051103 AS

Chemical Study of linseed oil and its films

DRAFT Document

Compiled by A. Sharma CERN
Nov. 5, 2003

Contents:

Introduction

Linseed oil, the largest volume drying oil, is obtained from flax, *Linum usitatissimum*. Flax is grown on different locations throughout the world in temperate zones located in the latitudes of roughly 30º to 60º nowadays. Nowadays the plant can be found on all continents: Argentina, Canada, Europe, India and the USA being major producers. The varieties can be divided into oleaginous flax (linseed) and textile flax (fibre flax). The conditions of farming and the effects of the climate will accentuate the differences between the two types. These factors are also important for the final composition of the oil that is obtained from the seeds. In general, the oil content of the seeds varies from 35 to 45 % of the dry weight.

The chemistry of traditional linseed oil begins with the method of preparation of the oil itself. The traditional manufacturing processes used for the oil production and work-up may lead to an alteration of the initial triacylglycerol composition.

Two methods, either a pressure method or a solvent extraction process are used to obtain the oil from the seeds of the flax plant. In both cases the seeds first have to be cleaned and separated from materials by subjecting them to processes such as blowing with air (to remove chaff, etc.) or screening (to remove particles of appreciably different size). In a next step, the seeds are ground to a fine meal, which facilitates the oil extraction. The meal then can be heated in a kettle prior to pressing, a process called “cooking”. The principle objective of this heat treatment is to coagulate the proteins in the walls of the oil containing cells and make the cells permeable to the flow of oil. At the same time, the

lowered viscosity of the oil at elevated temperatures also assists the flow of the oil from the seeds.

After the oil film is applied on a (primed) support the chemical drying of the viscous mixture starts due to the reaction of the unsaturated triacylglycerols with oxygen.

