Production of Branched-Chain Fatty Acids from Sterculia Oil[1]

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ABSTRACT

Methyl sterculate was rearranged by use of 0.5% of rhodium catalyst to isomeric conjugated diene fatty acid methyl esters containing both methylene- and methyl-branched isomers. The rearranged products were hydrogenated directly to saturated, methyl-substituted, branched-chain fatty acid methyl esters with the methyl substituent at one of the positions formerly occupied by the cyclopropenoid ring. The crude branched-chain fatty acids from these esters were purified by recrystallization from a mixed solvent of ethanol and water (80:20, v/v) and flash distillation; the product contained about 90% of branched-chain fatty acids (C_{19}:80%, C_{18}:10%). Esters of the branched-chain fatty acid were prepared with 2-ethylhexyl alcohol or trimethylolpropane, and the characteristic properties of these esters were investigated. The branched-chain fatty esters appear to have potential utility in lubricants; other uses may be possible.

INTRODUCTION

Several procedures are available for producing methyl-substituted, branched-chain fatty acids. Branched-chain fatty acids are produced along with dimeric and trimeric acids upon thermal treatment of oleic acids in the presence of mineral catalyst (1-3). Other branched-chain fatty acids are produced from olefins by the oxo-process (4). Also, various types of branched-chain fatty acids exist in living organisms (5). Tuberculostearic acid and its homologs, which have a methyl group substituted in the hydrocarbon chain, are found in *Tubercule bacilli* (6,7) and *Microbispora chromogenes* M-22 (8). Iso acids and anteiso fatty acids, which are substituted, respectively, on the next to last carbon and at the second from the last carbon, are obtained from a number of natural sources (9-13). Methylation of cellular lipid from the methyl group of methionine has been investigated in *Agrobacterium tumefaciens* (14), in *Corynebacterium simplex* grown on *n*-alkanes (15) and *n*-alkenes (16), and in *Mycobacterium phlei* (17). The mechanism for the biosynthesis of cyclopropenoid fatty acids from methionine has been investigated by Yano et al. (18).

It is known that cyclopropenoid ring has a high degree of strain in the structure, and it has been suggested that an allylic cation transition state may exist in the acid-catalyzed rearrangement; alternatively, compounds with methylene- or methyl-groups may result directly from a cyclopropyl cation (19). This ring rearrangement has been investigated in sterculene with Al_2O_3 (20) and in methyl sterculate with Pd (21).

In this report, the production of branched-chain fatty acids from sterculia oil, an oil of Southeast Asia known to possess high contents of cyclopropenoid fatty acids, was investigated by rearrangement of the cyclopropenoid ring, followed by hydrogenation of the rearrangement products.

EXPERIMENTAL PROCEDURES AND RESULTS

Oil Extraction

Sterculia seeds (601.4 g) were dehulled to obtain the kernels (306.2 g), which were allowed to stand in 1,500 mL petroleum ether overnight at room temperature. Sterculia oil (137.9 g) was obtained after filtration of the miscella and removal of petroleum ether at 40-50 C in a rotary evaporator. The yield of this oil was 45.0% of the kernel and 22.9% of whole seeds.

Transesterification

Sterculia oil (AV = 2.0) was washed in 1% KOH aqueous solution to remove free fatty acid from the crude oil. The alkali-refined sterculia oil (125.2 g, AV = 0.0) was transesterified with methanol (700 mL) and sodium methoxide (1.8 g) in a 3-necked flask at 49-51 C under N_2 for 3 hr. When the reaction mixture had cleared and the absence of triglyceride had been confirmed by thin layer chromatography (TLC) (silica gel plate; developing solvent: hexane/ethyl ether, 80:20, v/v), the reaction was considered completed. The reaction products were extracted with petroleum ether (400 mL), the petroleum ether extract was washed with water and then dried, followed by removal of solvent; 122.5 g of crude methyl esters was recovered. This methyl ester was analyzed by capillary gas chromatography (GC) after several months' storage (sample I, Table I). Peaks coinciding with the rearrangement products (described later) were found in capillary-GC. The origin of the rearrangement products was unclear; for example, adventitious catalyst during storage may have caused rearrangement. Therefore, a second sample of methyl ester, which was prepared carefully so as not to contact air and excess heat, was analyzed under the same conditions of capillary-GC. The result is shown in Table I. Ultraviolet (UV) spectra of methyl ester revealed a strong absorption band at 207 mμ (ϵ_{207} = 6.3 1/g cm). It was unclear whether this absorption was caused by methyl sterculate or other material in the sterculia oil that carried through the transesterification process.

