Studies in Vegetable Oils
Series
No. 3

ELEMENTARY CHEMICAL STUDIES
ON
I. ARACHIS OIL
II. HYDROGENATION OF VEGETABLE OILS

by

Munir D. Atiyeh

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May 25, 1945.
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</table>
PREFACE

Systematic chemical investigation of the important agricultural products of this country has been always a greatly felt need. The herein-described work, therefore, was performed during the academic year 1944-1945 in the laboratory of this institution with the aim of partially meeting this need in the field of vegetable oils.

In writing out this paper, undue discussions of analytical methods and theories of reactions were carefully neglected especially in Part I. Because, as there is no claim to originality in these fields, there could be no merit in including from a very bulky and easily accessible literature.

In Part II the aim was fixed on two objectives:

1. Practical success in hardening oils by catalytic hydrogenation and determination of the best (here-possible) conditions for it.

2. Examination of the hydrogenated products at different stages of the process to reveal their composition and decide on some characters of the reaction or reactions involved.

In acknowledgment, I wish to thank Professor N. D. Constan for kindly supervising the work, Professor H. W. Close for reviewing and correcting the manuscript, and all the members of the Chemistry Department Staff for their helpful and generous dealing.

May 25, 1945

M. D. Atiyeh
INTRODUCTION

I. THE PLANT

Its Botany, Present Agricultural Status and Prospects in Syria and Lebanon,
With Tables on Chemical Composition

ARACHIS HYPOGEA differently termed peanut, earth nut and ground nut, is known in this country as فاصوليا. A native of Brazil (some say Peru also) it was brought to West Africa by slave ships and thence to all the Mediterranean Basin.

Arachis Hypogeas is a legume belonging to the Leguminosae family - beneficial to the soil for its nitrogen-fixing nodules. It is one of five varieties of Arachis; the other four are not cultivated in this country nor anywhere extensively, because of their inferiority as oil-producing plants. This is an annual legume, the stem is usually prostrate, though some varieties have it erect, forming a cluster of leaves from 30-40 cms. in dry regions and 50-60 cms. in regions of abundant rainfall or irrigation. The leaves are of the alternate type, composed of two oval pairs of leaflets. The stem and the inferior faces of these leaflets are covered with hair. The flowers are of two kinds: in the first they are big, yellow with red striations and open among the leaves; these are sterile, in second they are small, called flower stems, and bend down, after the small single blossom has bloomed, and force the little pods into the soil where they develop and mature as fruits. (for chief microscopic structural characteristics, see Winton, Structure and Composition of Foods, Vol. I, p. 665).

It was about one hundred years ago that this country imported its culture from the Dark Continent, as its name in Arabic tends to indicate... Its cultivation remained very meagre with crops of practically no economic importance, until fifteen years ago when it was tried in a village in Akkar plain called El-Khuraybeh (عربية) from which it spread rapidly to all irrigated regions in this plain where it is now an important product of the agriculture of the district. It is also cultivated in all irrigated regions all along the coast from Tripoli to Latakia and to a limited extent in Al-Asi valley. Experts foresee with some certainty
the rapid extension of its agriculture to all irrigated districts of this country like the plain West of Homs ((Conv), all Al-'Asi Valley and El-Jezira, provided, they say, modern industries be established for exhaustive utilization of the crops.

The variety cultivated here is the Indian. The fruit usually contains two kernels. Due to practical reasons in harvesting, it is desirable that new varieties that mature earlier before too much rainfall in November, be introduced.

The cultivation season runs from the middle of April to the beginning of June and harvesting is done from October till December when peanuts are judged mature by the yellowing of the foliage and shedding of leaves. It is becoming a usual practice to interplant peanuts with corn, using a wide corn row with one or two peanut rows. This is said to be a perfectly healthy practice as peanuts mature later than corn and thus do not compete with it for moisture.

In selecting land for growing peanuts, the well-drained sandy loam or sandy clay soils have first choice. "In general peanuts do best on soils testing 5.6-6.6 with \( P_{2}O_{5} \) above 100, and \( K_{2}O \) above 100 pounds to the acre and 2.5% organic matter."1

In Syria and Lebanon there is no regular agricultural rotation; but of the many rotations irregularly run the one: Cereals - Peanuts - Cereals - Corn, is preferred to any other in practice.

The yield in this country might be fairly estimated as 1,500 - 2,500 kgs. per hectare. Improvement on this yield is possible through use of better methods and fertilizers.

**Chemical Composition:**

Overlooking the fruit here (which will be fully considered in a subsequent section) what remains of the plant is what is commercially known as hay. This, being the vegetative part of the plant together with some roots, is dried, pressed and marketed as cattle food. Reports on its chemical composition and relative nutritive value are found in almost any treatise on the subject. The three tables given below have been chosen to represent the composition of the hay. The first two are taken from Winton2, due respectively to Prapp and Brown.

