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# Alkaline fusion of nonsaturated fatty acids

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# ALKALINE FUSION OF NONSATURATED FATTY ACIDS

by A. Vazquez Roncero

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When a nonsaturated fatty acid is heated with melted potash the soap corresponding to a saturated soap with two carbon atoms less than the originating product is obtained with a good yield. This means that there is a possibility of manufacturing short and saturated acids from nonsaturated acids of eighteen carbon atoms which are the most common in nature and it is obvious that an industrial development of this process would be of a great economic importance, especially to the soap and detergent industry main user of these products. Therefore, we have considered it important to summarize in this paper the knowledge, up to date, on this reaction which, although known for more than a century, is seldom mentioned in general texts of Organic Chemistry and also is not very frequently found in specialized works.

## 1. The alkaline fusion of nonsaturated acids.

In 1840, Varrentrapp (1) observed, in his studies on the constitution of the oleic acid, that when fusing this acid with potash at 300°C, it transforms itself almost quantitatively in potassium palmitate and acetate, freeing a large amount of hydrogen.

We can express the global reaction by the following equation:

$$CH_3 - (CH_2)_7 - CH = CH - (CH_2)_7 - COOH + 2KOH \longrightarrow$$
$$\longrightarrow CH_3 - (CH_2)_{14} - COOK + CH_3COOK + H_2$$

These results were confirmed by successive experiments performed with the same oleic acid (2) (3) and the undecylenic acid which split itself, according to the aforementioned equation in acetic and pelargonic acids (4). However, the importance of this "Varrentrapp reaction" was not recognized from the beginning because it was erroneously inferred that the oleic acid was the 2 octadecenoic acid. At the end of the century the true position of the double link was proven and the importance of this reaction diminished which until recently has not attracted the researchers' interest.

The previous formula does not show anything about the Varrentrapp reaction mechanics. The study of these mechanics has always presented many difficulties, mainly due to the high temperature and speed (sometimes of an explosive character) produced during the acid decomposition and the freeing of hydrogen. Nevertheless, and in a first approach, we can assume that the splitting of oleic acid in palmitic and acetic is done in two successive stages: first, the isomerization, by which the double link displaces itself along the chain toward the carboxyl group to reach the position $\alpha\beta$ conjugate with it, takes place and then the molecule, favored by its new structure, shows hydroxylation and dehydrogenation at the double link which leads to its fast decomposition producing potassium palmitate and acetate and the freeing of hydrogen. This decomposition is only performed in substantial amounts over a certain temperature (280-300°); below it the isomerization fundamentally prevails.

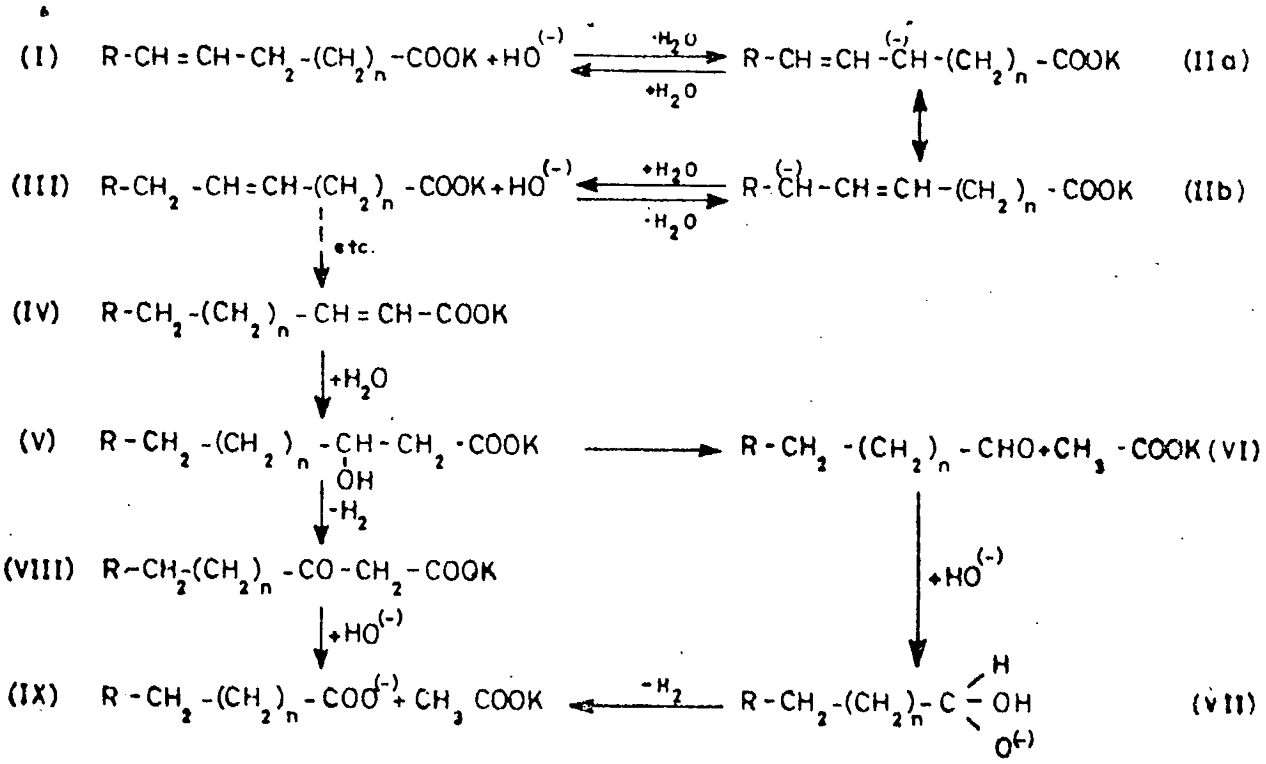
It is a fact that under certain conditions, the double links of unsaturated acids are displaced more or less easily along the chain. We can mention, as a few examples, the thermic isomerization by heating at high temperatures, the formation of isooleic acid during the hydrogenation or the well-known conjugation of double links, isolated when heated in the presence of diluted alkali. But our knowledge on these processes cannot be applied easily to the alkaline fusion because the special conditions in which this developed, will also require, undoubtedly, a proper reaction mechanism.