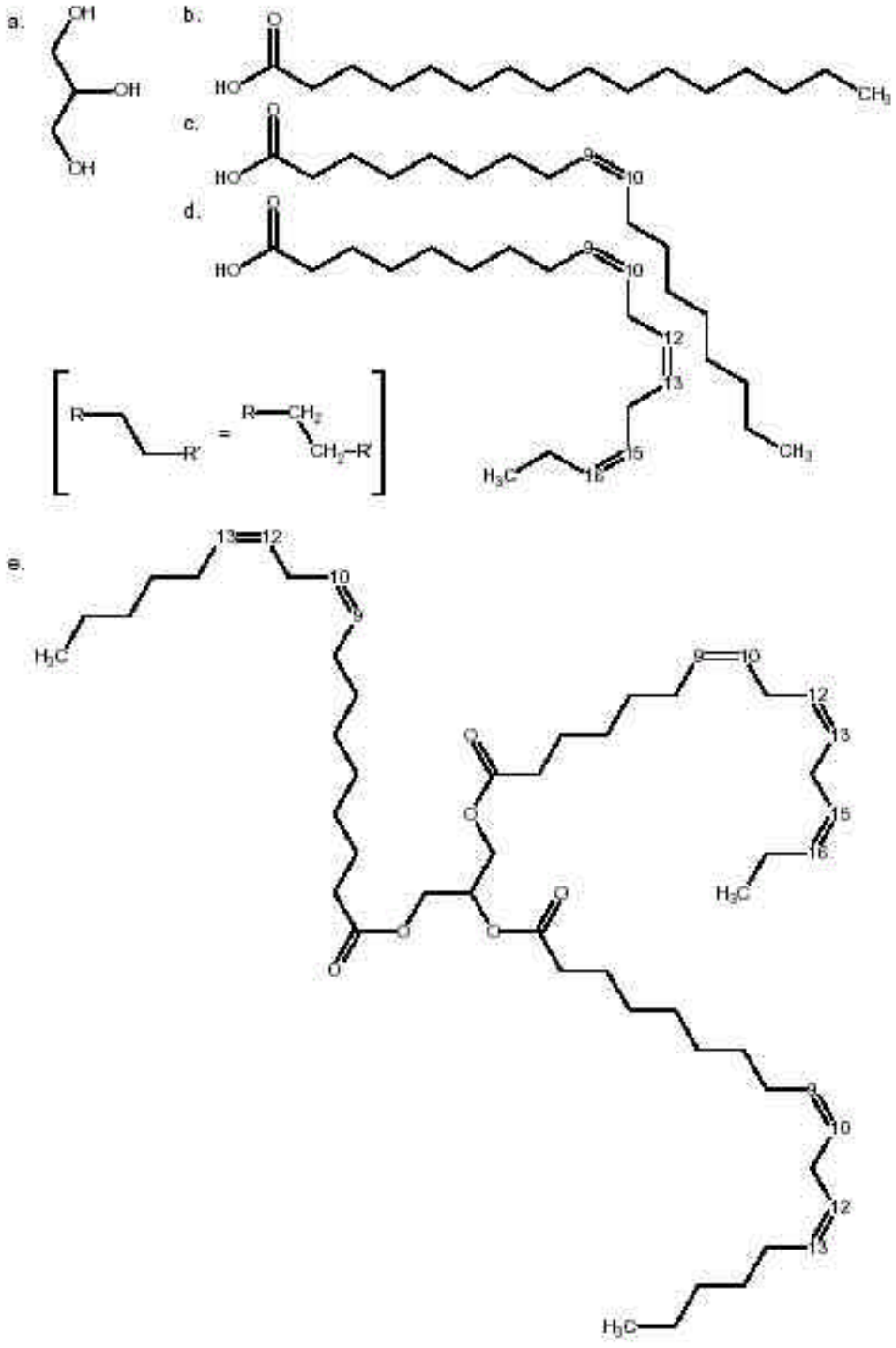


Figure 1. Constituents of linseed oil. (a) glycerol; (b) palmitic acid (C16); (c)

oleic acid (C18:1); (d) linolenic acid (C18:3), and (e) a triacylglycerol with C18:2-C18:2-C18:3 fatty acid moieties (TAG).

The composition of linseed oil

By far the largest proportion of the oil constituents are triacylglycerols, triesters of glycerol (1,2,3-propanetriol) with mixtures of fatty acids. The general structure of a triacylglycerol (TAG) and some fatty acids are depicted in Figure 1.

Oil	Fatty Acid (% of total FA)				
	Palmitic[a]	Stearic	Oleic	Linoleic	Linolenic
Linseed	4-10	2-8	10-24	12-19	48-60
Poppyseed	9-11	1-2	11-18	69-77	3-5
Walnut	3-8	0.5-3	9-30	57-76	2-16

Table 2. Fatty acid distribution in different linseed oils

Oil	Fatty Acid (% of total FA)				
	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Europe	4-6	2-3	10-22	12-18	56-71
Russia	6-7	3-6	15-23	14-19	49-60
Canada	5-6	3-4	19-20	14-16	54-61
India	9-10	7-8	10-21	13-15	50-61
Argentina	4-5	5-6	19-21	15-24	45-53

[a] These are the common names. The systematic names are hexadecanoic-, octadecanoic-, (9Z)-octadec-9-enoic-, (9Z,12Z)-octadeca-9,12-dienoic-, and (9Z,12Z,15Z)-octadeca-9,12,15-trienoic acid, respectively. Short-hand notation C16, C18, C18:1, C18:2, and C18:3 FA, respectively.

TAGs are the main components of the oil, but there are much smaller quantities of other materials present. Some of these can have a marked effect on the drying properties of the oil. Free fatty acids are always present, with an average composition reflecting the constituents of the TAGs. These are naturally found in the seeds or formed upon hydrolysis of the original TAG ester bonds. The proportion is commonly ranging from 0.5- 2 % of the total weight, but it may be much higher, depending on the identity of the oil, how it was obtained, and its history.

Water present naturally in seeds will also dissolve in the oil, although only in a small portion, usually about 0.1-0.2 %. For linseed oil around 0.2-0.4 % of phytosterols are present of which the two major compounds are brassicasterol ($C_{28}H_{46}O$) and stigmasterol ($C_{29}H_{48}O$) after being oxidised cause the more brownish colour of the oil.

Besides these species, trace amounts (0.01-0.1%) of normal and branched paraffins, waxes and triterpenic alcohol (0.15 %) have been identified as well, with squalene as one of the major compounds. An important class of constituents found is the tocopherols (around 0.1 %). These are the natural protectors of the oil because of their anti-oxidising properties. Their presence therefore will have a noticeable influence on the drying process.