---

### TABLE A

<table>
<thead>
<tr>
<th>Kind of hay</th>
<th>Samples</th>
<th>Water %</th>
<th>Protein %</th>
<th>Fat %</th>
<th>N.f. Ext. %</th>
<th>Fiber %</th>
<th>Ash %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without nuts (prepared by author)</td>
<td>10</td>
<td>9.50</td>
<td>9.55</td>
<td>3.08</td>
<td>45.35</td>
<td>24.30</td>
<td>8.24</td>
</tr>
<tr>
<td>Commercial: (From Texas Market)</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum</td>
<td></td>
<td>8.49</td>
<td>9.54</td>
<td>2.24</td>
<td>35.25</td>
<td>20.23</td>
<td>8.40</td>
</tr>
<tr>
<td>Maximum</td>
<td></td>
<td>10.18</td>
<td>10.28</td>
<td>6.61</td>
<td>48.60</td>
<td>28.37</td>
<td>11.80</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>9.21</td>
<td>9.89</td>
<td>4.35</td>
<td>42.67</td>
<td>23.77</td>
<td>10.09</td>
</tr>
</tbody>
</table>

The second table is on the mineral constituents of the ash obtained separately from stems and leaves, the ash being estimated as 15.71% by wt. of total hay:

### TABLE B

<table>
<thead>
<tr>
<th>Ash of</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaves</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td></td>
<td>15.00</td>
<td>7.26</td>
<td>50.77</td>
<td>10.89</td>
<td>4.85</td>
<td>3.57</td>
<td>5.60</td>
</tr>
<tr>
<td>Stems</td>
<td>19.23</td>
<td>7.52</td>
<td>25.80</td>
<td>19.67</td>
<td>5.54</td>
<td>7.42</td>
<td>9.98</td>
</tr>
</tbody>
</table>

For comparison as to nutritive value the following table is given:

### TABLE C

<table>
<thead>
<tr>
<th>Oats</th>
<th>Water</th>
<th>Protein</th>
<th>Fat</th>
<th>Fiber</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Détrefle</td>
<td>14.30</td>
<td>12.94</td>
<td>2.11</td>
<td>29.27</td>
<td>7.47</td>
</tr>
<tr>
<td>Luzerne</td>
<td>6.95</td>
<td>16.48</td>
<td>2.05</td>
<td>31.38</td>
<td>7.49</td>
</tr>
</tbody>
</table>

It is seen that peanut hay is superior to the first variety of oats and very well approaches the second.

1. cf. Ref. III, p. 50

Henry
II. THE FRUIT

The fruit or the nut is formed of a shell containing usually two, sometimes one or three, kernels. The kernel is composed of two oleaginous cotyledons, the germ and an enveloping thin usually red skin. Fleury gives as an average composition for a considerable number of observations the following table:

<table>
<thead>
<tr>
<th>Country of Origin</th>
<th>Shell</th>
<th>Skin</th>
<th>Germ</th>
<th>Cotyledons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Senegal</td>
<td>25.00</td>
<td>3.22</td>
<td>2.90</td>
<td>63.88</td>
</tr>
<tr>
<td>India</td>
<td>21.50</td>
<td>2.50</td>
<td>3.35</td>
<td>72.35</td>
</tr>
<tr>
<td>Plata</td>
<td>26.00</td>
<td>1.96</td>
<td>2.15</td>
<td>69.90</td>
</tr>
</tbody>
</table>

The following table is the average result for five varieties of shelled peanuts made at the U. S. Dept. of Agr.

<table>
<thead>
<tr>
<th>Moisture</th>
<th>Oil</th>
<th>Crude Fiber</th>
<th>Protein</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>3.42</td>
<td>47.40</td>
<td>2.45</td>
<td>30.85</td>
<td>2.90</td>
</tr>
</tbody>
</table>

Two samples of the fruit were examined, one from Tripoli the other from Tartus with the following results averaged for both:

<table>
<thead>
<tr>
<th>SAMPLES</th>
<th>Water in Kernels</th>
<th>Shells (by diff.)</th>
<th>Kernels (in Kernels)</th>
<th>Oil (in Kernels)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>4.72</td>
<td>30.11</td>
<td>69.89</td>
<td>48.12</td>
</tr>
</tbody>
</table>

1. Henry p. 50
2. Jamieson p. 182
III. THE OIL

Arachis oil is a viscous liquid lighter than water and insoluble in it, but is readily soluble in Carbon tetrachloride, chloroform, ether, carbon disulfide and to a limited extent in glacial acetic acid and hot 95% alcohol. When purified by ordinary methods (using no chemicals) for edible purposes, it has a light bright yellow color and a faint vegetable odor reminescent of its fruit. It is composed mainly of the triglycerides (simple or mixed) of linoleic, oleic, palmitic, stearic and presumably two other saturated acids of high molecular weight generally termed arachidic and lignoceric. The proportion of each of these esters in an oil is subject to small variations depending on soil, climate and variety of plant. As indicated by the magnitude of the acetyl value (assuming the absence of any hydroxy acids esters) it may contain a small amount of di- and monoglycerides together with around 1% of unsaponifiable matter consisting mainly of phytosterols and coloring pigments.

