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THE ANALYSIS OF CURED DRYING OILS BY SWOLLEN STATE ^{13}C-NMR SPECTROSCOPY

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Abstract—Swollen state ^{13}C-NMR spectroscopy is used to obtain information on the structures of cured drying oils used in alkyd paint manufacture. Examination of the individual drying components within these oils suggests that the behaviours of linolenate and linoleate groups are quite different. Low molecular weight materials produced during curing can be examined and their structures compared with those of the bulk insoluble product. The effects of catalyst upon the drying process can also be studied for the more reactive drying oils. Cured oils can be identified but the characteristic features are often reduced to low level components.

INTRODUCTION

Drying oils are a group of unsaturated triglycerides that are incorporated into alkyd paint binders to provide cross-linking sites for oxidative polymerisation [1]. Cured alkyds have received little attention in terms of non-destructive structural determination, except for limited study by infra-red and Raman spectroscopy [2–4]. In our laboratories we have shown that cured alkyds can be characterised by swelling in a chlorinated solvent and observing high-resolution ^{13}C-NMR spectra directly from the material [5]. In order to investigate the specific contributions to these spectra from the drying oil constituents, a range of drying oils was cured and the products examined in the swollen state using ^{13}C-NMR. By comparisons with solution spectra of the uncured materials, particular attention could be given to the mechanism of cross-linking and the products of the reaction. Where possible, specific structural assignments were confirmed by i.r. spectroscopy.

EXPERIMENTAL

Materials

The materials were of normal commercial quality.

Curing procedure

The drying oils (*ca* 2 g) were cured by adding a xylene solution (0.1 ml) containing cobalt naphthenate (25 μg) and lead naphthenate (58 μg). The mixture was stirred thoroughly and then spread onto a glass plate to a thickness of *ca* 0.5 mm. After 18 hr exposure, a tack free surface was obtained for all the materials except soya bean oil. After 2 days the characteristic wrinkled pattern was evident on the surface of the film. The materials were removed from the glass plates after 4 weeks exposure to air and light, when the underside was still tacky in some cases. A further 4 weeks air exposure produced films which were tack-free on both sides. In order to cure the soya oil film, it was necessary to heat the sample for 4 hr at 80 after 2 weeks exposure to air. In order to prevent oxidation of the film, the heating took place at a reduced pressure of 0.1 m bar. The underside of the film was treated in the same manner after removal from the glass plate. Samples of tung oil and blown oil were cured similarly without the use of catalyst.

Swelling procedure

The cured drying oil (*ca* 0.3 g) was packed into a 10 mm NMR tube containing a PTFE plug and covered with deuterochloroform. The sample was then left overnight to swell prior to NMR analysis.

NMR conditions

Both solution and swollen state ^{13}C-NMR spectra were recorded at 22.5 MHz on a Jeol FX 90Q instrument: chemical shift range -10 to $+250$ ppm (taking the central signal of deuterochloroform as 77.1 ppm from TMS); broadband proton decoupling; scan cycle time 1.0 sec; pulse width 30°. For solution spectra, *ca* 4000 transients were recorded; for swollen state spectra, 8000–50,000 transients were recorded.

^{1}H-NMR spectra were obtained using a Perkin–Elmer R32 instrument operating at 90 MHz, with a sweep width of 10 ppm and a sweep time of 5 min. All signals were measured relative to TMS.

Infra-red spectroscopy

i.r. Spectra were recorded as 2% KBr discs on a Perkin–Elmer 783 spectrometer operating under the following conditions: 4000–400 cm^{-1}; scan time 6 min; double beam; 5 spectral accumulations; resolution 2 cm^{-1}.

RESULTS AND DISCUSSION

Drying oils

Most drying oils used in alkyd resin manufacture are C_{18} triglycerides of vegetable origin [5]. The approximate chemical compositions of the drying oils used in this work are shown in Table 1. Not included in this list is a marine oil, pilchard oil, sometimes used as an ingredient in alkyd binders. The fatty acids in this material are generally longer chain and contain more unsaturation. A typical sample contains 25% C_{18} polyunsaturated chains and 25% C_{20} polyunsaturated chains in addition to about 25% of palmitic and stearic chains, the remainder being oleate and linoleate chains.

The mechanisms whereby the drying oils cure to form films are very complex and a complete understanding has not been established [6]. Most of the work has been carried out with the corresponding fatty acids or their simple esters, although this ap-

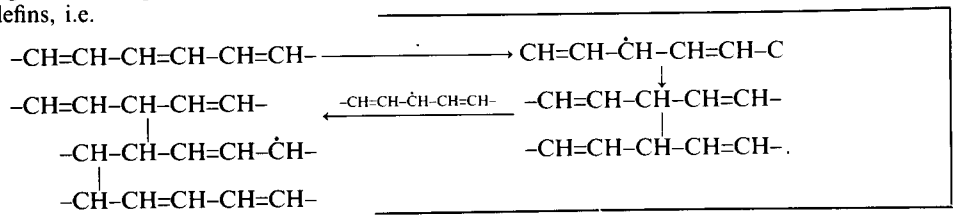
Table 1. Fatty acids present in a range of drying oils

	Linoleic	Linolenic	Oleic	Palmitic + stearic	Others
Soya	51	9	25	15	
Safflower	76	1	13	10	
Linseed	16	52	22	10	
Tung	4	1	6	9	*Eleostearic-80

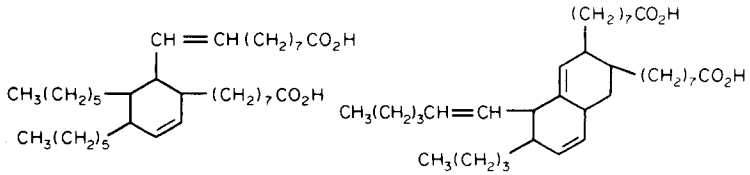
*$CH_3(CH_2)_3(CH{=}CH)_3(CH_2)_7CO_2H$.

proach ignores contributions from intramolecular reactions and mechanical interlocking of molecules that can occur with triglycerides. In the presence of oxygen, oils containing non-conjugated double bonds are thought to form hydroperoxides at the reactive methylene groups between the double bonds, particularly in the presence of polyvalent metal driers. The hydroperoxide can then break down to produce two free radicals and propagate the reaction. The reaction at the allylic position can lead to conjugation of the double bonds which in turn can lead to a Diels Alder reaction between the conjugated olefin groups and a double bond on another chain either intermolecularly or intramolecularly. The latter reaction leads to cross-linking and film formation. More recent work has suggested that the hydroperoxide breaks down to produce a carbonyl group adjacent to the double bond which then becomes the cross-link site [2]. There is also evidence that further oxidation is possible leading to cleavage of the chains. Volatile products are then lost and acid and hydroxyl end groups remain.

Far less work has been done on the curing mechanism of conjugated drying oils and the only material to have been studied is tung oil which contains eleostearate [6]. Hydroperoxides are not formed with tung oil but the conjugation already present may mean that Diels Alder type reactions are more likely than with non-conjugated drying oils. Certainly tung oil is readily cured without the addition of metal driers unlike most other oils described here. The conjugation may also serve to stabilise any free radicals that might be formed by reaction with air and cross-linking can take place as in the polymerisation of olefins, i.e.