Refining and heat processing of linseed oil

Blown linseed oil is produced by blowing air through the oil. The main characteristic of this oil is that no driers are added to the oil. Therefore the blowing usually has to be continued for a longer period until there is a pronounced rise in the viscosity (prepolymerization). At the same time the oil is mildly heated to a temperature in the range of 40 to 150 ºC. The exact changes that occur during blowing are complex and depend on various factors including temperature, exposure time, amount of air passed and so on. These factors will vary from one manufacturer to another. The oil usually is a clear brown or light brown fluid with a typical “oxidized” smell.

Autoxidation and film formation

The most important chemical reaction taking place during the production and processing of drying oil, and the curing and ageing of the oil film is a process in which oxygen from the atmosphere reacts spontaneously with the unsaturated (esterified) fatty acids of the oil. This process is generally referred to as autoxidation. The overall effect of this reaction on the liquid TAGs of drying oils is that they will start to cross-link to form higher molecular weight material. On the other hand, degradation resulting in smaller molecules will take place at the same time.

The basic overall reaction is the incorporation of molecular oxygen into the unsaturated fatty acid:

$RH + O_2$ ： ROOH,

with RH being the substrate, an unsaturated fatty acid (R) with a removable hydrogen (H) and ROOH the newly formed **hydroperoxide**. An important characteristic of autoxidation is that it is autocatalytic. Once the process has started the rate is to increase as the reaction progresses. At the start the rate is often so slow that there seems to be an induction period, because the rate is too small to be quantified. This behaviour is typical for radical-chain mechanisms. Comparable to other radical chain reactions the autoxidation can be divided into three separate steps: initiation, propagation and termination, as shown here:

Initiation: $In\bullet + RH$ ： $R\bullet + InH$ (1)
Propagation: $R\bullet + O_2$ ： $RO_2\bullet$ (2)
$RO_2\bullet + RH$ ： $ROOH + R\bullet$ (3)

Termination: $RO_2\bullet + RO_2\bullet$: ROOOOR (4)

$RO_2\bullet + R\bullet$: ROOR (5)

$R\bullet + R\bullet$: RR (6)

The initiation which is the key event of the whole process involves very small quantities of radicals which can be formed by thermal or photochemical hemolytic cleavage of the RH bond or by an initiator free radical (single electron transfer from the substrate or Oxygen or a metal atom present in the system). Figure 2 shows the rearrangement of a hydroperoxide radical, and a hydroperoxide cyclisation reaction.

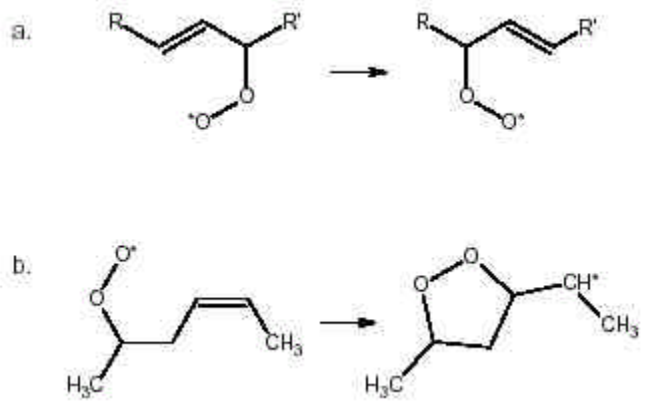


Figure 2. Rearrangement of a (a) hydroperoxide radical, and (b) a hydroperoxide cyclisation reaction.

Autoxidation of unsaturated lipids is affected by many factors, some of which increase and some of which decrease the autoxidation rate. The effect of any given factor depends on the reaction conditions, so that no factor can be classified exclusively as anti-oxidative or pro-oxidative. In general, the rate of autoxidation increases with increasing reactivity of the autoxidizing material, with increasing concentrations of the reactants (the number of active sites and concentration of oxygen), and as a result of physical factors like an increase in temperature or irradiation, but especially by increasing the rate of the initiation reactions. This is mainly done by factors that increase free radical concentrations such as UV light. On the other hand, the reaction rate can be suppressed by such factors as a decrease of the number of reactive sites, the decrease of partial oxygen pressure, or lower temperatures. The most important, however, is the reduction of the initiation rate by a decrease of the number of free radicals capable of chain initiation. This is done with so-called anti-oxidants.

Ozone, O_3, is a well-known industrial reagent for the oxidative cleavage of double bonds. Exposure to ozone results in an increased rate of oxidation and the subsequent formation of low molecular weight breakdown products, with azelaic acid as the main reaction product. The same catalytic effect has been shown for UV-light in the initial stage of drying.