The technology of working the oil out of the peanuts by expression (hot and cold) and extraction with different solvents, refining, bleaching, deodorization etc. is almost an exhausted topic in any reference work on oil. Thus I draw attention to the following references and exempt myself of any further discussion.

Once the oil is secured (in a fairly pure condition), its investigation according to the science of chemistry prescribes two general major undertakings:

1. The Analytical investigation of the oil to ascertain its composition, hence purity and adaptability to different conditions and purposes.

2. The Synthetic undertaking being an attempt, in the light of analytical data to utilize the oil in the building up of new compounds of different values in the chemical laboratory as well as in the market place.

This being the task, the following work occupies itself in Part I with the analysis and characteristics of Arachis oil run on a genuine sample which will be described below, and in Part II with a very important synthetical problem in relation

   Janieson, Chap. 1, pp. 182-183, 131-139.
   Wright & Mitchell, Chap. 9 and 11.
to all oils - hardening by catalytic hydrogenation for
the production of vegetatives and other butter substitutes
and the adaptation of some oils to new industrial uses.
PART I

(ANALYTICAL)

On The Composition, Chemical and Physical Characteristics of Arachis Oil

I. Historical

Chevreul, in his famous research at the beginning of the last century, established the constitution of fats and oils. His conclusions were but little modified and extended by Berthelot and Wurtz all to give us the present picture of the constitution of the fat molecule as a "neutral glyceryl ester" of higher fatty acids. The alcoholic part of these esters being common to all of them, the differences we observe and measure among oils of different origins must come from differences in the constitution of the acid part of the molecule. Thus the problem of classification of oils and fats boils down in the end to the relative abundance of a type of fatty acids in the sample under examination.

Three such representative types of acid radicals of frequent occurrence are:

1. Oleic Acid - \(\text{CH}_2(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}\) M.P. 140°C, and is the fundamental constituent of non-drying oils.

2. Linoleic Acid - \(\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}(\text{CH})_7\text{COOH}\) M.P. -11 and is the fundamental constituent of semi-drying oils.

3. Linolenic Acid - \(\text{CH}_3\text{CH}=\text{CH}\text{CH}_2\text{CH}=\text{CH}\text{CH}_2-\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}\) (\(\alpha\)-form) and is the fundamental constituent of drying-oils.

Lewkowitsch, while asserting the theoretical correctness of such a scheme for classification, suggests a more practical method. His method is based on two guiding principles, the first is the magnitude of the Iodine value which subsumes under it the former theoretical scheme, and the second is the origin of the oil - vegetable or animal as indicated by testing for phytosterols and cholesterol with digitonin.

Accordingly Arachis Oil is classified as a non-drying (edible) vegetable oil. Iodine values as high as 105 (Oliveri) and as low as 83.3 (Tortelli and Ruggeri) have been reported. Though such high iodine values give some foundation to its classification by some writers as a semi-drying oil, yet its general behaviour points clearly to its non-drying character.

1. Lewkowitsch, Vol. I, p. 3 et seq.
The analytical problem is dealt with according to two manners. The first and relatively recent one is the direct chemical analysis of the oil through the isolation of every component acid and its individual identification. The second, which is the older, consists of a series of empirical determinations to obtain "values". These "values" once determined on a sample are correlated and interpreted in the light of reference "values" for that oil and the composition and purity of the sample in question could thus be fairly ascertained. (A critical appreciation of both methods and newly introduced physical methods, and color tests will conclude this part.)

II. Experimental

The sample of Arachis oil used in this work was secured by crushing 2.25 kgs. of shelled sound nuts (from Akkar, 1944 crop) in a machine to medium size. The crushed mass was put in clean dry canvas bags and pressed in the cold (17°C. approx.) in a hydraulic press up to a pressure of 1½ tons/in.². The exuding oil was collected, washed immediately, in the course of 24 hours, four times with water. Then it was filtered with suction. The filtrate, still turbid, was re-filtered with "filter-aid" whereupon a clear bright-yellow liquid was obtained. After drying in the oven at 80°C. for five hours, it was put in a clean dry, brown, airtight-closed bottle and kept in a dark cool place.