Oligomers of linoleic acid are widely used for the manufacture of alkyds and as anti-corrosion additives [7, 8]. The acid itself is heated to induce polymerisation and the products fractionated as dimers and trimers. The species present in the dimers, which are referred to as dimer acid, have been examined [9]; although the exact products formed depend on the conditions, the following species are typical:



The ^{13}C spectrum of a refined dimer acid sample is shown in Fig. 1. There are many features in common with the spectrum of linoleic acid itself [10] such as the signals at 34.2, 32.0, 29.8, 24.8 and 22.8 ppm from polymethylene units in these structures. The allylic methylene signals are of much reduced intensity and the large signal at 37.2 ppm is not present in linoleic acid. A similar signal is observed in the spectrum of *n*-butylcyclohexane for both the substituted ring carbon atom and the methylene group bonded to it [11]. This seems clear evidence of a cyclic reaction product in the dimer acid. The small olefinic signals of 137.7, 129.9 and 126.5 ppm are further evidence of cyclisation. Substituted cyclohexanes have an olefinic signal at about 126 ppm and the more substituted olefinic group in the bicyclic structure above should appear at about 137 ppm. The remaining olefinic signal is similar to that observed in oleic acid for the olefinic group in the alkenyl side chains [10].

These olefinic signals in dimer acid are quite broad so perhaps accounting for their apparent low intensity. The Diels Alder cross-linking should only consume about 67% of the available olefinic groups. The broadness also suggests that there are many similar species formed giving over-lapping peaks in the olefinic region. This range of products also probably accounts for the smaller signals in the remainder of the spectrum.

Trilinolein and trilinolenin

Swollen-state ^{13}C-NMR can be used to observe cross-linking in most common drying oils. The disappearance of particular species can be observed by comparison of the cured spectra with the solution state spectra of the uncured oil. Newly formed species can be identified in the cured materials by referring to standard spectra. However the signals due to the new species are often smaller than expected, probably because of the failure of the swollen-state NMR technique to respond to rigid cross-linked components. Whilst this drawback must be borne in

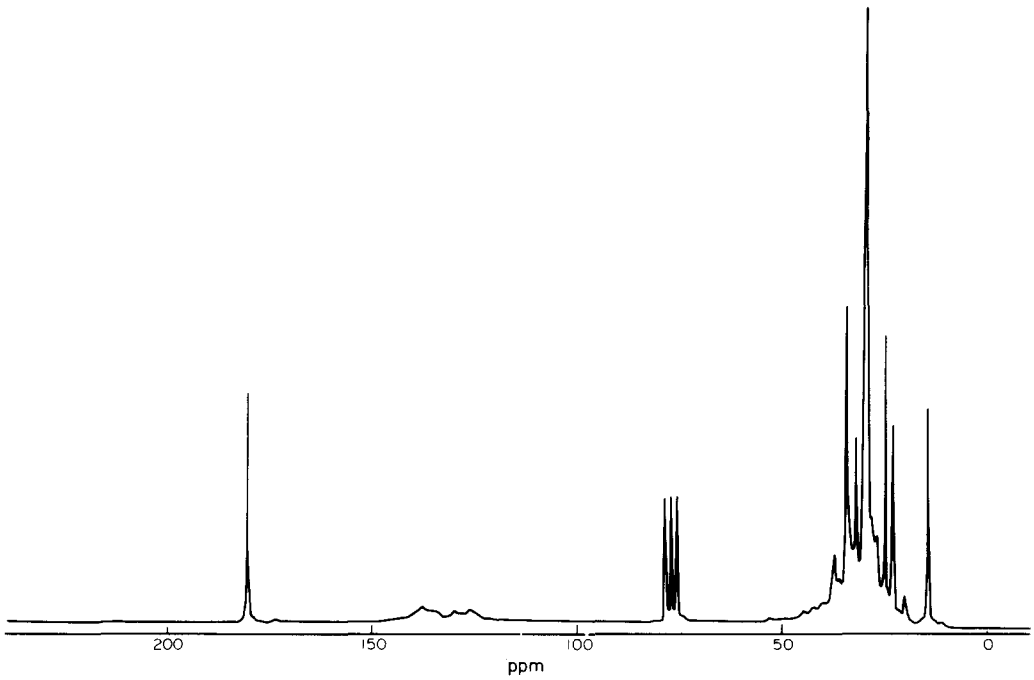


Fig. 1. Linoleic acid dimer (dimer acid).

mind, there is much useful information to be gained from the spectra.

In order to understand the behaviour of drying oils on curing, it is helpful to examine the contributions made to the curing by the linolein and linolenin units present. Samples of the triglycerides of linoleic acid and linolenic acid are commercially available and these materials were cured as films by adding catalyst.

The swollen state ^{13}C-NMR spectrum obtained from the cured triglyceride of linoleic acid, trilinolein, is shown in Fig. 2 underneath the solution state ^{13}C spectrum of the uncured material. The latter spectrum shows the same features as that of linoleic acid itself with four olefinic carbon resonances at 129.7, 129.6, 127.8 and 127.7 ppm. The methylene carbon between the two double bonds gives a signal at 25.4 ppm and the methylene adjacent to just one double bond gives a signal at 27.0 ppm. The features from the glyceride region of the molecule are also similar to those found in other triglycerides with the

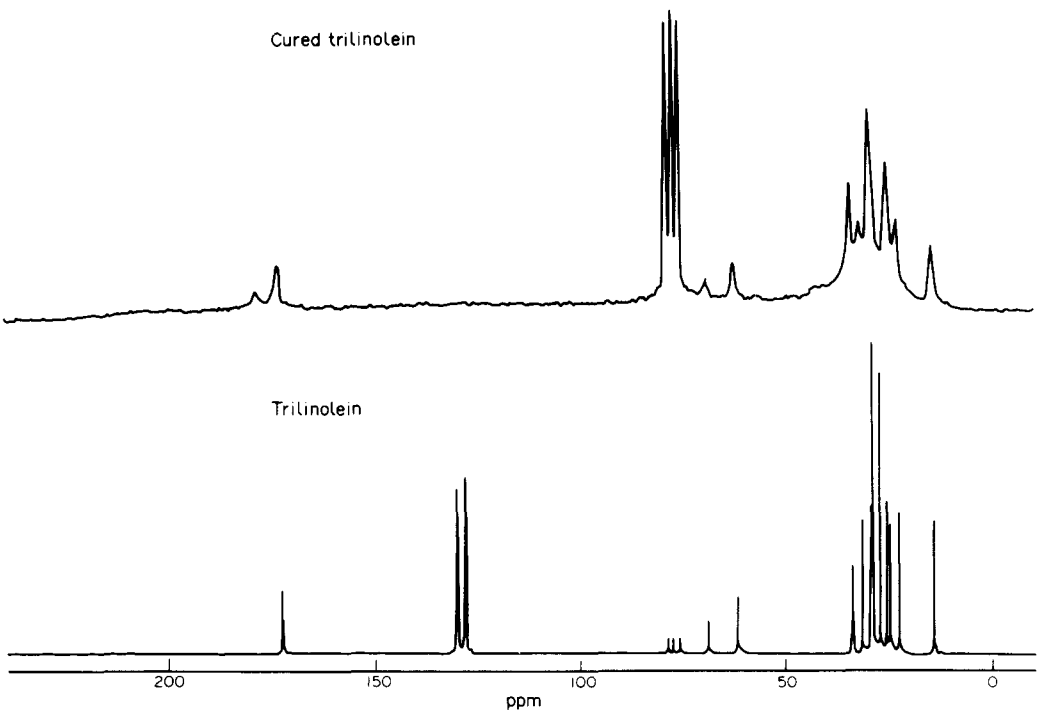


Fig. 2. Trilinolein/cured trilinolein.

primary position appearing at 61.8 ppm and the secondary at 68.7 ppm [12]. The separation of the carbonyl groups is smaller but two distinct signals are seen at 172.4 and 172.1 ppm.