Relevant Factors for Degradation

The formation of the volatile materials in the stages of drying oil already can be seen as the first steps in the degradation. However, the film itself stays relatively intact and no typical degradation phenomena like blistering, brittleness, cracking, and flaking are observed at that time. These phenomena are normally only first observed when the oil film is exposed to harsh condition in tests using high temperature, humidity, ozonization, or high doses of ultraviolet (UV) light. **The thinner the tested oil film is, the more dramatic the changes and loss of material will be**. The overall effect of strong doses of light on the oil film results in its decomposition forming carbon dioxide, carbon monoxide, water, and low molecular weight volatiles and (di)acids. The extreme breakdown of the thin surface layer leads to chalking. This is especially associated with certain components which are activated by **UV radiation** of which the most active wavelengths lie between **290 and 350 nm**. Lower layers are also affected because of the penetrating power of UV radiation. The changes in density are not similar for the top and lower layers. As a result of unequal contraction, stress and strain is built up in the oil film system, which can lead to failure of the film in the form of cracking or flaking. Another factor of importance in this process is the non-homogeneity of the different layers due to formation of pre-polymers within particular layers.

Heat is thought to be a less complex factor compared to other parameters involved in the degradation of oil. High temperatures are responsible for the alteration of the kinetics of the different processes like autoxidation, photoxidation, and hydrolysis, and furthermore volatile compounds will be lost faster from the film.

Water absorption in the film leads to the hydrolytic breakdown of ester bonds with an overall effect of gradual weakening of the film, so that the mechanical effects of alternate swelling and shrinking, or of movements of the substrate, should become more destructive with time. On the other hand, water can be absorbed and may collect at the interface of substrate and oil or layers, leading to loss of adhesion and peeling. Adhesion may be restored on drying, but eventually this cycle will produce an irreversible loss of adhesion. Blooming, the formation of stains on the surface on part or the whole of the surface, is occasionally observed under high levels of humidity as well. This last example can be seen as a change in the equilibrium between the three types of fatty acids present in the oil: esterified-, metal bound-, and free fatty acids. The increased rate of hydrolysis leads to an excess of the free fatty acids within the oil film, which are thought to migrate eventually to the surface of the film when not trapped by the reaction with oil layers.

Chemical Analyis: FTIR

Drying Linseed oil used for film are a mixture of (isomeric) triacylglycerols, with fatty acyl moieties with different degrees of unsaturation and number of carbon. This is clearly visible in the mass spectrum shown in Figure 3 that was obtained for a raw purified linseed oil. The bulk of the material was detected within scan numbers 40-54, but molecular information is detectable afterwards due to condensation/redesorption. The mass spectrum of scans 49-53 shows two clusters of molecular ions at m/z 850-860 and 852-886, corresponding to triacylglycerols with one C16, two C18 fatty acids and 6 to 1

double bonds and triacylglycerols with three C18 fatty acids and 9 to 2 double bonds, respectively. No distinct signals are seen for triacylglycerols with two or three saturated C16 fatty acids or three saturated C18 fatty acids.

Linseed oil is not a pure product and regional variations are expected. Fragment ions formed upon loss of an acylium ion from the triacylglycerols are observed at mass range m/z 619-611 with the lowest m/z representing a diacylglycerol containing two linolenic fatty acids (m/z 611). Complete loss of a fatty acyl chain is seen in the m/z range 605-594, with once more the last m/z representing a diacylglycerol containing two linolenic fatty acyl chains. Diacylglycerol fragment ions consisting of one C16 fatty acyl unit are detected from m/z 579 to 572, with the last ions consisting of a C16- and a linolenic fatty acyl moiety. Acylium and $[RCO+74]^+$ ions are seen for all fatty acids with those of the unsaturated fatty acids of highest intensity. The ratio of these, however, does not reflect the ratio of fatty acids present. The fragment ions $[RCO+115]^+$ and $[RCO+128]^+$ ions are hardly visible in the mass spectrum. Fragment ions arising from fragmentation of unsaturated fatty acids are observed in the low mass region with m/z 108 being the most intense one (50%). These are identical to those observed in the DTMS spectrum of linolenic acid previously described in Figure 2.