Thus it is obvious that the values and results given in Table I below are supposed to be standard ones for genuine Arachis oil.

It will be seen that values like Reichert-Meisel and Pålenske have not unrightfully been neglected.
### TABLE II

**Analytical "values" of genuine Arachis Oil**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>No. of determinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sp. Gr. (Pyknometer)</td>
<td>0.91705</td>
<td>1</td>
</tr>
<tr>
<td>(Westph. Balance)</td>
<td>0.9170</td>
<td>1</td>
</tr>
<tr>
<td>2. Ref. Index (20°C.)</td>
<td>1.4712</td>
<td>1</td>
</tr>
<tr>
<td>3. Acid Value</td>
<td>0.6170</td>
<td>2</td>
</tr>
<tr>
<td>4. Sapon. Value</td>
<td>185.73</td>
<td>3</td>
</tr>
<tr>
<td>5. Soluble Acids</td>
<td>0.0121%</td>
<td>1</td>
</tr>
<tr>
<td>6. Hehner Value</td>
<td>95.65</td>
<td>2</td>
</tr>
<tr>
<td>7. Sat. Acids (Pb soap–Ether method &amp; corrected by Ig. V.) in oil</td>
<td>14.58%</td>
<td>2</td>
</tr>
<tr>
<td>8. Unsat. Acids (same as 7) in oil</td>
<td>77.26%</td>
<td>2</td>
</tr>
<tr>
<td>9. Iodine Value of oil (Wijs)</td>
<td>98.875</td>
<td>3</td>
</tr>
<tr>
<td>10. &quot; &quot; Hehner Acids (Wijs)</td>
<td>100.58</td>
<td>2</td>
</tr>
<tr>
<td>11. &quot; &quot; Solid acids (Pb soap ether separation)</td>
<td>12.203</td>
<td>2</td>
</tr>
<tr>
<td>12. Iodine Value of liquid acids (Pb soap ether separation)</td>
<td>117.40</td>
<td>2</td>
</tr>
<tr>
<td>13. Thiocyanogen value of oil</td>
<td>76.124</td>
<td>4</td>
</tr>
<tr>
<td>14. &quot; &quot; Hehner Acids</td>
<td>76.975</td>
<td>2</td>
</tr>
<tr>
<td>15. Acetyl value (apparent)</td>
<td>19.48</td>
<td>3</td>
</tr>
<tr>
<td>16. Unsap. matter</td>
<td>0.786%</td>
<td>1</td>
</tr>
</tbody>
</table>

1. Except in few cases indicated in the table, all determinations were done twice, each time with fresh reagents and new standards. In case the two results were intolerably different a third and sometimes a fourth determination was run also with new standards and fresh reagents.
For a just appreciation of these results, Table II (following) has been constructed. The numbers in it were collected from authoritative reports on genuine Arachis oil and made to indicate the range of normal fluctuation in each value.

TABLE II

Range of Analytical Values of
Genuine Arachis Oil

<table>
<thead>
<tr>
<th>Value</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sp. Gr. (\frac{15}{4})</td>
<td>0.914 - 0.920</td>
</tr>
<tr>
<td>2. Ref. Index (20°C.)</td>
<td>1.467 - 1.4720</td>
</tr>
<tr>
<td>3. Acid Value</td>
<td>0.22 - 13.40</td>
</tr>
<tr>
<td>4. Sapon. Value</td>
<td>186 - 194</td>
</tr>
<tr>
<td>5. Reichert-Weisal Value</td>
<td>0.5 - 1.60</td>
</tr>
<tr>
<td>6. Hehner Value</td>
<td>95 - 96</td>
</tr>
<tr>
<td>7. Iodine Value of Oil (Wijs)</td>
<td>83 - 101</td>
</tr>
<tr>
<td>8. Iodine Value Hehner Acids (Wijs)</td>
<td>95.5 - 103.4</td>
</tr>
<tr>
<td>9. Iodine Value of liq. Acids (Wijs)</td>
<td>106 - 128</td>
</tr>
<tr>
<td>10. Solid (Satur.) Acids</td>
<td>16.3 - 22.8%</td>
</tr>
<tr>
<td>11. Liquid (Unsatur.) Acids</td>
<td>72.1 - 77.6%</td>
</tr>
<tr>
<td>12. Thiocynogen Value of Oil</td>
<td>63.02 - 78.5</td>
</tr>
<tr>
<td>13. Acetyl Value (true)</td>
<td>8.7 - 9.1</td>
</tr>
<tr>
<td>14. Unsapon. matter</td>
<td>0.27 - 0.54%</td>
</tr>
</tbody>
</table>

1. Values 1, 4, 6 & 7 are taken from Allen p. 109
2, 3, 10, 12, 13, 14 are taken from Jamieson p. 131
3. seq. & Appendix.
4. 5, 8, 9, are taken from Lewkowitsch Vol. II pp. 249-251.
5. 12, cf. Pauly.
III. Discussion of Results

Analytical values of oils such as those in Tables I & II belong really to two orders. In the first order fall those values that arise from direct measurement of differences due to:

1. Mean molecular weight i.e. the relative proportion of high and low molecular weight acids.

2. The relative number of double bonds depending upon the proportion of unsaturated acids.

These are simple, primary values. In the second order fall those values that are more general such as Sp. Gr. and M.P., being simply composites due to all the acids present. These are composite, secondary values.

