

tic samples. Exchange rate measurements were carried out in anhydrous trifluoroacetic acid at $20 \pm 0.1^\circ$ as previously described.²

8-Bromo-7-methoxybenzocycloheptane. 8-Bromo-7-hydroxybenzocycloheptane³ was methylated using dimethyl sulphate in alkali⁴ to yield the title compound in 75% yield, m.p. $54-55^\circ$ (from light petroleum). NMR: $\delta = 7.05$ and 6.46 ppm (s, 1H each, ArH); 3.74 ppm (s, 3H, $-\text{OCH}_3$); $2.8-2.4$ ppm (m, 4H, ArCH₂-) and $1.9-1.3$ ppm (m, 6H, aliphatic ring protons). The mass spectrum showed prominent peaks at *m/e* (rel. int. %) 257(9), 256(100), 255(10), 254(100), 215(8), 213(8), 175(22), 146(19), 115(13), and 91(11).

7-Hydroxybenzocycloheptane-6-(³H) (1). This compound was obtained from 8-bromo-7-hydroxybenzocycloheptane using the method described for 6-tetralol-7-(³H) in Ref. 2. Spec. act. $0.7 \mu\text{C}/\text{mmol}$.

7-Hydroxybenzocycloheptane-8-(³H) (2). 8-Bromo-7-methoxybenzocycloheptane (1.5 g; 5.9 mmol) was converted to a Grignard reagent which was hydrolysed using tritiated water (1 ml; 19 mC/ml) as described for 3,4-dimethylanisole-6-(³H) in Ref. 2. The crude product was demethylated using BBr₃ as described for 3,4-dimethylphenol-6-(³H) in Ref. 2. This afforded a mixture of 8-bromo-7-hydroxybenzocycloheptane and 7-hydroxybenzocycloheptane-8-(³H). The radioactive compound was separated by preparative TLC affording 140 mg (15%). Spec. act. $0.9 \mu\text{C}/\text{mmol}$.

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Lanthanide-Induced PMR Chemical Shifts in Triglycerides

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High resolution proton magnetic resonance (PMR) spectroscopy is a valuable tool in research on fats and oils, isolated¹ or in single seeds.² The present investigation was initially concerned with the evaluation of pig fat quality and of a method for more rapid selection among turnip rape genetic crosses. The latter project has so far been hampered by poor spectral resolution. As illustrated by Fig. 1, detailed information

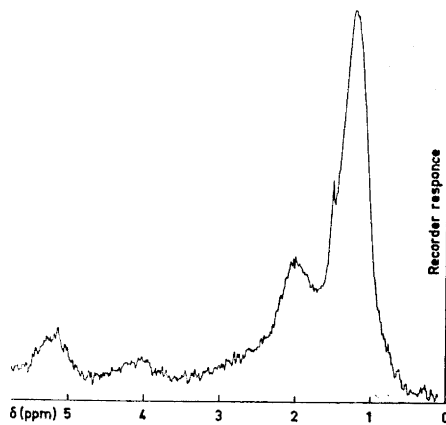


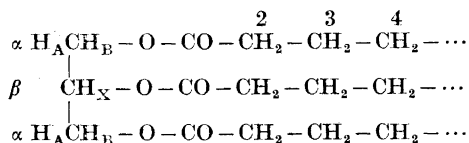
Fig. 1. 100 MHz PMR spectrum of a 5 mg turnip rape kernel, immersed in CCl_4 . The resolution did not improve appreciably on drying the kernel.

such as the iodine or saponification number cannot readily be obtained from the PMR spectrum.

For isolated fats, the situation has improved greatly with the advent of "shift

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reagents".³ These have been successfully applied to unsaturated fatty acid methyl esters⁴⁻⁶ and, quite recently, to triglycerides.⁷ For the latter class of lipids, we have obtained similar, but in some respects more detailed, results. Those for pressed almond oil are now reported. The protons are coded as shown.



The almond oil used contained 20 % linoleic, 77 % oleic, 1.5 % palmitic, and 1.5 % stearic acids, leading to an average triglyceride molecular weight of 883. The europium/triglyceride molar ratios (x) used were based on this value. When "Eu(DPM)₃" was added in sequential small portions up to the point of saturation to an almond oil solution, all shifts (δ) increased almost linearly with the following constant induced-shift-ratios:⁸

A	B	X	2 α	2 β	3 α
1.56	1.32	1.62	1.00	0.85	0.70
3 β	4	5	6	7	
0.60	0.35	0.14	0.05	0.01	

The assignment of separate signals to the α and β chains was based on the 2:1 intensity ratio of the corresponding PMR signals. Moreover, tripalmitin exhibited precisely similar signals. At 300 MHz, the nonequivalence of the 4 α and 4 β protons was also observed.