The ^{13}C spectrum of the cured material in Fig. 2 retains many of the features of the uncured material, albeit at lower resolution due to curing. However the most notable differences are the absence of olefinic signals and the presence of a significant carbonyl signal at 178.9 ppm. i.r. Spectroscopy of the film shows the presence of a shoulder at 1710 cm^{-1} implying the presence of a carboxylic acid carbonyl group. A recent i.r. study on a bodied linseed oil material showed the build-up of an acid carbonyl group during cure [2].

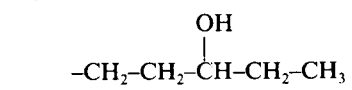
The total absence of olefinic signals in the cured sample is unexpected since curing is thought to occur to give products still containing isolated olefinic groups. It is assumed that it is the mobility of the molecule in the gel that overcomes the expected dipolar interactions to produce good resolution spectra. Sites which do not have this mobility, i.e. cross-links and their adjacent atoms, may not give signals. The ^{13}C-NMR spectrum would then not be representative of the whole sample. However, confirmation of the absence of olefinic bonds is given by Fourier transform i.r. and solid state NMR. The absence of unsaturation implies that Diels Alder type reaction products are not formed in the drying of linoleic acid. The disappearance of the unsaturation does not obviously correspond with the appearance of new signals from the polymerisation products.

At this point it is helpful to examine the saturated aliphatic region (10–40 ppm) of the spectrum of the cured material: certain signals are absent in comparison with the solution state spectrum; in particular those methylene groups adjacent to olefinic groups which give signals at 27.0 and 25.4 ppm are either absent or present as a small shoulder. A certain amount of methylene loss was reported in the FT-i.r. bodied linseed oil study although the fate of these species was not apparent [2].

In order to ensure that the spectrum obtained from the swollen material was in fact from the cured film and not from soluble impurities, the material was washed several times with deuterochloroform and reswollen. The ^{13}C spectrum obtained was unchanged, but a certain amount of soluble material was removed.

The ^{13}C spectrum of this extract shows it to contain soluble low-molecular weight products of the curing reaction of trilinolein. No olefinic groups are present and a definite carboxylic acid carbonyl signal can be seen. The ^{1}H-NMR spectrum of this sample shows only a very weak signal from olefinic protons. The strong similarity of the swollen state spectrum and the spectrum of the extracted material implies that the olefinic content of the cured material is quite low.

The ^{13}C spectrum of trilinolenin is similar to that of trilinolein, the major differences being the signals from the additional olefinic group seen at 126.9 and 131.5 ppm in Fig. 3. The extra double bond in the chain moves the signal from the 15-methylene group upfield to 20.4 ppm. The signal at 25.4 ppm for the methylene group between the olefinic groups is now much stronger due to the additional double bond. The swollen state ^{13}C spectrum of cured trilinolenin is shown in Fig. 3 as the upper trace, and there are noticeable differences from the spectrum of uncured trilinolein. There is very little evidence of an acid carbonyl signal at *ca* 177 ppm and the olefinic signals are still clearly visible. The lack of a strong acid carbonyl signal may imply that less chain cleavage occurs than for trilinolein. The other notable feature is the signal at 10.2 ppm, which seems to correspond to the terminal methyl signal of the species (I) since similar signals have been



(I)

reported in the spectrum of 3-pentanol, 3-hexanol, 3-heptanol and 3-octanol [13]. The methine carbon

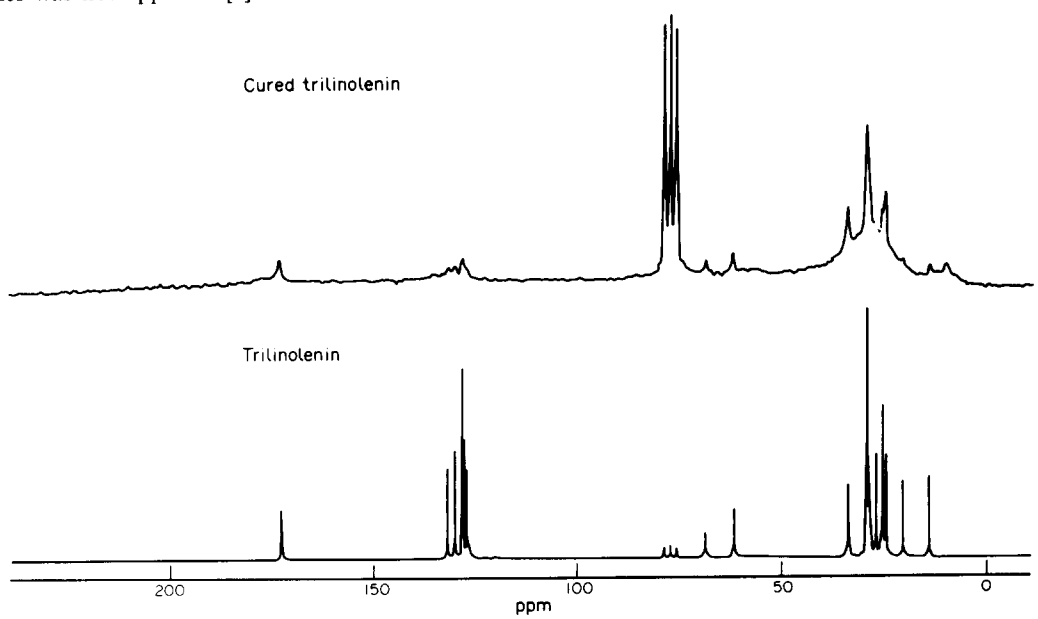


Fig. 3. Trilinolenin/cured trilinolenin.

attached to the hydroxyl group would give a signal in the region of the deuterochloroform and so would be difficult to detect. The use of an alternative solvent may well not overcome this problem. If a poorer degree of swelling were obtained, it would not be possible to observe the signal from the methine carbon atom. The FT-i.r. study of bodied linseed oil showed that hydroxyl groups were produced during curing but the location of these species could not be specified. The apparent intensity of this signal in the swollen state spectrum seems surprisingly large and further quantitative studies of this material are proposed.

A significant amount of cross-linking occurred in the trilinolenin since the signals adjacent to olefinic groups (27.3 and 25.8 ppm) are only present as small shoulders. Yet there still remains a significant amount of olefinic material. As with trilinolein, the cured trilinolenin was washed with chloroform and the swollen state spectrum remained unchanged. The ^{13}C spectrum has many similarities to the spectrum of uncured trilinolenin but the intensity of all the peaks associated with the curing process are of reduced intensity. Thus the olefinic signals at 132.1, 130,4, 128.4, 127.9 and 127.2 ppm are all smaller in the extracted material although the relative nature of these signals seems to be the same as with trilinolenin itself. The allylic methylene signals at 27.3, 26.7 and 20.7 ppm are reduced in intensity relative to the other methylene signals in the spectrum. It is thought unlikely that the extract contains only one component and so full quantification of the signals is of limited use, but it appears that a significant amount of chain scission has occurred to give some of the products. Further studies of this extract are being undertaken.