In 1888, G. Wagner (5) assumed that the wander of the double link in the alkaline fusion is performed by repeated additions and separations of a water molecule. This hypothesis was soon disputed by R. Fittig (6) and later by R.P. Linstead and collaborators (7), who, when studying the tantomery between forms $\alpha$-$\beta$ and $\beta$-$\gamma$ of nonsaturated acids, demonstrated that the addition of water to form hydroxyacids is a secondary and independent reaction from the double link displacement from one position to the other. This isomerization already occurs when heating but it is increased by alkalis and it is a result of the concentration rather than from the molecular proportion of the alkali used.

A. Lüttringhaus recently proposed a new process, which in our opinion has a good fundamental base, to which other later theories basically agreed (9) (10). This process is based on a prototropy which causes a reversible wander of double link along the chain until the $\alpha,\beta$ position is reached and where an irreversible splitting happens. Figure 1 shows the different stages.

## Figure 1

Fig. 1



Mecanismo de la reacción de Varrentrap

The Varrentrap reaction mechanics.

Let us consider first the isomerization phase shown in stages (I) to (IV) of this formula.

Simple olefines in allylic position will be anionized in the presence of organic sodium compounds, establishing a balance between both possible isomers having the double link in contiguous positions. Lüttringhaus assumed that this reaction can also occur under the conditions of the alkaline fusion and so the potassic salt forms an unsaturated acid (I), in a very alkaline mildew and at a very high temperature will anionize to produce IIa. Probably this only happens on a very small scale, but it is sufficient to establish the IIa ↔ IIb mesomery and then, although the hydrolysis of (IIa) leads again to (I), the hydrolysis of (IIb) will lead to the isomer (III), which double link is already displaced one space in direction to a carbonyl group. This compound now shows the same ionization and the process is repeated until it reaches a nonsaturated acid in a 3-4 position which will quickly isomerize to a 2-3 (IV) position due to the great reactivity of the methylene group in 2 position, located between the double link and the carboxyl.

Therefore, the double link prototropic displacement takes place gradually, passing by a series of intermediate unsaturated acids, some of which were already isolated by Egorov (II) and Eckert (12) when performing the alkaline fusion under reasonable conditions. It is hoped that if the structure of some carbon of the chain does not permit the normal development of this process, the wander of the double link stops and the molecule splits itself precisely by this carbon. This is the case, when there is a quaternary carbon atom and it has been brilliantly confirmed by Lukes and Hofman (13) in the alkaline fusion of branched fatty acids.