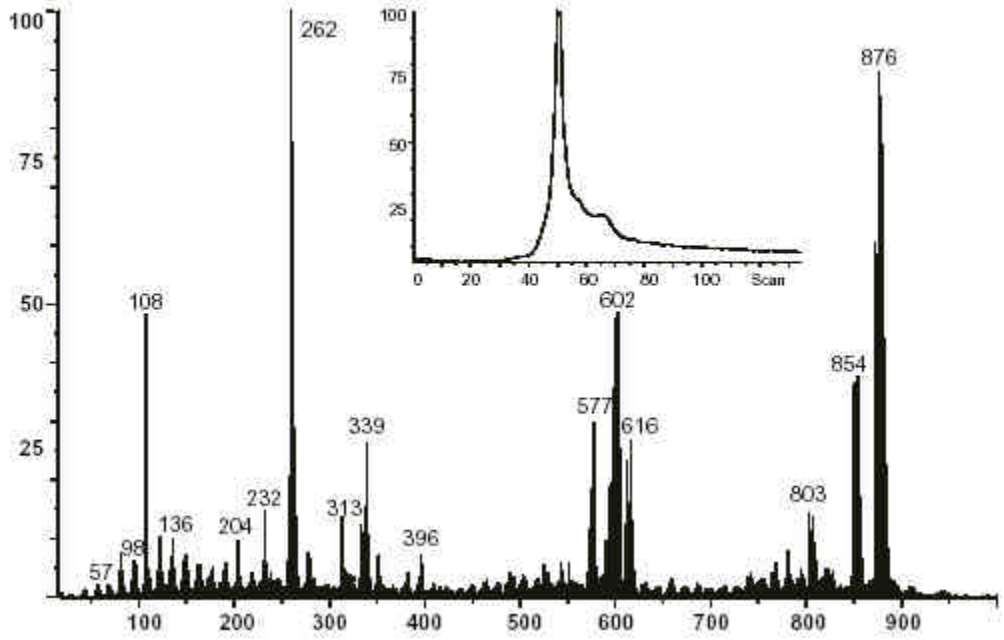
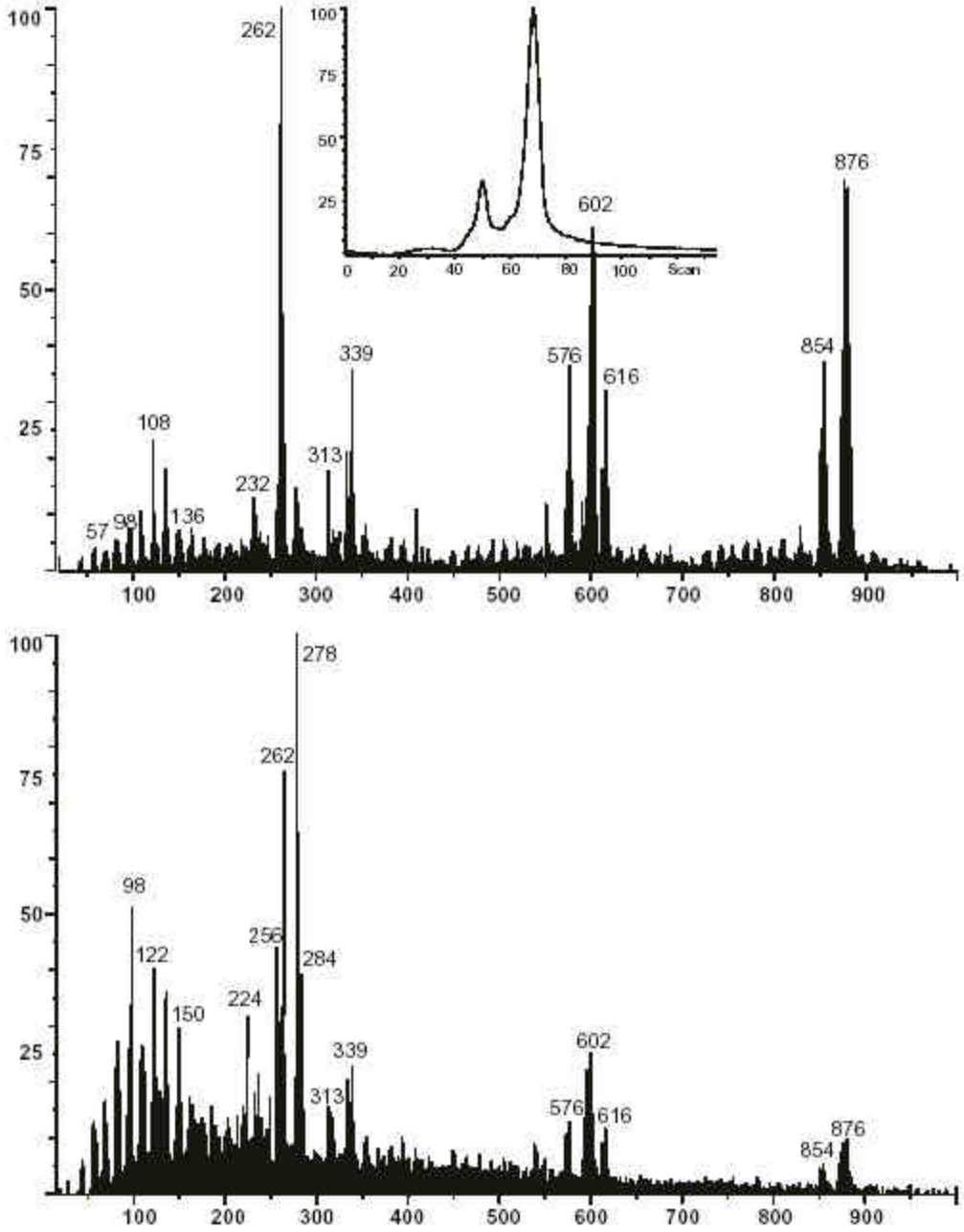


