

FORMATION OF CYCLIC FATTY ACIDS AT THE
HYDROGENATION OF LINSEED-OIL*József Perédi, Anna Ruzics, Eva Kurucz*

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Fatty acids of unsaturated fats first of all those of multiple unsaturatedness may undergo a considerable structural change on the effect of temperature rise, particularly in cases where heating takes place in the presence of a catalyst. One of the changes is cyclization, which recently was studied by many researchers. As a result of investigations many kinds of cyclized acid types have been rendered probable mainly by various authors [2-4, 7, 8, 10], also proved that many compounds of this type may be taken into consideration in fats exposed by cyclization effects. Also it became known that, mechanism of the process depends on prevailing conditions. Other products are formed on the single effect of temperature rise and again others on the combined effect of increased temperature and catalysts. Thus we know thermic and catalytic cyclization.

Mainly cyclohexadiene derivatives and to a lesser extent aromatic compounds, i.e. benzene derivatives are formed upon the effect of heat.

If a thermic effect takes place in the presence of alkalies, the number of cyclohexadiene isomers increases due to the more intensive displacement of double bonds and also bicyclic compounds (indane derivatives) can be formed by the so-called internal Diels-Alder reaction. In such a case aromatic compounds — benzene derivatives — and ω -phenylalkane carboxylic acids can also be detected in the product, hence according to our actual knowledge, this method yields the broadest variety of cyclic fatty acid types. If heat effect takes place in the presence of a metal catalyst, aromatic fatty acids — first of all orthosubstituted benzene derivatives — predominate, whilst cyclic monoene and cyclohexane derivatives are formed in the presence of hydrogen. Principal types of the manyfold cyclized acids are shown in Figure 1.