The process proposed by Lüttringhaus does not exclude the possibility that the prototropic displacement happens in the opposite way and in fact a statistic double link distribution occurs along the chain during the first phases of the reaction (8) (9) (14), but as from (IV) a series of one way reactions which leads to the final molecular fission, in practice all double links end by being displaced to the conjugate position 2-3. The analysis of the isomers mixture during successive phases of the fusion clearly shows that at the beginning the double link migrates almost equally in both ways and that the carboxyl group does not exert any influence during the first isomerization phases. However, this influence appears with more intensity as it approaches the conjugate position with the carboxyl.

Naturally, each double link displacement must be accompanied by a steroisomery, forming almost equal amounts of cis- and trans-isomers, as it has been proven recently (9).

It must be pointed out that all isomeric acids isolated as intermediate products have the double link, at least at the eighth carbon from the carboxyl group. The same Lüttringhaus (8) had only isolated isomers in C-6 or C-7 in the fusion of undecylenic acid. It seems that from here on the migration toward the carboxyl is much faster and maybe has a different process than the one already indicated, as it could be a direct trans-hydrogenation of the double link from the position 6 to 2, favored by the possible formation of intramolecular cyclic structures - 6 or 7 links - as intermediate steps. This fast displacement of the double link from C-7 has been experimentally confirmed by R.G. Ackerman and collaborators (9) when studying the behaviour of 6-octadecenoic, 2-octadecenoic and other unsaturated acid during their fusion.

Once the double link has reached the $\alpha\beta$ position, conjugated to the carboxyl, a series of reactions occur leading finally to the molecule split in two fragment acids. The chain is broken precisely at the double link without intramolecular transposition of any type, as it has been proven when working with acids marked in the carboxyl group or in the second carbon atom (10-15). This behaviour of 2-3 mono nonsaturated acids in the presence of concentrated alkalies is common, and well-known for a long time; however, we have little data on the possible mechanic of this decomposition.

The most probable and generally admitted is that a hydroxylation to B-hydroxy acid (V) characteristic of acrylic acids occur at the first place (fig. 1). The fact that actually it has been possible to isolate small amounts of hydroxy acids from secondary products of the reaction (6-11) and mainly because the chain gets broken precisely where carbon atoms are holding hydroxyl groups (12), supports this theory. This hydroxylation is reversible to a high temperature but it is followed by several degradation reactions which happen very quickly and displace the balance toward the right. The hydroxylate derivate degradation (V) can follow two different courses: either a dehydrogenation occurs with formation of a cetoacid (VIII) and this, in a strong alkaline mildew, suffers an "acid splitting" to palmitate and acetate (IX); or the hydro acid (V), in the presence of a highly concentrated base splits itself in acetate and fat aldehyde (VI) by a kind of a reversed aldol condensation. This would add a $HO^-$ group to produce (VII), which will dehydrogenize itself very quickly to form a palmitate (IX). Although not certain, there are several reasons in favour of the latter course (8) (9) (10) (16). A behaviour study of hydroxyacids and cetoacids during the alkaline fusion can effectively contribute more to clarify this point (17).

As we have already seen, the two successive isomerization and splitting phases generally are independent. Nevertheless, there is no doubt that a certain number of molecules split themselves before the double link has totally migrated toward the carboxyl group, as it is proved by the presence of intermediate length monocarboxylic acids among reaction products (18-19); it lets us assume that, at least during it first phases, the isomerization is partically competitive with the splitting mechanic.

The Varrentrapp reaction is quite extended, as it can be seen in the aforementioned global reaction, so that the resulting products are mainly composed by potassium acetate and soap of the corresponding saturated acid. But dicarboxylic, hydroxyacids and short monocarboxylic acids are also found in small amounts as by-products. We must not discard the possible presence of hydrocarbons which could transform themselves by a similar mechanic to the one produced, for instance, during the thermic decarboxylation of $\alpha/\beta$ nonsaturated acids (20).

The alkaline fusion practiced at the Laboratory does not imply special difficulties. Normally, it is sufficient to heat the fat acids together with two or three times their weight of potash, inside a silver, nickel or even stainless steel vessel. To heat it, the crucible is immersed in a metallic lead or lead and zinc alloy bath, previously heated slightly over the desired final temperature. The final temperature can also be gradually reached by heating slowly the fat acids and potash mixture, and in this way a more regular freeing of hydrogen is obtained. The reaction can be done in open or closed vessels. The latter ones permit to work in an inert atmosphere, decreasing the danger of hydrogen inflammability and eliminating the possibility of secondary oxidative reactions.