Rearrangement

It has been reported that an aged palladium catalyst is more effective than fresh catalyst for the rearrangement (21). Accordingly, rearrangement of methyl ester was performed with 5% palladium-on-carbon bought more than 10 yr ago, with palladium bought more than 15 yr ago (catalyst I) and with 5% rhodium-on-carbon bought 5 yr ago (catalyst II) (all from Matheson, Coleman, and Bell, Cincinnati, OH). In preliminary experiments, it was revealed that the palladium catalyst bought 10 yr ago was not a good catalyst for the rearrangement reaction, but that it was a good catalyst for hydrogenation. Catalysts I and II were investigated in detail for the preparation of branched-chain fatty acids. Methyl ester (3-5 g), decane, as solvent (100 mL), and catalyst (10% of whole catalyst, 0.5% of metal) were added to a 3-necked flask with agitator and heated at 149-152 C under N_2. The rearrangement reaction was conducted for 9 hr, and about 6 mL of sample was taken at 1, 2, 4, 6 and 9 hr of reaction time.

Product Characterization

The rearrangement products were analyzed by UV spectrophotometry and GC after the catalyst had been removed by filtration and the solvent had been removed by vacuum

[1]Presented at the AOCS meeting in New Orleans, May 1981.

TABLE II

Composition of Rearrangement Products[a,b] (%)

Peak no.	Component ECL	Component Methyl ester	Rearrangement reaction times (hr) 1	2	4	6	9
1	16.0	Palmitate	18.9	19.9 (19.4)	19.5 (19.8)	19.8 (21.2)	20.5 (21.0)
2	18.0	Stearate	2.0	2.4 (2.0)	2.2 (2.2)	2.5 (2.2)	2.5 (2.3)
3	18.3	Malvalate	3.8	1.7 (3.6)	0.3 (1.9)	0.0 (1.4)	0.0 (0.9)
4	18.5	Oleate	4.6	5.3 (4.9)	5.2 (5.1)	4.8 (5.4)	5.2 (5.3)
5	18.7	Rearrangement product (C_{18})	3.6	4.0 (2.9)	5.1 (3.0)	3.1 (3.4)	3.7 (2.6)
6	19.1	Sterculate	30.2	14.3 (26.7)	3.4 (17.5)	0.8 (11.3)	0.3 (5.9)
7	19.3	Linoleate	6.3	5.7 (6.1)	6.1 (7.0)	5.9 (6.5)	6.2 (6.5)
8	19.6	Rearrangement product (C_{19})	16.8	23.1 (11.5)	20.9 (13.5)	16.7 (12.4)	10.5 (10.7)
9	20.6	Rearrangement product (C_{19})	8.2	10.1 (17.8)	10.2 (22.8)	9.8 (25.1)	9.3 (27.0)
10	20.9	Rearrangement product (C_{19})	0.5	1.3 (0.6)	3.1 (1.0)	4.9 (1.3)	4.7 (1.8)
11	21.9	Rearrangement product (C_{19})	5.1	12.2 (4.5)	24.0 (6.2)	31.7 (9.8)	37.1 (16.0)

[a]Capillary-GC conditions. Equipment: Perkin Elmer 3920 (FID); column: Silar 10 C, 50 m long × 0.25 cm id, glass capillary; col. temp.: 170 C; inj. temp.: 250 C; interface (column to detector): 200 C; carrier gas: 30 psi, He.
[b]With rhodium (catalyst II). Corresponding values for palladium (catalyst I) are given in parentheses.