Conditions favouring cyclization may also occur at the large-scale

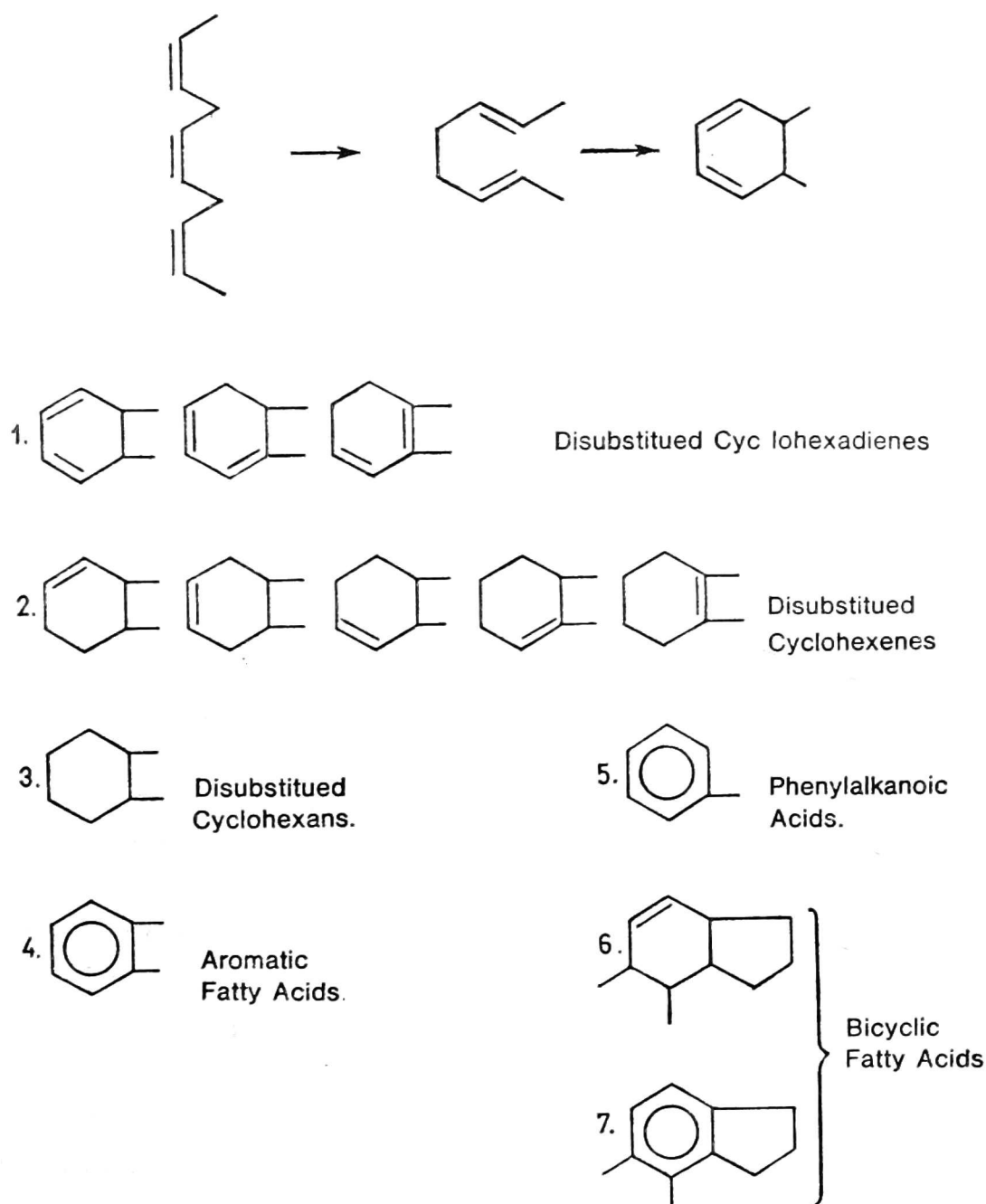


Fig. 1. Cyclic fatty acids

processing of fats, above all at the hardening thereof. For this reason we considered it necessary to identify these compounds, to determine their quantity and first of all the quantity of aromatic fatty acids formed.

MATERIALS AND METHODS

Since probability of cyclization increases with the unsaturated nature of the fat, linseed-oil was chosen to our experiments and this was studied:

— after cyclization with KOH in the presence of ethylene glycol (model substance),

— after hardening in the presence of nickel catalyst,

as well as

— by itself, without conversion (control substance).

Methods of preparation for the two products and more important parameters of the three substances are given below:

Cyclized linseed-oil (model substance). The oil was cyclized in N_2 atmosphere 6 hours at $220^\circ C$ with KOH of 10 per cent (in ethylene glycol), with 50 per cent excess alkali calculated on the oil. The product comprising some 40 per cent of cyclized substances was decomposed with hydrochloric acid, the fatty acids vacuum distilled.

Hardened linseed-oil. Hardening was carried out in plant operation on a discontinuous unit. Catalyst 0.2 per cent Ni; quantity of H_2 about 120 l/kg/hour; temperature $180-210^\circ C$. Slip point of the product was $33^\circ C$, composition of fatty acids: C_{16} 5.4 per cent, C_{18} 15.3 per cent, C_{181} 56.7 per cent, C_{182} 20.4 per cent, C_{183} 1.0 per cent. Other acids 1.2 per cent.

Linseed-oil (control substance). Refined plant product. Acid number 0.2, composition of fatty acids: C_{16} 5.4 per cent, C_{18} 4.0 per cent, C_{181} 18.6 per cent, C_{182} 14.0 per cent, C_{183} 58.0 per cent.

TESTING METHODS

Prior to testing cyclized fatty acids should be enriched due to their low quantity and also for the sake of purification. The urea-adduct method was chosen for this purpose and carried out according to the process described by Coenen and Wieske *et al.* [2]; the fat was saponified with alcoholic potassium hydroxide, the unsaponified part removed by ether, fatty acids liberated by hydrochloric acid, thereafter adducts have been formed with a fatty acid: methyl alcohol: urea proportion of 1 : 13 : 4. The non-adduct part (NA) was esterified with methyl alcohol and again an 1 : 4 : 4 adduct was formed. The second NA part obtained by decomposing the adduct was analyzed by itself, as well as after oxidative and reductive conversion.

Reduction was carried out by the method of Friedrich, I.P. [6] with Pd/C catalyst, at $60^\circ C$ and 2 hours in the presence of glacial acetic acid. Oxydation was performed by the method of Coenen and Wieske *et al.* [2] (H_2O_2 , mixture of glacial acetic acid and formic acid, reaction time 14 hours at room temperature).