Our results with the more electrophilic and soluble reagent "Eu(fod)₃" are shown in Fig. 2 and are characterized by larger β/α (including X/A and X/B) induced-shift-ratios than those produced by Eu(DPM)₃. With increasing x value, this effect ultimately disappears, since the originally *less* shifted α signals approach or, for the 2 α protons, cross over the respective β signals. Apparently, Pfeffer and Rothbart⁷ did not observe this cross-over effect. Their published spectra, corresponding to the molar ratio $x=2.32$, show the 2 α protons at higher frequency than the 2 β protons, which does not accord with the present results. However, this discrepancy could be due to a concentration or temperature effect⁸ or, less likely, to our own assignments of x -values. These may be slightly high, owing to traces of free acids

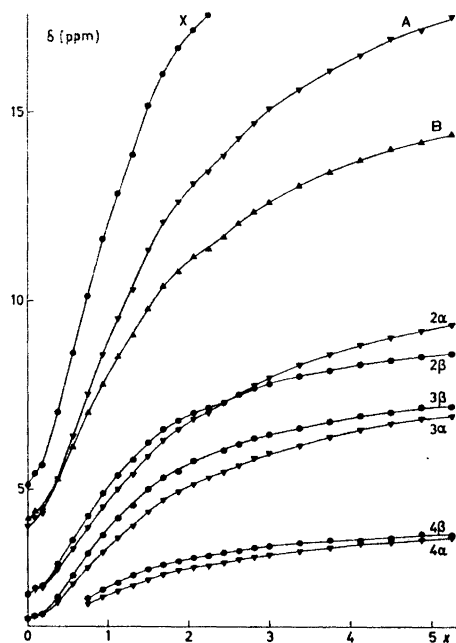


Fig. 2. PMR chemical shifts (δ) for almond oil in Eu(fod)₃-CCl₄ at 100 MHz. x is the Eu/triglyceride molar ratio.

or moisture, as indicated in Fig. 2 by the non-linearity observed for $x < 0.2$. The 5 α and 5 β signals were overlapped by others in most spectra, completely obscuring any possible separation between them.

Within the same acid chain, the observed Eu(DPM)₃ and Eu(fod)₃ induced-shift-ratios are similar to those produced by Eu(fod)₃ in methyl esters,⁴⁻⁶ but the ratios for the glyceryl protons are considerably larger than that for an ester methoxy group. This may be explained by assuming a triglyceride conformation, with widely diverging acid chains, in which only the glyceryl residue is necessarily always close to the carbonyl coordination site(s). The X proton is the most shifted one, as expected.

Eu(fod)₃ can accept two more ligands.⁹ The relatively small Eu(fod)₃ induced α shifts for $x \approx 1$ may therefore be explained by preferential bidentate coordination of the triglyceride through vicinal ester groups, leaving one α chain free. With increasing x , or with the weaker Lewis acid

Eu(DPM)₃, monodentate coordination could become more important. The bulky Eu complex may then prefer the sterically less crowded α ester groups. These interpretations are speculative at present, but they do fit well with the experimental data.

In PMR spectra of unsaturated fats or related compounds, the allylic signals are particularly important, because the olefinic signals usually overlap and are little affected by shift reagents. At 220 MHz, almost any double bond may thus be located within a fatty acid chain¹⁰ and its configuration established.¹¹ At 60 or 100 MHz, a 6–7 double bond can still be located using Eu(fod)₃.^{4,5} Our results may further permit assignment of such bonds to an α or to the β chain of a triglyceride, since overlap should not obscure any Eu(fod)₃-induced separation of the allylic 5 α and 5 β signals. Similar assignment of functional groups and chain-branching at positions 2–6 could also be made. Despite favourable results for individual triglycerides,⁷ a general method for identification of the unsaturated acid chain(s) in natural fats is still lacking.

For that purpose, we have followed a recent suggestion of the formation of additional coordination sites at the double bonds.⁵ Thioacetic acid was chosen as the reagent, since even a slight nonequivalence between thiolacetate groups can be detected owing to the singlet nature of their PMR signals. Unlike thiobenzoic and mercaptoacetic acids, thioacetic acid reacted rapidly and quantitatively with almond oil under ambient conditions. In the PMR spectrum of the adduct, Eu(fod)₃ addition caused doubling of the thiolacetate singlet, the less shifted peak being about twice as large as the more shifted one. A maximum splitting of 0.07 ppm occurred for induced shifts between 1.0 and 2.3 ppm, corresponding to $0.8 < x < 1.6$. For $x > 2$, the peaks appear to cross, but this effect is largely obscured by line broadening. Similar results were obtained with the adducts from a 3:1 mixture of methyl oleate and methyl linoleate. Hence, the two thiolacetate singlets shown by the almond oil adduct apparently correspond to the oleyl and linoleyl chains present rather than to the α and β chains.

An investigation of the lanthanide-induced ¹³C-NMR shifts is now in progress.

Experimental. The fatty acid analysis was performed at the Department of Animal Breeding, Agricultural College, Uppsala. With

the exception of a few 300 MHz spectra measured by Varian Associates, Palo Alto, the PMR spectra were recorded at 100 MHz and 31° on a Varian HA-100D instrument. Each sample (20–25 mg) was dissolved in spectroscopic grade carbon tetrachloride (0.50 ml), which had been dried azeotropically and distilled. The shift reagent was added in 5 or 10 mg portions. Eu(DPM)₃¹² and thioacetic acid¹³ were prepared and purified according to the literature. Eu(fod)₃ was purchased from Merck Sharp & Dohme Canada Ltd. and used as received. The almond oil–thioacetic acid adduct was prepared by mixing equal volumes of the neat reactants, resulting in an immediate temperature increase. After a few minutes, the excess acid was removed by repeated rotary evaporation with carbon tetrachloride.

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