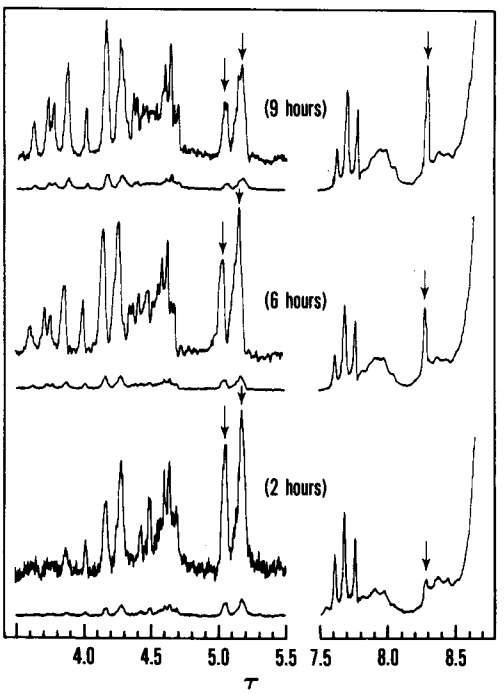

FIG. 4. NMR of rearrangement products after 2, 6 and 9 hr of reaction.

hydrogenated at room temperature in 40 psi H_2 pressure for 1 hr. After catalyst filtration and solvent distillation, the hydrogenation products were analyzed by UV, infrared (IR) and GC. Absorption bands of UV spectra at 222, 232 and 238 mμ (observed in the analysis of the rearrangement products) disappeared. Absorption bands of IR spectra at 10.37 μ due to *trans* bonds and at 6.2 μ and 11.4 μ due to unsymmetrically substituted double bond also disappeared.

Hydrogenation Product Characterization

The hydrogenation products with catalyst I were hydrogenated again with added fresh Pd catalyst (0.5% metal based on ester), at room temperature, with 30-40 psi of H_2 pressure for 2 hr. Capillary GC analysis of these hydrogenation products is also presented in Table III.

The hydrogenation product with catalyst II was analyzed by GC-MS. The mass spectrum of peak b by GC

TABLE III

Composition of Hydrogenation Products[a]

Peak	ECL	Composition: Catalyst I, Rehydrogenation Before	Composition: Catalyst I, Rehydrogenation After	Composition: Catalyst II
a	16.0	22.7	22.9	17.2
b	17.1	3.4	6.2	6.6
c	18.0	16.4	15.8	12.7
d	18.3	26.0	47.1	58.8
e	18.4	10.2	0.7	1.3
f	18.6	15.1	1.7	1.6
g	19.0	6.2	5.6	1.8

[a]Capillary-GC conditions. Equipment: Perkin Elmer 3920 (FID); column: Silar 10 C, 50 m long × 0.25 cm id, glass capillary; col. temp.: 170 C; inj. temp.: 250 C; interface (column to detector): 200 C; carrier gas: 30 psi, He.

showed typical ion fragments for a methyl side chain at positions 8 and 9 that were:

m/e 171, $(CH_3\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_6\overset{\overset{CH_3}{|}}{CH}\text{-})^+$ and

m/e 185, $(CH_3\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7\overset{\overset{CH_3}{|}}{CH}\text{-})^+$.

The parent peak was shown at m/e 298. Also, the mass spectrum of peak d by GC showed typical ion fragments for a methyl side chain at positions 9 and 10 that were:

m/e 185, $(CH_3\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_7\overset{\overset{CH_3}{|}}{CH}\text{-})^+$ and

m/e 199, $(CH_3\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_8\overset{\overset{CH_3}{|}}{CH}\text{-})^+$.

The parent peak was shown at m/e 312.

Purification of Branched-Chain Fatty Acids

To purify the hydrogenation product, recrystallization was carried out with a mixed solvent consisting of ethanol and water (80:20, v/v). Crude, branched-chain fatty acids (10.9 g) were dissolved in 110 mL of mixed solvent and allowed to stand at 0 C for 2 hr; the resultant crystals (2.6 g) were

TABLE IV

Purification of Branched-Chain Fatty Acids by Recrystallization with the Mixed Solvent

Peak	Recrystallization component (%)		
	Crude branched-chain fatty acid	Filtrate	Crystal
a	17.3	6.6	41.4
b	6.6	9.0	1.3
c	12.9	1.9	40.6
d	58.1	76.4	14.2
e	1.1	1.1	0.6
f	1.8	2.2	1.6
g	2.2	2.8	0.3

filtered. The filtrate produced 7.1 g of material after removal of solvent and was analyzed with capillary-GC. The results are shown in Table IV.