Once the heating is over - it takes from 15 to 60 minutes at temperatures of 300° to 350°C - the mixture is cooled and soaps are dissolved in water which is extracted with ether to eliminate the possibly formed insaponifiable products. The water is acidified and extracted with ether or petroleum ether, finally obtaining from 85 to 90 per cent of saturated fat acids. These results vary according to the time and temperature reached. As a guide to the reader we are transcribing a concrete example.

Data from an alkaline fusion experience on total fat acids from olive oil have been gathered (21). The essay was performed in an open vessel, gradually heated and samples taken under the conditions indicated for each test.

TABLE I

Alkaline fusion of olive oil fat acids

| Test | Temperature (°C) | Minutes | Iodine Index |
|---|---|---|---|
| 1 | - | 0 | 93 |
| 2 | 130 | 15 | 89 |
| 3 | 180 | 30 | 89 |
| 4 | 230 | 45 | 85 |
| 5 | 280 | 60 | 78 |
| 6 | 290 | 75 | 75 |
| 7 | 310 | 90 | 69 |
| 8 | 320 | 105 | 38 |
| 9 | 320 | 120 | 2 |

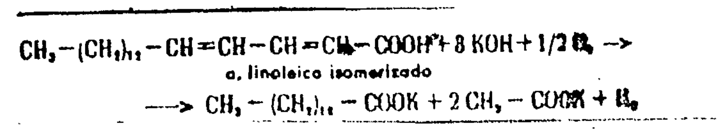
It can be seen that until about 300°C is reached a substantial decrease of the iodine index is appreciated, which practically decreases to zero when the 320°C is reached. The final product neutralization index in this essay was 220, almost equal to the palmitic acid.

When this experiment is repeated under the same temperature conditions but working with a closed autoclave the saturated acid yield is very poor (22), due probably to the negative influence exerted by the pressure of the liberation of hydrogen and, therefore, on the free development of the reaction. Under these conditions, it is necessary to increase the temperture and thus, by oleic or petroselenic acid fusion in closed vessel at 360°C during 30-60 minutes, it is possible to obtain up to 80-85 per cent of palmitic acid (9).

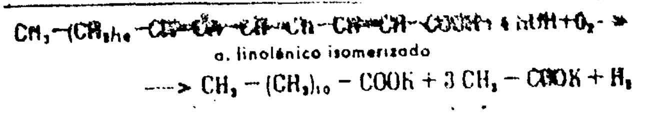
## 2. Alkaline fusion of poly nonsaturated fat acids.

The presence of two or more double links in the chain of poly nonsaturated acids, extraordinarily increases the reaction possibilities, so that it is not expected that the alkaline fusion of these acids occurs by an entirely similar process to the one described for the mono nonsaturated acids. For instance, the known isomerization of double links isolated from conjugated systems, which later displacement toward the carboxyl does not exactly match the aforementioned schema must be taken into consideration. Furthermore, a temperature of over 200°C is extremely favorable to the formation of cyclic and polymer products (23) which contributes to decrease the final yield of saturated acids.

However, it is expected that the alkaline fusion of poly nonsaturated acids follows, to a great extent, the same line of the mono nonsaturated, thus,a double link migration toward the carboxyl group, until they are conjugated with the same, occurs first and then the molecule decomposition takes place eliminating several groups of acetic acid and a shorter saturated fat acid; according to this schema, in the alkaline fusion of linoleic and linolenic acids, for instance, substantial amounts of myristic and lauric acids are obtained respectively:



to isomerize linoleic acid



to isomerize linolenic acid

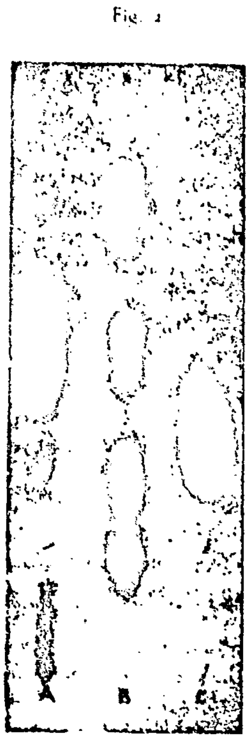
This hypothesis has been recently confirmed when studying the alkaline fusion of ethyl linoleate and linolenate (21). Esters are dissolved with three times their weight of potash, by heating them at 310°C from 30 to 60 minutes. The identification of products resulting from the reaction has been preferably done by chromatography on paper, as can be seen in Figures 2 and 3.

It can be observed that the main products obtained are the myristic acid, in the first case and lauric acid in the second case, although they always are accompanied by small amounts of longer saturated acids.