A glance at the two tables suffices to show that simple, primary values in both are in perfect agreement as are also the secondary values. Furthermore secondary values in Table I are logical composites of the primary values. The acetyl value obtained is intolerably different from any one recorded in the literature. Recording it here as 19.45 necessitates a more thorough experimental justification which cannot now be offered.

Composition:

The work of Prof. H. Kaufman\(^1\) suggests a method for calculating the amounts of different unsaturated acids together with the total of the saturated acids present in an oil as glycerides, provided the iodine value and the Thiocyanogen value have been determined and the oil contains no unsaturation higher than linoleic, or as has recently been stated, linoleinic.

Arachis oil does not contain unsaturated acids other than oleic and linoleic.\(^2\) From the Thiocyanogen and iodine values

1. Pauly
2. cf. infra pp. 13 et seq.
recorded in Table I and by application of Kaufman's formula the following percentages are calculated:

TABLE III

<table>
<thead>
<tr>
<th>As Glyceride of:</th>
<th>In Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linoleic Acid</td>
<td>26.37%</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>62.03%</td>
</tr>
<tr>
<td>Saturated Acids</td>
<td>11.60%</td>
</tr>
</tbody>
</table>

When the iodine and thiocyanogen values have been determined on the free fatty acids of the oil, the percentages of various acids may be calculated, not as glycerides but as percent of acid according to a formula derived and recommended for adoption by The American Chemical Society in a report on "Analysis of Oils and Fats". Through use of this formula the following table could be given:

TABLE IV

<table>
<thead>
<tr>
<th>Acids</th>
<th>In total Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linoleic</td>
<td>26.02%</td>
</tr>
<tr>
<td>Oleic</td>
<td>59.77%</td>
</tr>
<tr>
<td>Saturated</td>
<td>14.21%</td>
</tr>
</tbody>
</table>

It is worthy to note here that results in table IV are in better agreement with the results of the Pb Soap - Ether analysis. In fact they might be almost identical if allowance is made of inevitable experimental error, and provided those

1. Jacobs, pp. 217-218
in Table I are reduced to percentages in fatty acids and not in oil.

The saturated acids are reported to contain Palmitic acid identified by Coldwell, Stearic Acid by Hehner and Mitchell, Arachidic Acid reported by Gossman, and Lignoceric acid by Kreiling.

Other than the two unsaturated acids reported above, there were some conjectures by Gossman, Schorder and Hazura as to the presence of a third, Hypogesic acid (C₁₆H₃₀O₂).

Lewkowitz in trust of the results reported by Freinsteiner (who isolated only 6% of linolic acid from the insoluble tetrabromide; and also states that besides oleic he could report 30.3% of liquid acids) assumes that hypogesic acid is present but its bromide is soluble in petroleum ether. Alike, though less acute dispute waged until recently on the presence or absence of behenic acid (C₂₂H₄₄O₂).

Jamieson, Baughman and Bruns¹, in an attempt to settle these disputes and determine qualitatively and quantitatively the composition of Arachis oil, have followed a very assuring technique. Having got the oil from two varieties of peanuts, Virginian and Spanish - by expression, they worked on each sample separately. First they separated the liquid from the solid acids according to the Pb Soap -Ether method.

They examined the liquid acids mixture through their bromine addition products. The absence of linoleinic acid was confirmed, by failure to have any hexabromide precipitate in ether below 10°C. In petroleum ether they could secure a precipitate of tetrabromide; the dibromide was secured by evaporating the filtrate. By boiling each of these precipitates with HNO₃ and AgNO₃ the amount of bromine was quantitatively determined and then the percentages of linoleic and oleic acids.

Hypogesic acid was tested for by fractional crystallization from alcohol and subsequent determination of the melting point, and repeatedly proved to be absent from their two samples.

The saturated acids were separated by repeated fractional distillation of their methyl esters in vacuo and subsequent individual identification by melting point determination and elementary analysis. Behenic acid is reported by them to be absent. They give the following figures as representing the

¹. Ind. Eng. Chem. 43, 1372 (1921)
composition of Arachis oil for the two samples they worked with.