Characterization of Purified Branched-Chain Esters

To investigate their characteristic properties, about 30 g of the branched-chain fatty acids were produced by the procedures just described, followed by rapid distillation under reduced pressure without fractionation. The properties of these branched-chain fatty acids were: acid value, 189.9 (mg KOH/g); melting point, 21.1-22.5 C; fatty acid composition, palmitate (5.0%), C_{18} rearrangement product (9.8%), stearate (0.4%), C_{19} rearrangement product (78.2%), unknown (peak e, trace), unknown (peak f, trace), unknown (peak g, 6.6%).

Preparation of Lubricant Materials

Esters of the branched-chain fatty acids with 2-ethylhexyl alcohol or trimethylolpropane were prepared and their characteristic properties such as viscosity, pour point and wear scar on mini 4-ball tester (22) were measured. Oleic acid (Pamolyn 100) esters and isostearic acid (Emersol 871) esters were also produced to compare with branched-chain fatty esters. Branched-chain fatty acids (10 g), oleic acid (50 g) or isostearic acid (50 g) that had been distilled, 2-ethylhexyl alcohol (10 g for branched-chain fatty acids and 46 g for oleic and isostearic acids, respectively) and *p*-toluenesulfonic acid (0.6% of fatty acid weight) were added to a 3-necked flask with agitator and Dean-stark trap and were esterified under nitrogen for 4.25 hr at 200-220 C to an acid value of 0.3 or less. Similarly, branched-chain fatty acid (20 g), oleic acid (50 g) or isostearic acid (40 g), trimethylolpropane (14% of acid weight), *p*-toluenesulfonic acid (0.6% of acid weight) and xylene (5 mL) were refluxed under nitrogen for 5 hr at 200-220 C. The reaction mixture was washed with 1% KOH aqueous solution, followed by washing with water until the waste water became neutral, and then drying and removal of 2-ethylhexyl alcohol or xylene with a vacuum pump. The crude 2-ethylhexyl alcohol esters were vacuum-distilled to provide 60.2 g of oleate ester, 54.2 g of isostearate ester and 11.0 g of branched-chain fatty ester, and the crude trimethylolpropane esters were bleached with 3% of activated clay at 100-115 C for 15 min in vacuo to purify them. The characteristic properties and lubricant test results of these esters are shown in Table V.

Oxidative stability of the branched-chain fatty esters was investigated; 6 g of sample was added to a test tube and heated at 95 C, with air sparging at 1.20 mL/sec for 100 hr. Acid value, viscosity and color of oxidized esters were compared with that before oxidation. The results are shown in Table VI.

DISCUSSION

Because cyclopropenoid rings have a high degree of strain in the structure, they may be rearranged to compounds in which the ring has opened by exposure to heat or oxygen or even under conditions of storage, extraction, transesterification or GC.

UV spectra of the rearrangement products with catalysts I and II (Fig. 1) revealed very strong absorption bands at 222, 232 and 238 mμ. Thus, the rearrangement products have a large proportion of compounds containing conjugated diene with different structures and the ratio of conjugated diene compounds are changed during the rearrangement reaction.

It was recognized from the equivalent chain length (ECL) that peaks 1, 2, 3, 4, 6 and 7 in Figure 2 were palmitate, stearate, malvalate, oleate, sterculate and linoleate,

TABLE V

Characteristic Properties of Fatty Esters

Properties	Oleic ester	Isostearic ester	Branched-chain fatty ester
2-Ethylhexyl ester			
Acid value (mg KOH/g)	<0.1	<0.1	<0.1
Color (Gardner)	<1	2	<1
Viscosity (cst, 37.8 C)	9.65	13.14	12.94
Freezing point (C)	-36	-25	-41
Pour point (C)	-39	-28	-43
Wear scar diameter (mm)[a,b]	0.391	0.431	0.470
Coefficient of friction[b]	0.121	0.108	0.109
Trimethylolpropane ester			
Acid value (mg KOH/g)	<0.1	<0.1	<0.1
Color (Gardner)	<1	3	<1
Viscosity (cst, 37.8 C)	53.5	103.4	93.6
Freezing point (C)	-35	-15	-38
Pour point (C)	-36	-16	-38
Wear scar diameter (mm)[b]	0.607	0.552	0.484
Coefficient of friction[b]	0.100	0.127	0.106

[a]Wear scar diameter and coefficient of friction of di-2-ethylhexyl sebacate were, respectively, 0.655 mm and 0.144.