Examination of the two key components of most drying oils has shown that the additional olefinic group in the linolenate side chain greatly alters the oxidation characteristics when compared to linoleate side chains. Drying oils also contain some partially esterified glycerol and the curing behaviour of this group of materials can be examined using dilinolein, formed by the reaction of two molecules of linoleic acid at the primary positions of glycerol. This material cross-links in the presence of catalyst to form a film and the swollen-state ^{13}C-NMR spectrum is shown in Fig. 4.

The latter spectrum is very similar to that of trilinolein except for the glyceride signals. The substituted primary groups appear at 64.8 ppm and the unsubstituted position at 67.7 ppm. There are noticeably more impurities in the sample in this region and some of these peaks at 72.1, 62.4 and 61.3 ppm can be clearly seen in the spectrum of cured dilinolein. They are from the 1,2-isomer. The cured dilinolein shows no olefinic signals in its ^{13}C swollen state spectrum and the allylic methylene signals at 27.0 and 25.4 ppm cannot be seen. A strong acid carbonyl signal appears at 178.2 ppm as for trilinolein. The small peaks at 160.7 and 42.6 ppm were not seen with cured trilinolein and their broadness may mean that other associated peaks are present but are too broad to be seen.

In virtually all naturally-occurring drying oils, linoleate and linolenate groups are present and they can cross-link randomly. A 3:1 mixture of trilinolein and trilinolenin was cured and the spectrum obtained

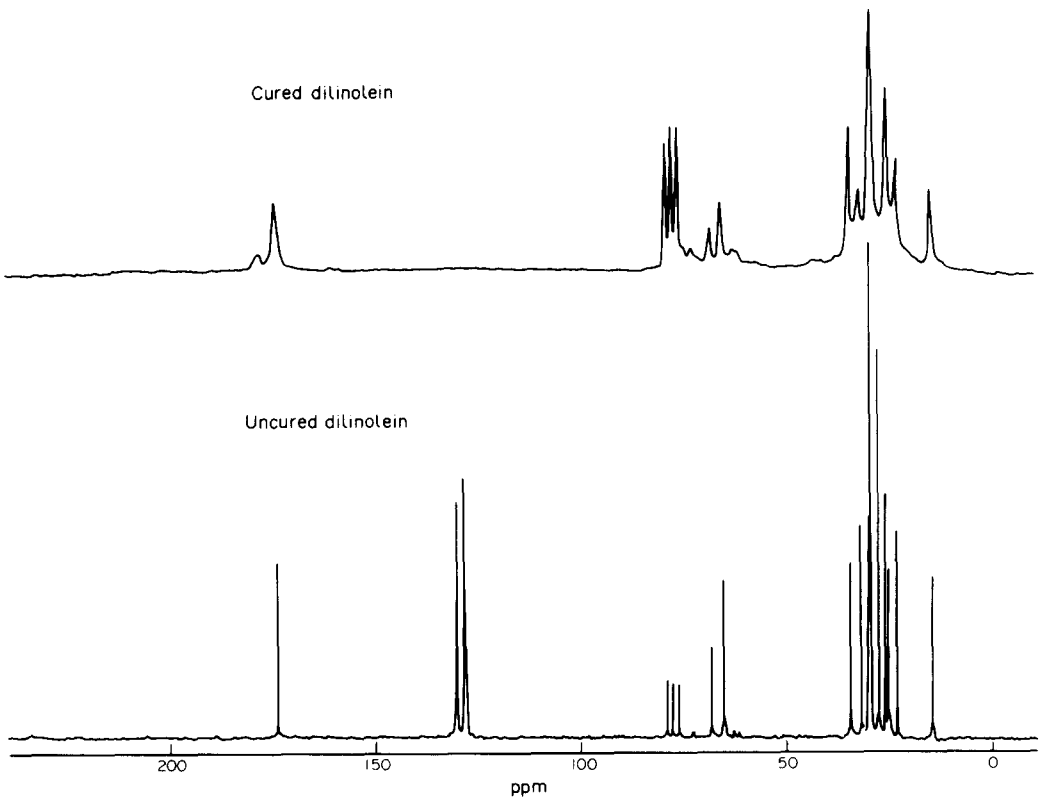


Fig. 4. Dilinolein/cured dilinolein.

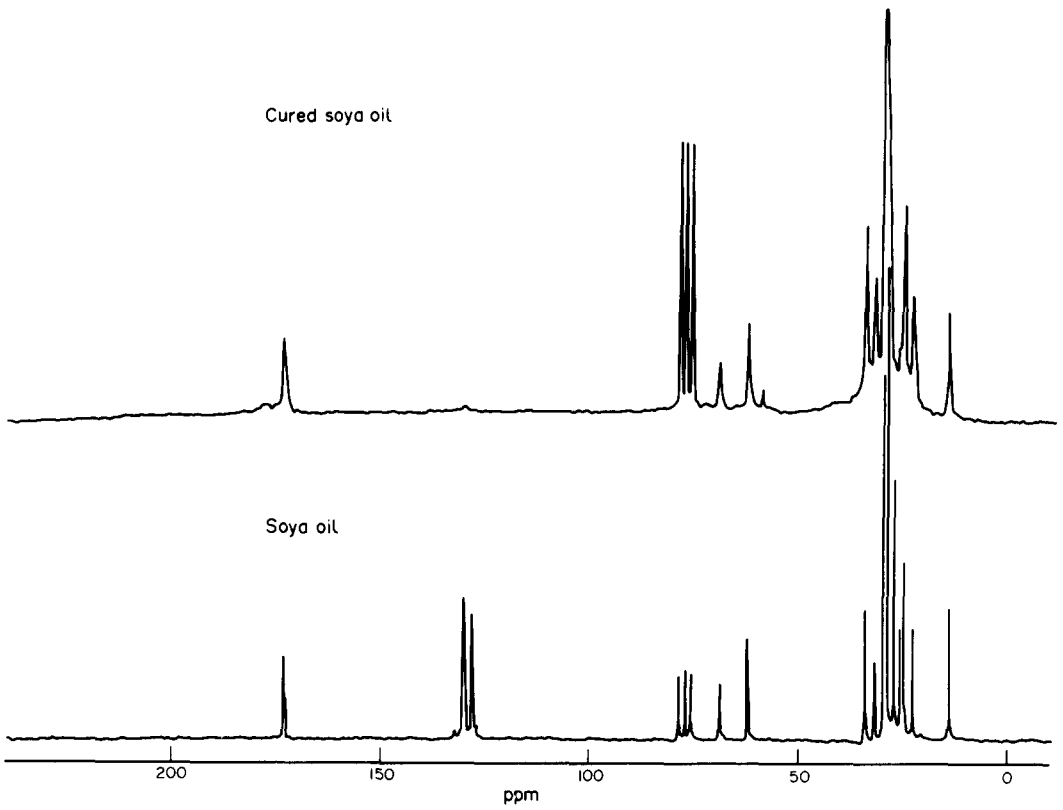


Fig. 5. Soya oil/cured soya oil.

is a composite of the upper traces in Figs 1 and 2, except that no olefinic signals are now seen. The other expected features are present such as the acid carbonyl signal of 178.0 ppm and the absence of the allylic methylene signals. Clearly the level of linolenate in a drying oil affects the appearance of the swollen state spectrum in the olefinic region.