The enriched substances simplified by reduction and oxydation resp. have been investigated by

— gas chromatography (Pye Unicam device; ethylene glycolsuccinate 10 per cent; Chromosorb E of 100-120 mesh; 40 to 50 mls N_2 /min;

$H_2/air = 1:1$; injection temperature $240^\circ C$; temperature of column $188^\circ C$, charbed with about 0.1 micro liter),

— IR spectrophotometry (Zeiss VR device, layer thickness 0.25 mm),

— thin-layer chromatography (Kieselgel G; petroleum ether: ether: glacial acetic acid = 90:10:1; developed with iodine vapour and phosphorus-molybdic acid resp.).

In order to prove the presence of cyclic components by faster means which in addition are widely accepted in practice, our investigations were mainly concentrated on the utilization of gas chromatography and thin-layer chromatography.

RESULTS AND CONCLUSIONS

MODEL SUBSTANCE

According to the results obtained, effect of cyclization was vigorous: picture of fatty acid methylesters (Me) corresponding to the known composition is visible on the chromatogram of the original linseed-oil, whilst in case of the untreated substance large quantities of new compounds appear at places corresponding to methylesters of a carbon number higher than C_{18} -Me, particularly within the range of C 19.5 — C 23.0 calculated on the basis of saturated acid methylesters, (Figure 2, 3).

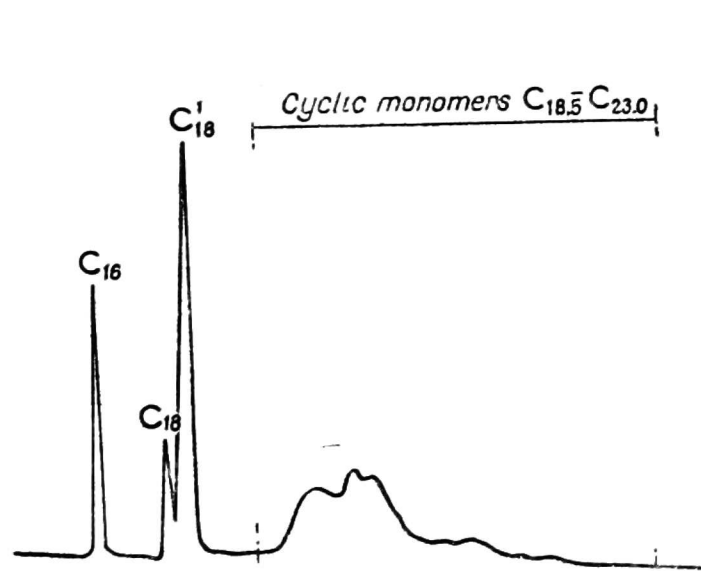


Fig. 2. Gas chromatogram of methyl esters from cyclised linseed fatty acids

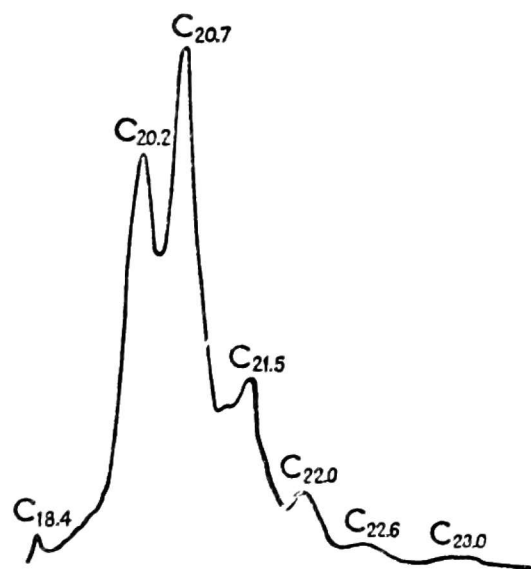


Fig. 3. Gas chromatogram of urea non adduct of cyclised linseed fatty acids methyl esters

All cyclized types occur at these places — aside from some compounds formed by chain cleavage — according to literature references. Indane derivatives occur farthest, aromatic compounds nearer, then diene and cyclohexane derivatives [1, 6, 8]. For enrichment of the cy-

clized products distillation of their fatty acids and repeated adduct forming proved well. We obtained large quantities [37 per cent] of NA which consisted — according to the gas chromatogram in Figure 3 — almost entirely of cyclized product and comprised relatively small amounts of linear fatty acid esters. This statement was also supported by the results achieved at hydrogenation of the product (Figure 4).