These results fully concur with those reached recently by R.G. Ackmand and his collaborators (16) who obtained in the linoleic acid fusion up to 60 per cent of myristic acid accompanied by 5 per cent of palmitic acid and small amounts of nonsaturated acids of eighteen carbon atoms. The methyl linoleate fusion at lower temperatures seems to lead to the formation of palmitic and conjugated linoleic acid.

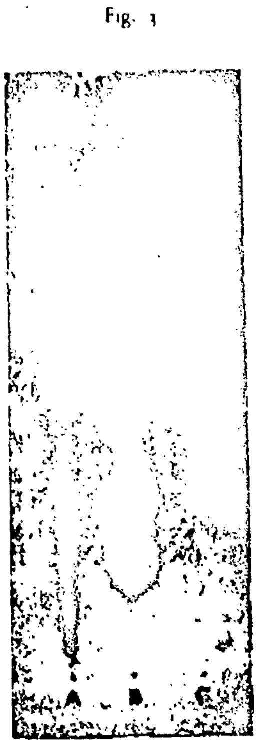
There is still very little known about the possible mechanic of these reactions. Previous authors (16) presumed that the double link system migrates at the first

Fig. 2



Alkaline fusion of ethyl linoleate

Fig. 3



Alkaline fusion of the ethyl linolenate

(A: Ester melted with KOH. B: Mixture of lauric, myristic, palmitic and stearic acids. C: Free acid - linoleic or linolenic corresponding to the used ester.)

moment in both ways and that the formation of the myristic acid can be explained by the 2-4 dienoate scission or by successive splitting of intermediate 2-enoates originated by the conjugation of an isolated double link with the carbonyl of COOH group. We are favorably disposed to the second possibility, which means that the conjugated double links, formed at the beginning of the reaction, disappear before total splitting of the molecule takes place.

We have been able to experimentally prove this by studying the absorption variation in the ultraviolet during the alkaline fusion of the full fat acids of the linseed oil (21). Fat acids, with 170 iodine index, were melted with seven times their weight of potash in an open vessel and gradually heated. Figure 4 shows absorption curves of different samples, according to the experimental conditions indicated in Table II. The iodine index of the final product was only 20.

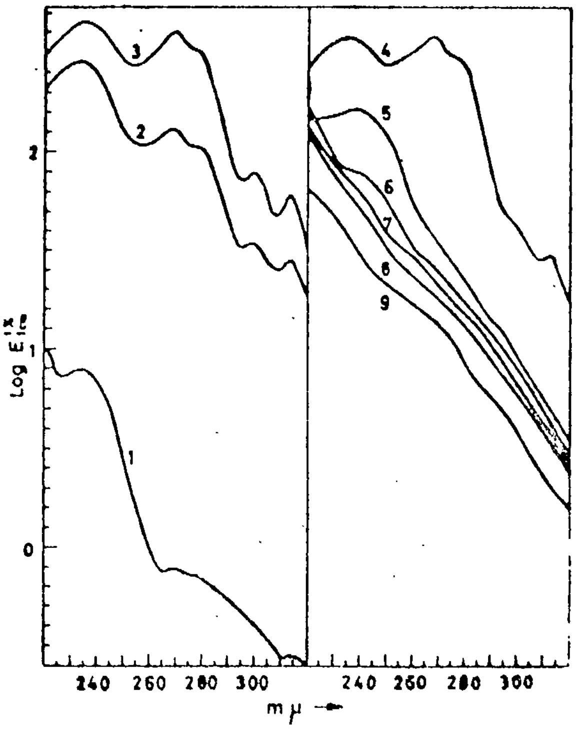
It can be appreciated that when the temperature is increased the amount of conjugated dienos, trienos and tetraenos corresponds to a normal alkaline isomerization, until approximately 180°C is reached (curve 3). At higher temperatures trienol and especially tetraenos start decreasing and completely disappear when the 260°C is reached (curve 5). If we continue increasing the temperature we can see that a 280°C, when the fusion starts, there only are but few conjugated dienos (curve 6) which completely disappear over the 300°C (curves 8 and 9) coinciding with the final decomposition of the molecule

## TABLE II

Alkaline fusion of fat acids from linseed oil

| Test | Temperature (°C) | Minutes |
|---|---|---|
| 1 | - | 0 |
| 2 | 140 | 25 |
| 3 | 180 | 42 |
| 4 | 225 | 64 |
| 5 | 260 | 85 |
| 6 | 280 | 95 |
| 7 | 305 | 140 |
| 8 | 310 | 180 |
| 9 | 310 | 200 |

Fig. 4



Alkaline fusion of the fat acids of linseed oil.
Ultraviolet absorption spectrum.