From Table 1, linseed oil normally contains about 50% of linolenate so it is to be expected that the spectrum of cured linseed oil should show some olefinic signals whereas the other drying oils with lower linolenate contents would not. At this stage it is not clear if the absence of olefinic signals is due to the higher reactivity of linoleate groups or if the products are too rigid to give a signal in the swollen state.

Cured drying oils

The spectra from cured drying oils should match those obtained from trilinolein and trilinolenin. The only features absent from the latter materials which might be of importance are the oleate chains. Triolein, the oleate equivalent of trilinolein and trilinolenin, will not cure at room temperature using a catalyst solution but Diels Alder cross-linking could be possible between the oleate double bond and a conjugated double bond system formed from linoleate or linolenate by a free radical reaction.

Table 1 shows that soya oil contains a high proportion of linoleate (*ca* 50%). Even so it will not form a film at room temperature using a drier solution. To overcome this, the material was heated at 80° under vacuum having first allowed sufficient air to be absorbed into the material to enable cross-linking to occur. Heating in the presence of air produced a dark brown oxidised film.

The swollen state ^{13}C spectrum obtained from the vacuum heated soya oil is shown in Fig. 5, above the solution-state spectrum of the uncured oil. The presence of small shoulders of 27.3 and 26.1 ppm due to the allylic methylene groups shows that a high degree of cure has occurred in an analogous fashion to trilinolein. An acid carbonyl signal is present at 178.9 ppm and there is a definite olefinic signal at 130.4 ppm. The latter signal probably corresponds to oleic olefinic signals that are not properly resolved in the swollen state. Soya oil contains quite a high level of oleate material which is why it will not form a film at room temperature. Thus it is probable that the oleic chains do not participate in the curing process. The signals at 137.7 and 126.5 ppm in dimer acid are not seen here as might be expected. There are other peaks in this spectrum similar to those seen with dilinolein. The peaks now seen at 72.2 and 65.1 ppm are not present in the uncured oil. A small signal at 161.0 ppm is just visible; it corresponds to an unassigned signal at 160.7 ppm seen in cured trilinolein. These features suggest that, during the curing, deesterification occurs at the glycerol units. Signals associated with both the 1,3 and 1,2 products can be seen if 65.1 ppm is from the former and 72.2 ppm is from the latter. There is also a small broad signal at 42.8 ppm, which appears in the spectrum of cured trilinolein. However the presence of the signal at 59.0 ppm is unexpected. It probably corresponds to

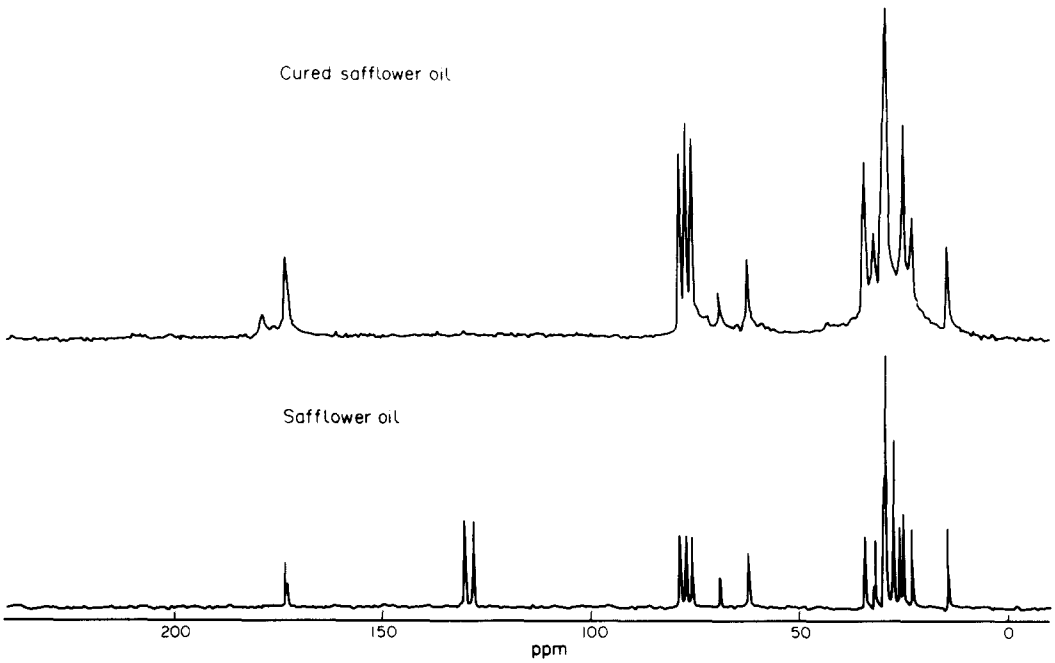


Fig. 6. Safflower oil/cured safflower oil.

the methylene carbon of a glycerol unit modified during curing.

There is some soluble material present in the cured soya oil and its ^{13}C spectrum shows many similarities to the cured soya oil spectrum such as a small olefinic signal at 130.4 ppm, a modified glycerol signals at 72.4 and 65.1 ppm and an acid carbonyl signal at 179.0 ppm. The latter signal appears more intense in the extract but this may be due to the better resolution of the spectrum. However there is no sign of the signal at 59.0 ppm which may mean that this species is only seen in the higher molecular weight material. As expected, the allylic methylene signals at 27.3 and 25.7 ppm are not seen in the soluble material.

Safflower oil can be used to produce a non-yellowing alkyd due to the low levels of linolenate present (*ca* 1%). The high linoleate content enables the oil to cure to form a film at room temperature in the presence of catalyst. The swollen state spectrum of the cured oil and the uncured oil spectrum are shown in Fig. 6. Upon expansion, the cured oil spectrum shows many similarities to that of soya oil including small signals at 16.1, 130.5, 72.1, 65.0, 59.0 and 42.8 ppm. This is to be expected since safflower oil and soya oil essentially contain different amounts of the same fatty acids. However the acid carbonyl signal at 178.6 ppm in cured safflower oil is much more definite and when the gain of the spectrometer is increased there are two peaks at 136.6 and 209.6 ppm not seen previously. A small peak at 37.6 ppm is also present in the cured safflower oil spectrum, and this can be taken as evidence of the Diels Alder cross-link site in the spectrum of dimer acid. The signal at 136.6 ppm may correspond to an olefinic group within such a cyclic unit.

The signal at 209.6 ppm seems to correspond to a ketone carbonyl in a six-membered ring and here the i.r. spectrum of the cured safflower oil helps in confirming this. Careful examination of the carbonyl region of the i.r. spectrum from 1750 to 1680 cm^{-1} shows there to be perhaps as many as 4 different signals. The ester carbonyl appears as expected at 1740 cm^{-1} and the acid carbonyl is a shoulder at 1710 cm^{-1}. A smaller shoulder at 1730 cm^{-1} may well correspond to the carbonyl signal from a cyclohexanone derivative of some kind. It might be expected to contain an olefinic group since the likely means of formation of such a ring is the Diels Alder type cross-linking reaction of the drying oil chains. If so, it cannot be conjugated to the ketone group otherwise the i.r. signal would appear at *ca* 1680 cm^{-1}.