**TABLE V**

Composition of Arachis Oil

*(Due to Jamieson et al.)*

<table>
<thead>
<tr>
<th>As Glycerides of:</th>
<th>In Spanish Oil</th>
<th>In Virginian Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic Acid</td>
<td>52.9%</td>
<td>60.8%</td>
</tr>
<tr>
<td>Linoleic Acid</td>
<td>24.7%</td>
<td>21.6%</td>
</tr>
<tr>
<td>Palmitic Acid</td>
<td>8.2%</td>
<td>6.3%</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>6.2%</td>
<td>4.9%</td>
</tr>
<tr>
<td>Arachidic Acid</td>
<td>4.0%</td>
<td>3.3%</td>
</tr>
<tr>
<td>Lignoceric Acid</td>
<td>3.1%</td>
<td>2.6%</td>
</tr>
<tr>
<td>Unsap. matter</td>
<td>0.2%</td>
<td>0.3%</td>
</tr>
</tbody>
</table>

"At least the absence of hypogeaic acid is ascertained."

Heiduschka and Felser report on the composition of Arachis oil as follows:

**TABLE VI**

*(Due to Heiduschka and Felser)*

<table>
<thead>
<tr>
<th>As Glycerides of:</th>
<th>In Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic Acid</td>
<td>79.9%</td>
</tr>
<tr>
<td>Linoleic Acid</td>
<td>7.4%</td>
</tr>
<tr>
<td>Palmitic Acid</td>
<td>4.0%</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>4.5%</td>
</tr>
<tr>
<td>Arachidic Acid</td>
<td>2.3%</td>
</tr>
<tr>
<td>Lignoceric Acid</td>
<td>1.9%</td>
</tr>
</tbody>
</table>

1. Winton, 1931.
However, Jamieson et al. comment on figures in Table VI saying: "Our knowledge of the general character of Arachis oil lead us to doubt these figures."

An attempt to separate the components of the solid acids mixture, secured by the lead soap-ether method, was made by the writer. A weighed quantity of solid acids was refluxed for twelve hours with excess, freshly distilled, absolute methyl alcohol saturated with dry HCl gas. The methyl esters, after washing them from methyl alcohol several times with ether, were distilled in vacuum (Press. below 5mm. Hg.) Three fractions boiling respectively at 182-186, 188-195, 195-222 degrees C. came over and a dark brown high-boiling residue was left behind. As the quantities were very small no further work was done on these individual fractions (due to high probability of error and lack of proper micro-apparatus.)

Tests:

There is no special color reaction for Arachis oil. Its detection and approximate determination depends upon the separation of Arachidic-Lignoceric acids mixture. It is assumed that arachis oil contains 85% of these acids which, due to their insolubility in cold alcohol, can be easily separated and their melting point determined as well as their weight. If the weight of these acids so secured is very close to 5% of the total weight of the oil sample and the melting point is between 74-75°C., then the oil is thought to be genuine 100% arachis oil provided rape and mustard seed oils have been proved absent. This is the process suggested by Renard, extended and modified by Beller and Evers. This is one of the best tests in oils, being most reliable in its qualitative aspect but quantitatively it ought to be interpreted with much reservation.

A tempting color test is Kreis' for rancidity. The production of pink coloration with phloroglucinol and diluted HCl is said to be due to heptylic aldehyde which latter is assumed to be one of the products of the rancidity process. At its best it could only be of use if it is positive and then only in a very general qualitative manner.

However, the Kreis test and all other color tests for rancidity in oils and fats have been rejected as unreliable by the German Commission of Standard Methods of Analysis; only taste and odor are criteria.²

2. Ind. Eng. Chem., 15, 1051 (1923)
3. Chem. Abs., 6174 (1950)
IV. Summary and Conclusion

In general, therefore, it could be stated that Arachis oil is a vegetable non-drying oil; chemically, it is composed of the glycerides of several fatty acids, the composition of which is shown in Table V. The physical and chemical characteristics of genuine samples of Arachis oil, expressed in this laboratory (no chemicals used in its purification) were very accurately determined always in duplicate and when necessary three or even four times. The results are collected in Table I. A comparison with recorded standard values, as could be had by looking at Table II, revealed perfect agreement except in the case of acetyl value.

Through the formula developed by H. Kaufman, recommended and extended by the American Chemical Society, and from the estimation of the saturated and unsaturated fatty acids by the Pb soap-ether method, the proportion of different unsaturated acids and acid glycerides and the total of saturated acids and their glycerides were calculated. An attempt to separate the individual components of the saturated acids through the distillation of their methyl esters in vacuo, was made. This could be ascertained that at least there are four different components, as testified by three fractions and a residue.