Figure 3. DTMS summation spectrum of fresh linseed oil (Talens). (scan 49-53).
Insert: TIC.

Aged linseed oil

In the case of a cured or aged oil film, a complex mixture of oxidised acylglycerols is expected due to incorporation of different numbers and types of functional groups containing oxygen, specific breakdown reactions occurring upon autoxidation and hydrolytic processes. In Figure 4 a,b the result of a DTMS analysis of a 4-year old aged

linseed oil film is depicted. Most of the material is desorbed and / or pyrolysed at higher scan numbers relative to the fresh oil as can be seen in the insert.



13.

Fig. 4 DTMS summation spectrum of fresh stand oil (Talens) (a) scan 45-55 Insert: TIC, and (b) scan 65-72.

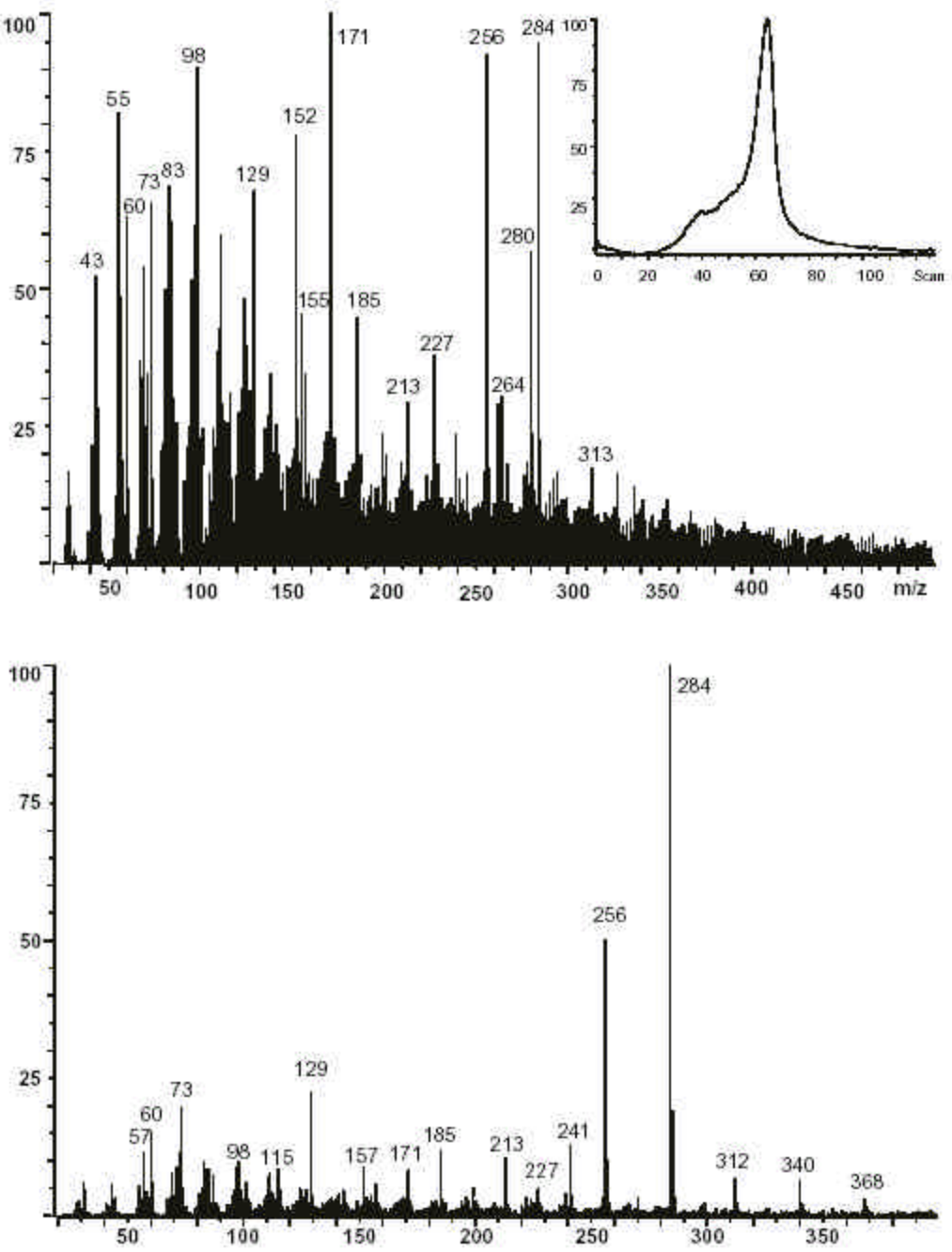


Figure 5 DTMS summation spectrum of 4-year-old dried linseed oil (Talens) (a) scan 56-64 Insert: TIC, and (b) scan 1-15.

This is indicative for the presence of more polar and high molecular weight material. Peaks representative for polar compounds are seen at m/z 152 and m/z 155 in the summed mass spectrum of scans 56-64. These masses can be ascribed to fragment ions of oxidation products: a C9 diacid and a 9,10- epoxyoctadecanoic acid, respectively. Furthermore, a high intensity peak at m/z 171 is observed which is seen in a number of spectra already encountered, but always with a relatively low intensity. This fragment ion

is thought to be indicative for FAs that are substituted with oxygen on the 9-position. The large number of low molecular weight masses in combination with the absence of diacyl- or triacylglycerols (fragment) ions suggests that most of the TAGs originally present have reacted away and that pyrolysis of cross-linked material has taken place. The molecular ions of palmitic and stearic acid at m/z 256 and 284 were observed within two scan regions. Besides