Linseed oil is the drying oil most commonly used for the manufacture of air-drying alkyds. Unlike soya oil and safflower oil, the main drying units are linolenate chains. Perhaps because of this, linseed oil itself will cure in air without using a catalyst, although slowly. The swollen state ^{13}C spectrum of catalyst-cured linseed oil is shown in Fig. 7. This particular linseed oil is alkali refined to remove acidic impurities. The presence of linolenate in the uncured material can be seen by the presence of the C_{15} allylic methylene signal at 20.4 ppm and the additional linolenate olefinic group at 127.0 and 131.6 ppm. The presence of a small amount of partially esterified material can be seen by the signal at 64.9 ppm which was seen above with dilinolein. The catalyst-dried linseed oil spectrum shows only a small residual olefinic signal at 130.4 ppm. Thus despite the high level of linolenate in this material, the olefinic region of the spectrum is quite different from that for cured trilinolenin. The cured mixture of trilinolein and trilinolenin described above also showed little evidence of trilinolenin olefinic material. This sample was based on a 3:1 excess of trilinolein whereas from Table 1 it can be seen that linseed oil is based on a 3:1 excess of linolenate over linoleate. Despite the high level of linolenate in linseed oil, it does not

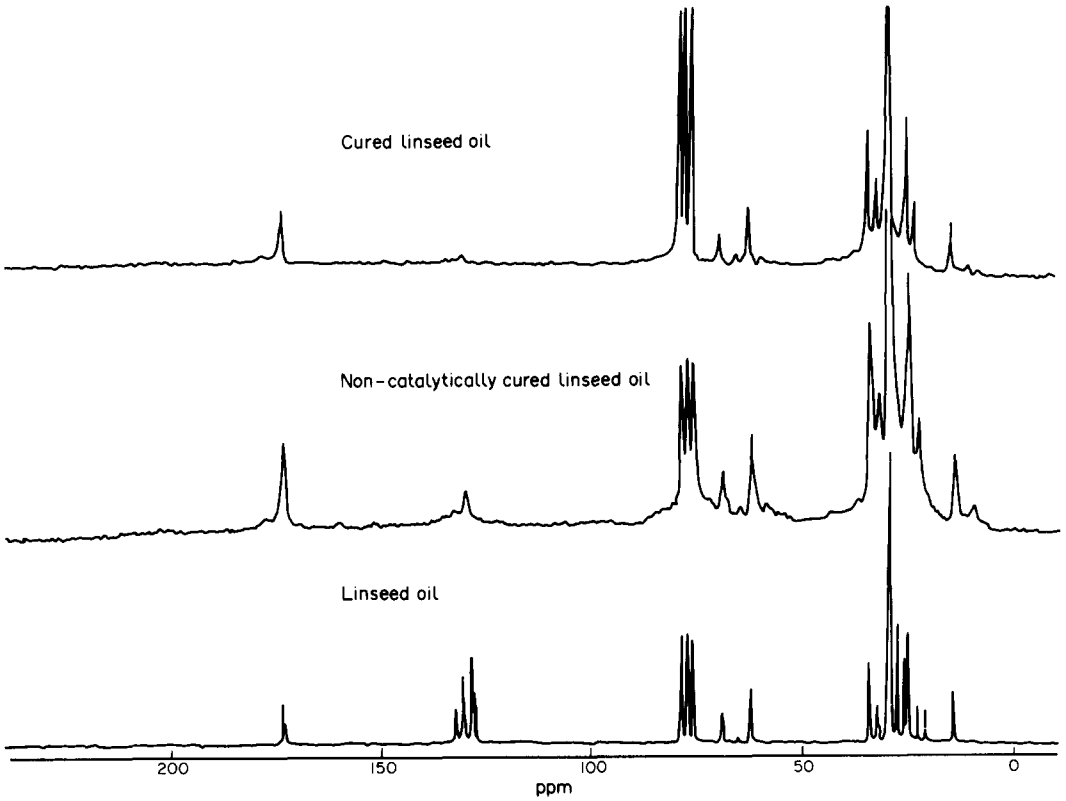


Fig. 7. Linseed oil/cured linseed oil/non-catalytically cured linseed oil.

appear to cure in a similar fashion to trilinolenin itself if a small amount of linoleate is present. However there are some features in the cured linseed oil spectrum which are seen with cured trilinolenin, viz. the signal at 9.8 ppm for the terminal methyl group in a chain that has been oxidised at the 15 position. Compared to the spectra of cured soya oil and cured safflower oil, the acid carbonyl signal at 178.1 ppm in cured linseed oil appears smaller relative to the ester carbonyl at 173.3 ppm. This would be expected if cured linolenate chains do not form acid groups on curing. Thus the evidence for the curing of linolenate chains in a real drying oil is slightly contradictory although it is possible that the expected linolenate olefinic signals are for some reason suppressed in swollen state NMR spectroscopy. The other features in the spectrum are similar to those described above especially the presence of signals at 59.1 and 37.3 ppm.

However there are some significant differences seen in the swollen state ^{13}C spectrum of a sample of non-catalytically dried linseed oil, shown in Fig. 7. This sample might be expected to be less cross-linked than catalyst-dried linseed oil, and the olefinic signals certainly appear to be larger. However the signal at 132.5 ppm is smaller than that of 130.0 ppm and may arise from a new olefinic species formed by a Diels Alder reaction, since the olefinic signal at lowest field in trilinolenin occurs at 131.6 ppm. The remaining additional features in this spectrum are the signals at 160.3, 72.3 and 43.8 ppm, observed with soya oil and safflower oil. A slightly more puzzling feature of the non-catalytically dried linseed oil spectrum is that the resolution is poorer than in the catalytically-dried spectrum. A less cross-linked material might be expected to give better resolution in its swollen-state spectrum and so this result raises the possibility that the molecular weight of the sample is higher and therefore that further oxidation of the material occurs when a catalyst is present. The catalytically-dried linseed oil in fact contains material soluble in chloroform as observed above with other drying oils. This material has a spectrum similar to the swollen state spectrum and may be the product of further oxidation. There is a limited range of drying oils in which this behaviour in curing can be studied since few oils will cross-link without the use of a catalyst. Tung oil and blown oil will cure without catalyst and are discussed below.

Linseed oil is normally refined prior to use in alkyds. The linseed oil described above was refined with alkali to remove acid impurities. The spectra of cured and uncured unrefined linseed oil, hereafter referred to as raw linseed oil, are shown in Fig. 8. It is interesting to note that alkali refining removes impurities such as those giving signals at 177.4, 160.3, 71.8 and 9.5 ppm. These are the very signals that appear in the spectrum of the cured, refined linseed oil, and would appear to be oxidation products of the linseed oil itself. This should mean that the identity of the species could be established by attempting to isolate them from the raw linseed oil. However other products of the curing reaction which give rise to signals of 59.1 and 42.7 ppm seem not to be present. This is probably merely a question of degree and that they are present in small but undetected amounts.