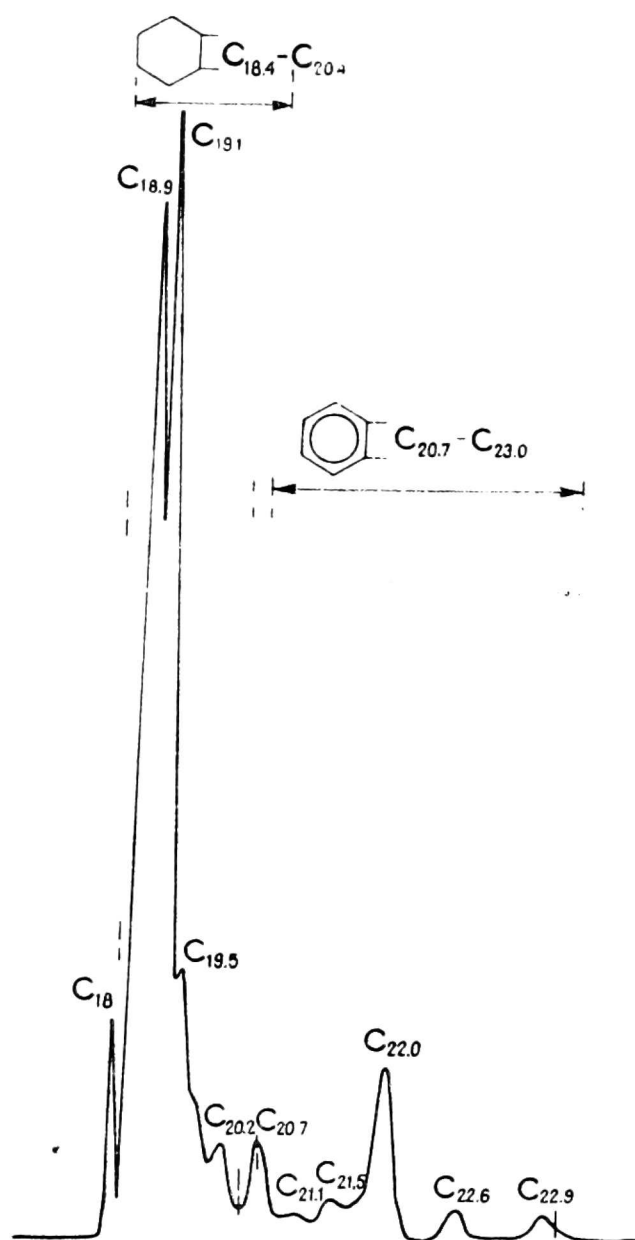


Fig. 4. Gas chromatogram of hydrogenated urea non adduct

Namely the C₁₈-Me peak scarcely raised at hydrogenation, with other words only few linear methylesters were present in the substance. The majority of compounds was displaced towards the cyclohexane region of C 18.4-C 20.4 after hydrogenation, indicating the presence of larger cyclohexadiene fatty acid Me quantities. Identification of the place of appearance as well as of the type of aromatic fatty

acids (AFA) was enabled by the hydrogenation. On the effect of treatment the region of AFA-methylesters (AFA-Me) of C 20.7-C 23 — confirmed by literature references — "became cleaned" of cyclized fatty acid methylesters (CFA-Me) and the pictures of unchanged AFA-Me's and of those formed of dienes on the effect of catalyst appeared. These consisted according to Figure 4 of three main constituents and of three other compounds of minor quantities. They appeared at C 22.0, C 22.6, C 22.9, C 21.5, C 21.4 and C 21.1. Considering the deviation of column load, the result is in good accordance with results of researchers dealing with gas chromatographic analysis of AFA's, whilst it could be proved that they are *o*-substituted benzene-alkyl acid methylesters with an ethyl, methyl, propyl (in largest quantities) side chain or eventually longer side chains (Table 1).

Our model substance was also tested on the IR-spectrophotometer. The spectrum shows characteristic absorptions induced by functional groups of CFA's and AFA's, (705 cm^{-1} : *o*-disubstituted cyclohexadienes, 942 cm^{-1} disubstituted conjugated dienes, 1602 cm^{-1} , 1485 cm^{-1} aromatic compounds, 760 cm^{-1} *o*-disubstituted aromatic compounds). Analyzed by thin-layer chromatography the NA product could be separated in five groups (Figure 5).