the detection at scans 56-64, inspection of the early region of the TIC in Figure 4a shows that these peaks are also present at low temperature. This indicates that free fatty acids are present. This is obvious from Figure 4b which depicts the summed mass spectrum of scans 1-15. The ratio of the molecular ions of palmitic (m/z 256) and stearic (m/z 284) acids (P/S ratio = 0.5) in this figure is not in agreement with the range of 1.1 to 2.1 as has been determined for different linseed oil oil films. This may be explained by unequal evaporation during drying of the sample and /or insertion of the analytical probe into the hot ion source. Upon heating the relative amount of C18 fatty acids increases due to enhanced evaporation of the more volatile C16 fatty acids with a factor of approximately 4, as has been suggested by Schilling et al. The P/S ratio of 1 observed in Figure 14a seems to match better. These fatty acids, at the time of analysis, are derived from TAGs and their oligomeric material and therefore no discrimination will occur upon drying. Besides these two saturated fatty acids also low intensity molecular ions of C20, C22 and C24 fatty acids are observed at m/z 312, 340, and 368, respectively. These are known to be present in fresh oils in trace amounts and most probably are better retained within the oil film due to their reduced volatility. No (fragment) ions are observed that point to the presence of unsaturated fatty acids. These must have reacted away by autoxidation forming oxidised compounds and/or are incorporated into crosslinked material.

Refs:

Identification of non-cross-linked compounds .. in cured and aged linseed oil .. using gas chromatography, Journal of Chromatography A (2002) 195-211

MOLART Report: Molecular Studies of fresh and aged varnished. Gisela Doelen 1999 Van den berg

Other related web resources