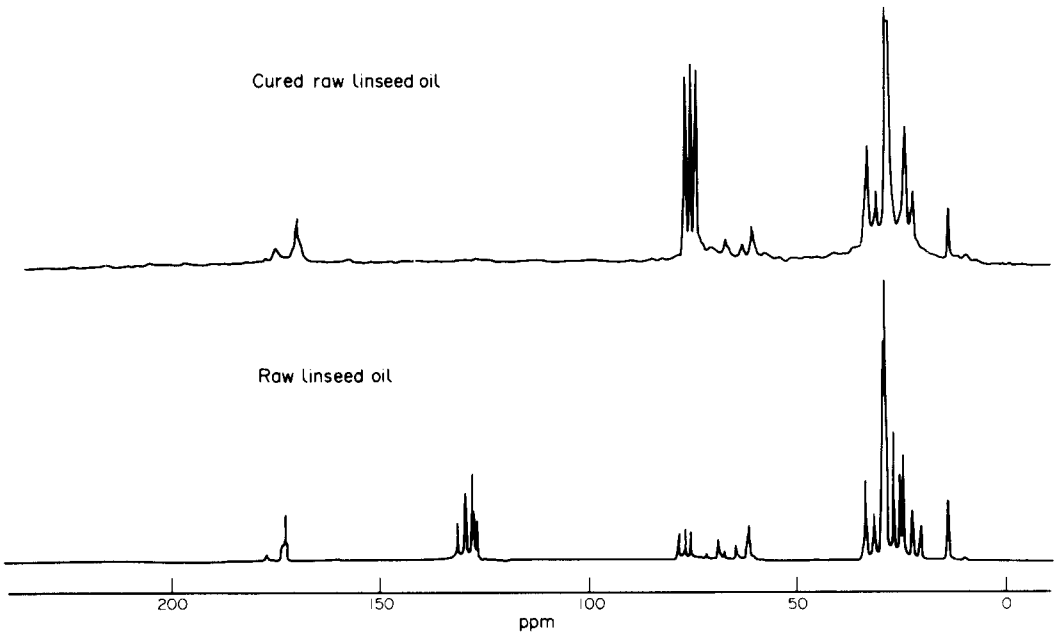


Fig. 8. Raw linseed oil/cured raw linseed oil.

The cured spectrum of raw linseed oil shows all the expected features except that now the acid carbonyl signal of 178.7 ppm is larger than would be expected even allowing for the fact that a small amount of acid carbonyl was present in the raw oil. There is also a significant difference between the chemical shifts of the 2 acid carbonyls at 1.3 ppm which could mean that the acid group present in the raw oil was attached to an alkyl chain of different length from that in the cured material. Clearly examination of the impurities in raw linseed oil could help characterise the key oxidation products observed in cured drying oils.

Pilchard oil is a typical marine oil in that the fatty acid units are generally larger than those of typical vegetable drying oils and contain more unsaturation. The oils themselves are not widely used but the spectra of the pilchard oil shown in Fig. 9 may

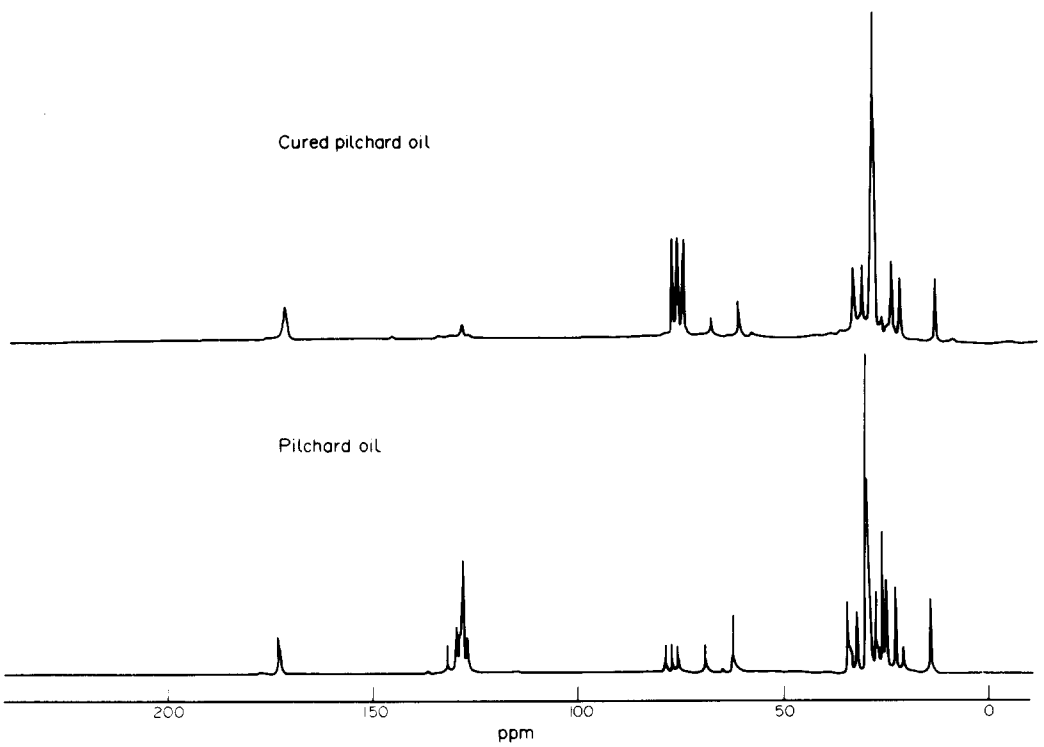


Fig. 9. Pilchard oil/cured pilchard oil.

assist the understanding of the curing behaviour of vegetable drying oils.

The uncured spectrum of pilchard oil in Fig. 9 shows many of the features associated with linolenate groups, i.e. the large signals at 25.6 and 20.5 ppm from the allylic methylene groups and the C_{14} and C_{15} olefinic signals at 131.9 and 127.0 ppm. Although the exact side chain groups present in this pilchard oil sample are not known, it is clear that they are similar to linolenate. The relative ratio of the peaks at 25.6 and 20.5 ppm here is higher than with linolenate suggesting that the side chains are generally longer and contain more unsaturation. One thing that is clear about this pilchard oil is that it contains few linoleate chains, since no signal at 31.5 ppm is present. The allylic signal from the oleate groups is quite large at 31.9 ppm and this combination of drying oil chains may explain the poor properties of cured pilchard oil films. Impurity peaks are present in the pilchard oil such as an acid carbonyl at 177.5 ppm and the signals at 39.4 and 9.6 ppm described above. There may also be a small amount of vinylic material in the material as indicated by signals at 136.5 and 114.7 ppm.

The swollen state spectrum of cured pilchard oil is also shown in Fig. 9. There is a wider range of olefinic signals in this spectrum than in other cured drying oils. Although the signals are not as intense or as sharp as those for cured trilinolenin, definite peaks can be seen at 135.4, 132.8, 130.0, 129.8, 128.8 and 116.5 ppm when the gain of the spectrometer is increased. Apart from 130.0 and 129.8 ppm which are probably from residual oleate groups, these signals are not present in the uncured pilchard oil spectrum and so are likely to be the products of a Diels Alder cross-linking reaction. It is interesting that the peak at 114.7 ppm in the uncured material, thought to be vinylic, has been shifted downfield to 116.5 ppm by the curing. A small acid carbonyl signal is present in the cured oil at 178.1 ppm, but its intensity relative to the ester carbonyl signal seems much smaller than in the uncured oil.