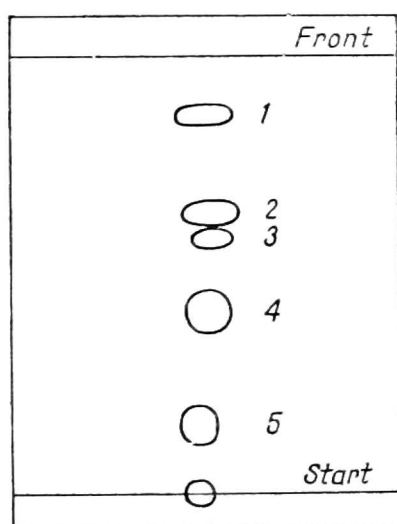


Fig. 5. TLC of urea non adduct

Among these the majority of the substance was placed in two groups, at the place of linear fatty acid methylesters and directly below (spots 2, 3). R_f values of the spots (0.70 and 0.64 resp.) are nearly identical with the values of Sagredos [9] who came to the same conclusions concerning the visible places of CFA's and AFA's. Also our presumption was confirmed by the infra-red spectra of products eluated from the individual groups: the presence of diene and of aromatic compounds in both main components could be established.

Thus processing and investigation of our model substance served as a good example to the gas chromatographic and thin-layer chromatographic detection of CFA's and AFA's, in addition furnished a basis for the study of hydrogenated linseed-oil.

HARDENED LINSEED-OIL

Cyclization ensued during plant hydrogenation according to various investigations of the product. After careful removing of the unsaponifiable part and repeated adduction, the amount of residual non-adduct part was 1.6 per cent. The infra-red spectrum changed as compared to that of starting oil particularly at wave number of 1602 cm^{-1} and 760 cm^{-1} , the latter serving for the detection of *o*-disubstituted aromatic fatty acids according to Coenen's proposal. Consequently, mainly *o*-disubstituted aromatic compounds are formed at hardening. Similar results could be obtained at the gas chromatographic analysis of the product (Figure 6).

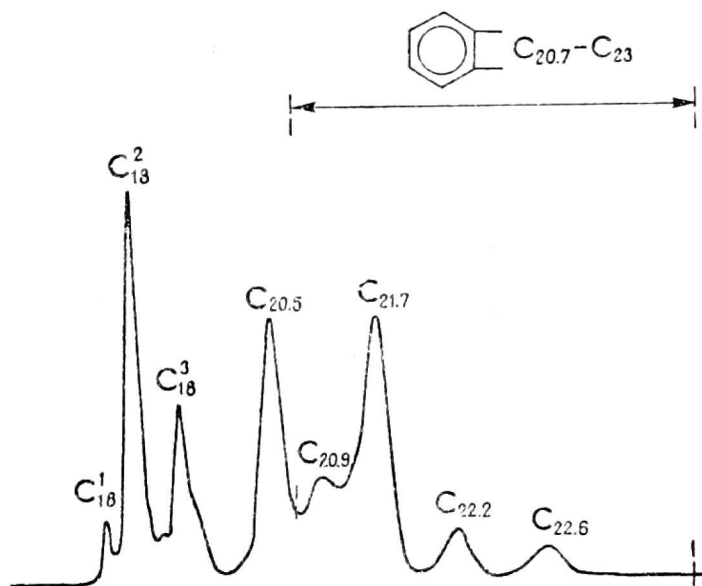


Fig. 6. Gas chromatogram of urea non adduct

On the gas chromatogram $C_{18}1$, $C_{18}2$ and $C_{18}3$ methylesters of hardened linseed-oil can also be seen, however, after the C_{20} methylester the majority of compounds appeared in five well separated peaks. Pattern of the gas chromatogram shows a considerable difference in comparison to the pattern of non-adduct part of the product, obtained by cyclization with potassium hydroxide, it was more simple and better to evaluate, indicating that lesser types of cyclized fatty acids are formed a hardening as compared to alkaline cyclization.

According to their places the substances of the last three peaks (C

21.7, C 22.2, C 22.6) are compounds of aromatic character. (Places of *o*-disubstituted benzene-alkane acid methylesters with propyl, butyl, ethyl side chains). Only inferior quantities of cyclohexadiene, cyclohexene and cyclohexane derivatives have been formed according to the gas chromatographic pattern.