In conclusion, the following figures can be given to represent the chemical composition of the Arachis oil that was studied:

| TABLE VII |
| CHEMICAL COMPOSITION OF |
| LEBANESE ARACHIS OIL |

<table>
<thead>
<tr>
<th>As Glycerides of:</th>
<th>In Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linoleic Acid</td>
<td>21.372%</td>
</tr>
<tr>
<td>Oleic (Palmitic acid = 6.3%)</td>
<td>60.032%</td>
</tr>
<tr>
<td>Saturated (Stearic acid = 4.9%)</td>
<td>18.296%</td>
</tr>
<tr>
<td>(Arachidic acid = 3.3%)</td>
<td></td>
</tr>
<tr>
<td>(Lignoceric &quot; = 2.6%)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>17.1%</td>
</tr>
<tr>
<td>Unsap. Matter</td>
<td>0.786%</td>
</tr>
</tbody>
</table>

Table IV gives as good or even better idea of the composition of the total fatty acids of the oil.

\* Due to Jamieson, Baughman and Bruns.
PART II
(SYNTHETICAL)

On Catalytic Hydrogenation of Some vegetable Oils and the Changes Produced therefrom with Observations on the character of the Reaction(s)

I. Theory and History

The catalytic hydrogenation of vegetable oils is a process of reduction consisting of the saturation of a carbon-carbon double bond or bonds (seldom a triple bond) with hydrogen under such conditions that an added foreign substance (catalyst) can hasten the reaction, thus making it of practical importance. By "catalytic" here is implied a purely practical distinction, as we recognize in practice two other forms of reduction or hydrogenation: chemical and electrolytic. For reasons which space does not allow of their enumeration and discussion, the catalytic form of reduction has been found the most convenient in the hydrogenation of vegetable oils.

Theoretically, hydrogen can be added in the presence of a catalyst to any unsaturated carbon-carbon bond; but, in practice the ease of addition is affected by the following variables: 1

1. Position of unsaturation.
2. Nature of adjacent groups.
3. Temperature.
4. Pressure.
5. Kind, quantity and condition of the catalyst.

(Since the experimental work described below is concentrated on only two definite olefinic compounds, the first two variables are really so only within very narrow limits - the difference between oleic and linoleic unsaturation.)

In contrast to chemical reduction, simple olefins are usually hydrogenated catalytically more easily than are conjugated olefins. 2 The ease of hydrogenation decreases according

1. Attention is drawn throughout the reading of this section to the excellent comprehensive review of the subject of Hydrogen addition to carbon-carbon bonds by K.N. and B.K. Campbell, Chem. Rev., 31, 77, (1942).
2. Ibid., p. 138
to the following order: monosubstituted, symmetrically di-
substituted, unsymmetrically disubstituted and finally tri-
and tetra substituted olefins.\footnote{1} Former and Galey in England
observed that the rate of hydrogenation of unsaturated acids
increased as the double bond was removed from the carboxyl
group.

The size and degree of the branching of the alkyl groups
has an effect on the rate of hydrogenation. In a perfectly
general manner it can be stated that the more the branching
the less is the ease of hydrogenation.

When there are two ethylene groups in a molecule and they
are not conjugated with one another (\textit{viz. linoleic acid}), it
is sometimes possible to effect consecutive hydrogenation and
to isolate the intermediate monoolefins. In such cases, the
double bond with fewer substitutions and farther from the
carboxyl group is hydrogenated first.\footnote{2}

The effect of temperature and pressure is of a purely
physical significance. Preference of a certain temperature
and pressure for a certain hydrogenation process springs
solely from the nature of the catalyst and the chemical
constitution of the compound to be hydrogenated. Often these
two latter factors allow of a wide range of fluctuation for
those two variables, in which cases the limits of advantageous
operations have been found empirically. Considering pressure
more basic, MacDougall\footnote{3} defines the relation between the rate
of adsorption\footnote{4} on the surface of a catalyst and the pressure of
the gas, at equilibrium, by the following relation:

\[ \Theta = \frac{k_1P}{k_2 + k_1P} \]

where \( \Theta \) is the fraction of "available" surface covered with
the gas at equilibrium under a pressure \( P \). It is quite
obvious that as \( P \) increases \( \Theta \) approaches unity as a limit.
Hence there is a certain value for \( P \) (this value depends on
kind, nature and state of subdivision of the catalyst) for
which \( \Theta \) is very near to unity, and any increase of pressure
above that value brings a practically negligible increase in
\( \Theta \).

\begin{itemize}
\item \footnote{1}{Ibid. pp. 159-143}
\item \footnote{2}{Ibid. pp. 143-145}
\item \footnote{3}{MacDougall p. 432 et seq.}
\item \footnote{4}{Refer to theories of Heterogeneous Catalysis.}
\end{itemize}
In practice, however, temperatures from 150-350°C. and pressures from below atmospheric to 12 atmospheres have been found advantageous when nickel is the catalyst.