The degree of cure of the oil is quite significant due to the low intensity of the allylic methylene signals at 27.3 and 20.5 ppm. The signals at 59.1, 37.3 and 9.8 ppm are not seen in the uncured pilchard oil spectrum and so correspond to oxidation products similar to those for the other cured oils. The latter signal is associated with a linolenate type terminal methyl group and careful examination shows a shoulder at 10.3 ppm. This is likely to be the terminal methyl signal from the longer side chains in pilchard oil that have undergone similar oxidation. Overall, the behaviour of pilchard oil is interesting because it suggests that reducing the amount of linoleate chains in the oil affects the curing the linolenate type chains so that more olefinic signals can be seen in the swollen-state spectrum.

With the remaining drying oil studied, the influence of the catalyst on the cross-linking of the oil can be examined. Tung oil is different from the other oils examined in that the drying units are based on the triply conjugated eleostearate group. There is no evidence for hydroperoxide formation during the cross-linking of tung oil and the dominant reaction is thought to be Diels Alder coupling [6].

The solution state spectrum of uncured tung oil is shown in Fig. 10. The multiple unsaturation present

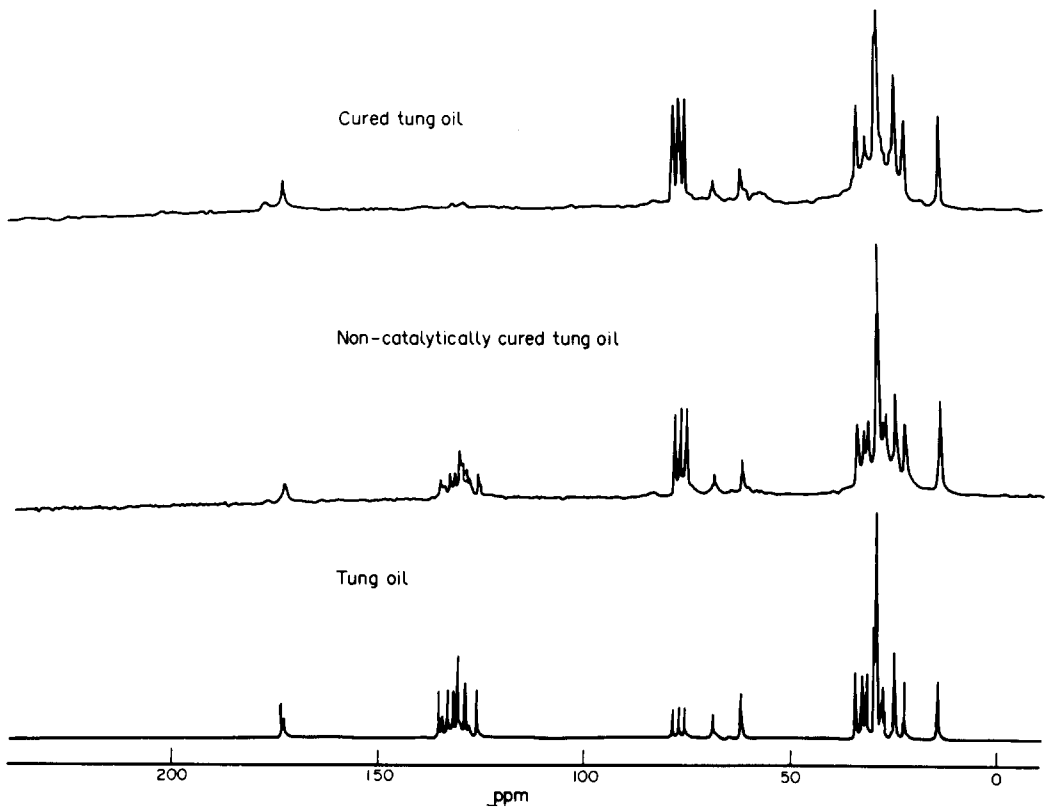


Fig. 10. Tung oil/cured tung oil/non-catalytically cured tung oil.

can be seen via the olefinic peaks from 126.0 to 135.1 ppm. Exact assignments of these signals are hampered by the fact that probably only 80% of the side chains are eleostearate the remainder being from saturated acids, oleate or linoleate. The allylic methylene signals appear at 30.8 and 27.8 ppm and these signals can no longer be seen in the swollen-state spectrum of the catalyst dried oil, which is also shown in Fig. 10. Some olefinic signals remain after curing, at 132.3, 130.1 and 129.0 ppm, and they are probably species formed by the cross-linking Diels Alder reaction, although it is possible that 130.1 ppm corresponds to oleate in the material. The broadness of those signals at 132.3 and 129.0 ppm suggests that the cross-linking gives rise to a wide range of species with over-lapping chemical shifts. Like linoleate chains, eleostearate is oxidised to give an acid carbonyl signal at 178.2 ppm. This is important since it shows that the anomalous behaviour of trilinolenin on curing is not simply due to the presence of an addition olefinic group. The presence of the small signals at 59.2, 43.9 and 37.5 ppm shows that there are similar side reactions during the curing of tung oil as described above for the non-conjugated drying oils. However there are also some previously unobserved signals, i.e. 57.7 and 56.3 ppm suggesting that the greater reactivity of tung oil leads to a wider range of reactions.

The swollen state ^{13}C spectrum obtained from tung oil cured without catalyst is shown in Fig. 10. The extent of cross-linking is quite low in the sample as indicated by the intensities of the signals at 32.6, 31.6, 27.9 and 27.3 ppm. The olefinic signals from this sample are still quite intense with no apparent change in the relative ratios seen with the uncured oil. However there appears to be a definite acid carbonyl signal at 178.0 ppm and some of the smaller peaks seen in the spectrum of the catalyst-cured tung oil, such as 85.8, 83.9 and 57.6 ppm, can be seen in Fig. 10, showing that oxidation reactions begin before the material has cross-linked to any great extent. There is a possibility that isomerisation of the conjugated double bonds may also be visible in the non-catalytically dried tung oil since the relative ratio of the signals at 27.9 and 27.3 ppm appears to have changed from that in the uncured tung oil.

CONCLUSIONS

A wide range of drying oils, covering virtually all those used in alkyd manufacture, can be cured and investigated by ^{13}C-NMR after swelling the films in deuterochloroform. The overall curing mechanism can be followed and particular functional groups formed can be identified. Fingerprint identification of the cured oil is possible but relies upon the presence of small amounts of characteristic components.

In some cases the results of previous studies are confirmed, or are found to be true for other types of drying oils, e.g. the formation of acidic groups and Diels Alder type during the curing processes. Examination of low molecular weight products in the cured oils suggests that they contain similar functional groups to the bulk insoluble material and that both are lower in olefinic material than might be expected by current mechanistic ideas.

Studies on the linoleate and linolenate components of drying oils shows that their behaviour upon oxidation is quite different and that when mixed together this behaviour is modified.

Initial investigations into those oils that will cure without catalyst shows that there may be some differences in the reactions in comparison to the catalyst dried systems.

Overall, ^{13}C-NMR is very useful tool investigating the structures of insoluble, cured drying oils and new developments such as solid state NMR and 2-dimensional NMR should further open up this area for detailed structural investigations.

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