Oxydative treatment of the product resulted in the pattern shown in Figure 7.

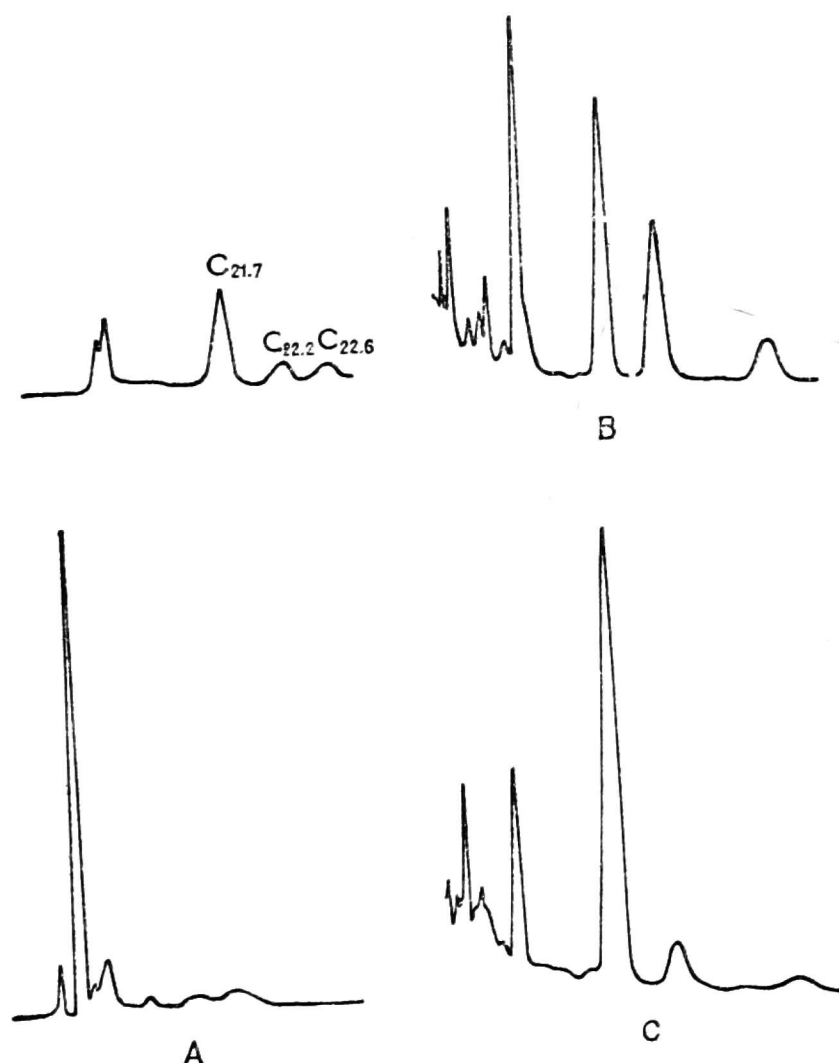


Fig. 7. Gas chromatogram of oxidized urea non adduct

Fig. 7A. Gas chromatogram of urea adduct (L.O.)

Fig. 7B. Gas chromatogram unsaponifiable matter (L.O.)

Fig. 7C. Gas chromatogram of unsaponifiable matter (H.L.O.)

The last three peaks of Figure 6 can be invariably seen on the basis of gas chromatogram of the oxydized non-adduct part, which refers to the aromatic character of the same, proved also by Coenen and Wieske *et al.* [2] by means of this method. For this reason we established that, from the size of peaks appearing in the range from C 21.1 to C 23 on the gas chromatogram of the non-adduct part a conclusion can be drawn on the extent of cyclization (in our case quantity thereof amounted to 39 per cen of the gas chromatographic region). At the

same time also the proportion of non-adduct part being volatile under gas chromatographic conditions can be established by means of an internal standard. This were 42 per cent in our product.

The proportion of AFA-Methylesther in the NA was also 16,4 per cent (in fats 0.26 per cent) and this value was practically identical with the value obtained by the IR-spectrophotometric method. If the unsaponifiable part is not removed during the determination, disturbing peaks will also appear on the gas chromatogram of NA part in the case of control-oil (Figure 7A).

