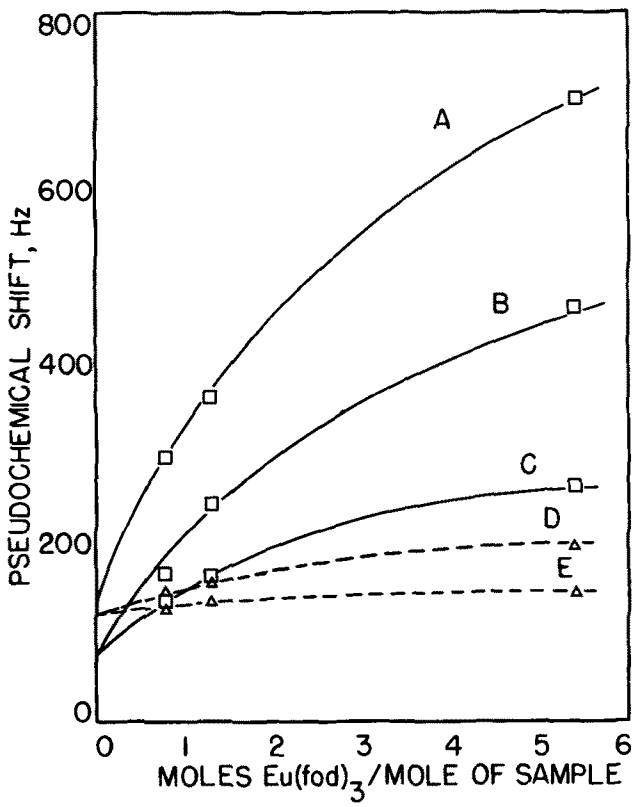

FIG. 2. Pseudochemical shifts as related to molar concentration of Eu(fod)$_3$: A, protons alpha to carbonyl group; B, protons beta to carbonyl group; C, protons gamma to carbonyl group; D, protons alpha to olefinic group (No. 5 C-atom); E, protons alpha to olefinic group (No. 8 C-atom).

eighteen carbon atom monounsaturated fatty acid methyl esters having unsaturation in the 6-7 to 13-14 carbon atom region. Figure 1-II illustrates a spectrum of methyl petroselinate to which has been added the pseudo contact shift reagent, $Eu(fod)_3$. It is obvious that considerably more information is readily available. First to be noted is the shift downfield of a triplet (A) representing the methylene protons alpha to the carbonyl group. Next to be considered are (B) and (C), the quintets resulting from methylene protons split by methylene protons on either side. Since (D) is a quartet which results from splitting owning to both methylene and methine protons, it is therefore adjacent to an olefinic group; thus the unsaturation (E) is reasoned to be in the 6-7 position. This is confirmed by (F), a second quartet as a result of the methylene and methine splitting of the methylene protons next in the carbon chain.

The technique just described would seem to be ideally suited to locating double bond positions in monounsaturated acids in which the double bond is positioned beyond the 5-6 position. Other techniques besides the use of shift reagents can be used when the unsaturation is nearer the carbonyl group (4,5). However the effectiveness of the shift reagent diminishes as the quantity of $Eu(fod)_3$ is increased.

The technique just described was also used with varying degrees of success on methyl oleate, 11-eicosenol and oleic acid. The resolution obtained for methyl oleate at the high molar ratios of reagent was not sufficient in order to position the olefinic group in the chain. Spectra obtained for 11-eicosenol using $Eu(fod)_3$ still showed no improvement in the resolution of the methylene protons beyond the eighth carbon atom. Contrary to what had been expected, the shifts observed in the oleic acid spectrum were less than those of the corresponding ester for a given molar ratio of the reagent. This was perhaps owing to the presence of competing OH and C=O groups or a break down of the reagent. The effectiveness of the chemical shift reagent is illustrated in Figure 2 in which the chemical shift of the methylene group proton alpha to the carbonyl is plotted against the molar ratio of the europium complex to sample. Maximum effectiveness of the complex is obtained up to about a molar ration of 3:1 thereafter decreasing with increasing amounts of the complex. The $Eu(fod)_3$ was found to be completely soluble in the methyl ester. The viscosity of the mixture was great enough to require dilution with carbon tetrachloride. The shift obtained was determined to be dependent only on the molar ratio of the complex to the sample and relatively independent of the quantity of CCl_4 used, which affected only the signal strength. Another more serious problem encountered as a result of high molar ratios of the complex was a downfield shift of the $Eu(fod)_3$ proton signal which tended to mask the methylene signals at about 75 Hz as shown by the dotted line in Figure 1-II. It would also appear that the "sphere of influence" of the europium complex is an important factor. This is illustrated in Figure 2 in which it is noted that the chemical shifts of those protons on the C-atoms farthest removed from the carbonyl group are the smallest and are least affected by increases in the concentration of $Eu(fod)_3$.

Although it had been reported that shift reagents do not normally affect olefinic groups (3), a shift was observed from 315 to 352 Hz for methyl petroselinate. Since the methylene protons along the carbon chain were observed to be shifted in order of their proximity to the carbonyl group, the proton on the olefinic group closest to the carbonyl would therefore be influenced first, causing an increase in the magnitude of the downfield shift of the C_6 proton, thus making the olefinic protons nonequivalent and changing their splitting pattern. A further increase in the molar ratio shifts the protons enough to give a complex symmetrical splitting pattern of 10-12 lines which could not be analyzed as first order splitting. The proton shifted further downfield is that of the C_6 atom and that shifted least is on the C_7 atom. The implication is that substituents added to an olefinic group could thus be located positionally on the chain under optimum concentration conditions.

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A New Colorimetric Method for Estimation of Argemone Oil

ABSTRACT

Argemone oil is toxic even in low concentrations for human consumption. The author suggests a new colorimetric method in which an orange color is developed when antimony trichloride solution is added to the extracted alkaloid. The developed color is measured in a colorimeter and compared against known standards of the alkaloid. The alkaloid content of argemone oil has been found to be about 1.0%. This method determines an admixture of argemone oil as low as 0.005% in other edible oils.

Argemone oil, a common adulterant of mustard oil in India, causes serious physiological consequences to the consumer such as nausea, vomiting and headache as acute symptoms, and glocuma, edema, etc., by prolonged consumption. Even a low concentration, i.e., 0.01% of argemone oil in edible oil, is marginally safe when the edible oil is consumed in normal amounts (National Institute of Nutrition, Hyderabad, India, unpublished experiment). The seeds of Argemone mexicana resemble mustard seeds in outward appearance. Further these have a high oil content (30.0%). The alkaloids of argemone oil are known to be responsible for the toxicity of the oil. Therefore their detection in other vegetable oils and in oil cakes for animal feed is very important.

It was observed by the author that both the alkaloids of