[b]Determined under conditions specified in ref. 22: load, 20 kg; angular velocity, 184 rad/sec (1750 rpm); duration, 1 hr; temperature, 75 C.

TABLE VI

Oxidative Stability of 2-Ethylhexyl and Trimethylolpropane Esters[a]

Ester	Acid value (mg KOH/g)	Color (Gardner)	Viscosity (cst at 37.8 C)
2-Ethylhexyl			
Oleate	75.8	4	77.4
Isostearate	1.1	5	14.3
Branched-chain fatty ester	0.6	<1	13.3
Trimethylolpropane			
Oleate	50.5	4	4463
Isostearate	0.6	5-6	104
Branched-chain fatty ester	0.6	<1	97

[a]Test conditions: air flow rate = 1.20 mL/sec, temperature = 95 C, time = 100 hr.

respectively. It was presumed from ECL determined by GC and GC-MS analysis that peak 5 in Figure 2 was the rearrangement product of malvalate and peaks 8, 9, 10 and 11 in Figure 2 were the rearrangement products of sterculate. The rearrangement compound eluted as peak 8 increased until 2 hr of reaction time in catalyst II, or until 4 hr in catalyst I, and decreased after those reaction times. The rearrangement compound eluted as peak 11 continued to increase for the whole reaction time (Table II and Fig. 3). It was presumed that the peak 8 compound was changed to the peak 11 compound. The rhodium catalyst was as effective on malvalate as on sterculate in producing increased amounts of the rearranged products.

NMR spectra of rearrangement products at 2, 6 and 9 hr of reaction time showed a peak at τ5.1 was due to a terminal vinyl group and a peak at τ8.3 was due to CH_3 attached to olefinic carbon (Fig. 4). Furthermore, it was observed that the intensity of the peak at τ5.1 decreased and that of the peak at τ8.3 increased with reaction time after 2 hr, compared with other peaks in NMR of rearrangement products. This indicates that, after 2 hr of reaction time, the amount of compounds containing terminal vinyl group decreased and that the amount of compounds containing CH_3 attached to olefinic carbon increased with reaction time. It was confirmed from these results that the compounds containing conjugated dienes, such as:

$$\underset{\|}{CH_2} \qquad \underset{|}{CH_3} \qquad\qquad \underset{|}{CH_3}$$

(-CH=CH-C-), (-CH=CH-C=CH-) and (-CH=CH-CH=C-),

were produced in rearrangement reaction of methyl sterculate with rhodium catalyst as previously noted with palladium catalyst (19) and acid catalyst (17,18). Furthermore, it is suggested that the rearrangement reaction of the cyclopropenoid ring proceeds in the manner shown in Figure 5.

With rhodium catalyst, the rearrangement products were successfully hydrogenated upon exchanging gaseous hydrogen for gaseous nitrogen and lowering the temperature of reaction mixture to room temperature without added fresh catalyst. However, with palladium catalyst, such hydrogenation was not enough to change all of the conjugated dienes into saturated chains because of the weaker catalytic activity compared to rhodium catalyst (19).

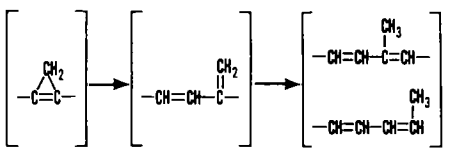

FIG. 5. Rearrangement reaction of the cyclopropenoid ring.

It was confirmed from GC-MS that C_{18} branched-chain fatty acids substituted at position 8 or 9 of the carbon chain were produced and that C_{19} branched-chain fatty acids substituted at position 9 or 10 of the carbon chain were produced. These acids were produced almost quantitatively from sterculia oil by the rearrangement reaction followed by hydrogenation.

Recrystallization with mixed solvent of ethanol and water was valuable for purifying the crude branched-chain fatty acids containing saturated straight-chain fatty acids (palmitic and stearic acids). This method separated the crude branched-chain fatty acids into the filtrate containing more than 85% of branched-chain fatty acids and into crystals containing more than 80% of saturated, straight-chain fatty acids.