This interfering substance will also appear on the gas chromatogram of the unsaponifiable part in forms of two peaks and according to the results of our experiments (internal standard) they amount to about 7-10 per cent of unsaponifiable part (Figures 7B, 7C). Consequently this disturbing effects can also reach to about 0.07-0.1 per cent of fat (the max. of the unsaponifiable part is 1.0 per cent). Therefor the removal of the unsaponifiable part is important in case of fats containing only low cyclized fatty acid.

According to our IR-spectrophotometric investigations (760 cm^{-1}) carried out so far, petroleum ether used to extract the unsaponifiable part dissolves no perceivable quantities of AFA methylesters.

Thin-layer chromatographic pattern of the non-adduct part (Figure 8) corresponds with that of the model substance.

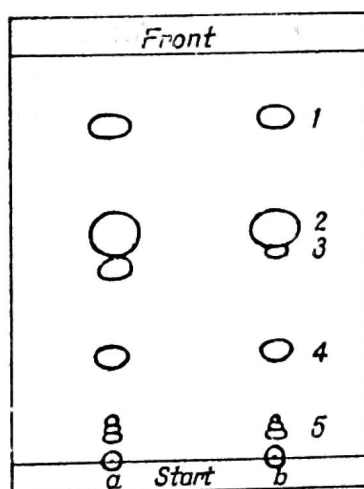


Fig. 8. TLC of urea non adducts: *a* — from hardened linseed oil, *b* — from linseed oil

Also it is very similar to the pattern of non-adduct part of the control substance (linseed-oil) with this difference that, the spot attributed to AFA can only be guessed. However, the difference is not definite to such an extent that quantity of AFA could be estimated on the basis of the thin-layer chromatogram.

SUMMING UP

We studied by means of various methods the cyclic and aromatic fatty acid species occurring in alkali cyclized and hydrogenated linseed oil. According to our experiences, gas chromatogram of the non-adduct part obtained by repeated adduction from hard fat relieved of its unsaponifiable part indicates relatively few components and is properly evaluable. The quantity of volatile ingredients in the non-adduct part can also be determined with relatively low scattering, by means of an internal standard. So far we did not observe a reduction of AFA quantity caused by the removal of unsaponifiable part. If this finally can be proved, a gas chromatographic method will be available enabling the detection of low AFA quantities — in case of fats comprising fatty acids with chains up to C_{18} — which are not detectable by the known IR-spectrophotometric method.

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POWSTAWANIE ZWIĄZKÓW CYKLICZNYCH PODCZAS UWODORNIENIA OLEJU LNIANEGO

Streszczenie

Podczas ogrzewania olejów w wyższych temperaturach, w obecności katalizatorów, następuje cyklizacja nienasyconych łańcuchów kwasów tłuszczowych, szczególnie gdy są one wielonienasycone. Zjawisko to zachodzi także w przypadku uwodornienia oleju lnianego przy następujących parametrach: temperatura 180–200°C i w obecności katalizatora niklowego.

Badając ten proces, stwierdzono obecność związków cyklicznych, określono ich skład oraz ilość niektórych z nich. W rezultacie badań stwierdzono, że cykliczne związki, powstałe podczas uwodornienia są cyklicznymi dienami lub monoenami, jak również pochodnymi cykloheksanu i związków aromatycznych.

Analizy wykonano, stosując metody TLC i GLC oraz IR-spektrofotometrię dla frakcji izolowanych za pomocą adduktów z mocznikiem.

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ОБРАЗОВАНИЕ ЦИКЛИЧЕСКИХ СОЕДИНЕНИЙ ВО ВРЕМЯ ГИДРАТАЦИИ ЛЬНЯНОГО МАСЛА

Резюме

Во время нагревания масла в высоких температурах в присутствии катализаторов происходит циклизация ненасыщенных цепей жирных кислот, особенно в случае их многоненасыщенности. Это явление наблюдается также в случае гидратации льняного масла при следующих параметрах: при температуре 180—200°C и в присутствии никелевого катализатора.

Исследования этого процесса которые обнаружили наличие циклических соединений, позволили определить их состав и количество некоторых из них. В результате исследований установлено, что циклические соединения образованные во время гидратации, являются циклическими диенами или моноенами, а также производными циклогексана и ароматических соединений.

Анализы проводились с использованием метода TLC и GLC, а также инфракрасной спектрофотометрии для фракций изолированных с помощью аддуктов с мочевиной.