Fig. 5

Fig. 5

Alkaline fusion of fat
acids of olive

Fig. 6

Fig. 6

Alkaline fusion of fat
acids of linseed

Figures 5 and 6 show chromograms of the alkaline fusion of full fat acids of olive and linseed oils. At the points A the mixture of the acids obtained during the fusion was deposited and at B the standard mixture of lauric, myristic, palmitic and stearic acids.

It can be seen that from olive oil palmitic acid and some myristic acid is presently obtained but approximately equal amounts of lauric, myristic and palmitic acid are obtained from linseed oil. In both cases small amounts of stearic acid which already existed in the original oils are observed.

Recently some tests of alkaline fusion of fat acids with triple link have been performed. Taking into consideration the general behaviour of acetylenes it is expected that in the acetylenic acid fusion with alkalines the triple link migrate along the chain through a sequence of acetylene-allene-acetylene structures until the dienic system which precedes the scission is formed when the C-4 position is reached. It has been experimentally proven in the stearolic acid (9/octadecenoic) case which generates during its fusion up to 57 per cent of myristic acid and small amounts of palmitic acid, together with 5 per cent of polymerized products (16). Acetylenic acids with the triple link close to the carboxyl group (starting from C-4) completely decompose themselves by the concentrated alkalies action.

## 3. The alkaline fusion in industry.

As we have seen in previous pages the alkaline degradation of nonsaturated fatty acids constitutes a general method to obtain short saturated fatty acids (lauric, myristic, palmitic) from common vegetal oils and even cheaper products such as fish oil and residual paste from refinery.

However, although the possible economic importance of this process was recognized from the beginning and even tests to its industrial exploitation were made (25). the fact is that we are not even in the first phases of its development. It is due to several causes such as the difficulty to work in a continuous system, the necessity of an excessive use of potash, the frequent formation of coloured subsidiary products and mainly that the fusion is very violent and accompanied by hydrogen freeing which makes it difficult to regulate and even dangerous.

We are going to make a brief summary of the main works done to industrialize the Varrentrapp reaction, many of them protected by patents. This lack of information, in the majority of cases, has forced us to dispense with a critical study of the methods and results indicated by several authors.

E. Segesseman and N.M. Molnar (26) heated alkaline soaps from tall oil with a concentrated potash solution at 290ºC in a closed iron vessel during six hours. In this way they obtained a mixture of myristic palmitic and stearic acids with partially hydrogenated resinic (?) acids which, according to the authors, can be attributed to the hydrogen freed during the reaction.

H.G. Kirschenbauer (27) obtained better results, up to 90 per cent of palmitic acid from cottonseed and wheat oils, heated at 320°C with an excess of potash after having been selectively hydrogenated to eliminate poly nonsaturated acids.

At higher temperatures, between 350 and 450°C, and in presence of potash and water (20% of the fatty acids weight) at a pressure of about 100 kgs/cm$^2$ saturated alkaline soaps are obtained from vegetal oils and marine animal fats (28). Under these circumstances less alkali than ordinarily is required and also the use of water permits to obtain slightly colored products despite the high temperature and the prolonged treatment. On the contrary, K. Appuhn (29) advocated the fusion at 300°C and normal pressure, without water, to obtain ordorless and solid soaps from low quality oils and fats. In order to decrease the violence of the reaction, this author recommended the addition up to 40 per cent of lanolin or sperm oil.

For economic reasons it has been tried to substitute the potash by the cheaper sodium hydroxide although, naturally, the cation nature is not completely indifferent to the alkaline fusion development (8). Personally,we could prove that the reaction does not go as well with soda as with potassium hydroxide (22) which is in accordance with other authors' results (30). Nevertheless, according to W. Schrauth (31) by heating a 50 per cent soda solution at 10 atmospheres, during 6 hours up to a 85 percent of palmitic acid from oleic acid, is obtained. More recently palmitic acid has also been obtained, under similar conditions, from pastes of cotton oil refineries.

Finally, W. Stein and his collaborators (33) obtained the degradation of alkaline soaps of soya or olive oil by sodium hydroxide, working at 200 atmospheres and 350 - 400°C in presence of Cd, Pb, Bi and Tl or their alloys metallic catalyzers.

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