Esters of refined branched fatty acids with 2-ethylhexyl alcohol and trimethylolpropane had low freezing point and low pour point, as did those of oleic and isostearic acids. These branched-chain fatty acid esters had smaller wear scar diameter and coefficient of friction in a mini 4-ball tester than did di-2-ethylhexyl sebacate (Table V). Oxidative stability of these branched-chain esters was at least the equivalent of the isostearate ester and was much better than the ester of oleic acid (Table VI). The branched-chain fatty esters appear to have potential utility in lubricants.

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Analytical ^{13}C NMR Spectroscopy of Fatty Quaternary Amines

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ABSTRACT

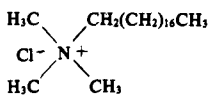
Natural abundance ^{13}C nuclear magnetic resonance spectroscopy (CMR) has been used for the rapid, nondestructive analysis of fatty quaternary ammonium compounds. Quantitative analysis of mixtures of mono-, di- and tri-fatty ammonium chlorides can be accomplished under conditions that do not involve heat or extremes of pH and that are independent of solvent present. In order to determine optimal conditions for quantitative studies, carbon spin lattice relaxation times (T_1) and nuclear Overhauser effects (NOE) were determined for each of the components. The method of internal standard addition was used to determine reproducibility and accuracy of the method for the measurement of mono- and tri-fatty quaternary components in material consisting predominantly (i.e., greater than 90%) of di-fatty-dimethyl ammonium chloride.

INTRODUCTION

Comprehensive studies of carbon-13 nuclear magnetic resonance spectroscopy (CMR) of aliphatic amines have been reported (1-3). None of these has adequately addressed the specific topic of quaternary amines. Fatty quaternary ammonium compounds have been of significant economic interest for many years. Their utility as fabric softeners, dispersants, emulsifiers and sanitizers is widely appreciated (4).

The properties of fatty quats vary widely and are dependent both on the distribution of the substituent fatty chains and on the nature of the substitution at the quaternary nitrogen. The substituent fatty chain distributions can be easily ascertained by examination of the precursors, but it is of significant importance that something be known about the quaternary substitution.

The primary focus of this paper is on compounds like those shown in Scheme I. Model compounds prepared from pure stearyl precursors were used, as were those having a hard tallow distribution. Only the signals from those carbon atoms directly bonded to nitrogen were used for quantitation. The method is, therefore, independent of chain length or distribution. One of the primary goals of this study was to obtain a method of general applicability.



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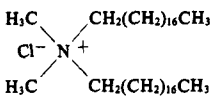

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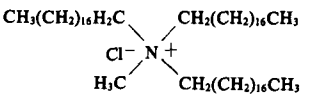

(3)

SCHEME I

Attempts to determine mono-, di- and tri-fatty substitution by gas liquid chromatographic (GLC) methods are complicated by the involatility of the materials, their chemical inability to form volatile derivatives, and their susceptibility to thermal decomposition or rearrangement (i.e., Hofmann degradation, dealkylation/realkylation). Pyrolytic methods yield information about the composition of the chains but are inconclusive with respect to the nature of the nitrogen substitution (5).

The use of liquid chromatographic methods, particularly ion-pairing, has shown some promise (6). Separation, however, is hindered by the surface-active nature of the compounds and there are considerable difficulties in detecting them at low concentration. Thin layer chromatography may ultimately prove to be a viable method but may present problems for the quantitative assessment of small amounts of contaminant quat in a matrix of other quaternary species.

CMR spectroscopy, on the other hand, does not suffer from any of the previously mentioned difficulties. The sample need only be dissolved in a suitable deuterated solvent (e.g., $CDCl_3$) for spectra acquisition. There is no chance for thermal alteration of the sample and all components of the mixture are measured simultaneously and with equal sensitivity. This makes CMR spectroscopy ideal as a method for the evaluation of other methods. This method cannot, however, be considered routine. It requires a highly sophisticated and expensive NMR spectrometer and frequently needs hours of accumulation time for trace contaminant measurement.

A number of precautions must be taken in the quantitative interpretation of CMR data (7). Paramagnetic relaxation reagents are quite frequently used in this situation to