Probably the most determining of all the variable factors is the catalyst. In heterogeneous catalysis, the catalyst is usually a certain form of the free metal or its oxide in the solid state. Metals recognized as somewhat active are Zn, Cr, K, Rb, Cs and Ca. But the highest activity so far observed is in Ba, Fe, Co, Cu, Ni, Pt and Pd. O. Schmidt ascribes this high level of activity to the liability of these metals to form solutions with hydrogen and to their failure to form solid stable hydrides. The unstability of their hydrides (or that of a form of their oxides) has been thought responsible for the transfer of hydrogen to the double bond.

The theories of the poisoning of catalysts, their mode of action, activity and life are all fully considered in any treatment of "heterogeneous catalysis".

From the foregoing considerations it looks possible to effect the saturation of one bond in preference to the other(s) through the proper choice of catalysts and conditions. Early workers on the subject thought they were converting oleic and linoleic etc. acids into stearic which they recognized as solid. While the validity of this opinion is not denied in modern investigation, yet two points are recognized:

1. From the practical (economic) viewpoint it is never desirable in most instances to have the process of hydrogenation going so far as the point of complete saturation of all the components of the oil.

2. From the scientific point of view, the reaction mechanism and character must be better understood in order to better control and develop it.

Thus the current of modern research on this subject has been mainly flowing in these two directions — really one.

II. EXPERIMENTAL

Four different oils (Arachis, Olive, Cotton-seed, and Sojabeen oil) were hybridized under different conditions of temperatures and pressures. The amount of the catalyst and its kind were two constant factors in all the experiments performed. For the catalyst in each case was secured by reducing with hydrogen (purified and dried) the required weight of NiCO₃ (on Kieselghur) which latter was one and the same for all (for its preparation see below).

Four experiments were performed. The first two each on a differently purified Arachis oil samples — labels A & B.

The third experiment was on cotton seed oil.

The fourth one was on olive oil and sojabeen oil.

In all these experiments the samples used for hydrogenation were purified with NaOH as no acidity is desirable, thoroughly washed with distilled water, dried with anhydrous Na₂SO₄, and filtered with 'filter aid'.

In experiments I and II the samples were taken originally from commercial edible arachis oil in Beirut market.

In experiment III the sample was taken from a bottle of cotton seed oil (decolorized) delivered by Messrs. Jabre and Quannaty and intended for edible purposes.

In experiment IV the olive oil sample was taken from the finest edible oil of this country, produced by cold expression. The sojabeen oil sample was supplied by Mr. A. Sherif who secured it from the crushed beans by cold extraction with benzine; however, benzine smell was perceptible in it.

The catalyst was prepared in the following manner: thirty grammes of Merck (puriss.) Ni(NO₃)₂·6H₂O dissolved in 40 ccs. of distilled water, were ground for 15 minutes in a mortar with 25 grammes of HNO₃ - washed Kieselghur (Merck) until the mixture was apparently homogeneous and flowed like a lubricating oil. It was then slowly added to a solution prepared from 19 grammes of Merck (Puriss.) (NH₄)₂CO₃·H₂O and 100 ccs. of distilled water. The resulting mixture was filtered with suction, washed three times, each time with 25 ccs. of distilled water, dried overnight in the oven at 110°C., and kept on a clean watchglass in a CaCl₂ dessicator.

The set-up in all these experiments (except Exp. II where a slight modification was introduced for producing pressure) consisted of a hydrogen generator (HCl and Zn foil) followed by a wash bottle containing lead acetate sol. (S² and Cl₂ are catalyst poisons) then another containing conc. H₂SO₄ from which the hydrogen passed into the reaction flask through a U-tube containing pure solid NaOH (to entrap any Cl₂ and other acid radicals). The reaction vessel contained the oil and consisted of an ordinary round-bottom flask closed fittingly with a two-holed rubber stopper and dipped in an oil bath. Through one of the holes passed the hydrogen delivery tube right to the bottom (that secured proper agitation) and through the other another glass tube opened the system to the atmosphere through a second solid-NaOH U-tube. Where pressure was to be measured (Exp. II) a mercury manometer was made to intercept the apparatus at the right place. All connections were made with new glass and rubber tubes fitting tightly into one another and sealed with paraffin.

Conditions and Products

Exp. I:

Sample: "A - ARACHIS OIL" - light yellow with a faint greenish tinge, characteristic vegetable odor.
Catalyst: - 2% (by weight of oil) (Approx.) of Ni on Kieselgur, reduced from above - mentioned NiCO₃ with H₂ and cooled in an atmosphere of hydrogen; then quickly transferred to the reaction flask containing the oil.
Pressure: Atmospheric.
Temperature: 170-175°C. (registered by an ordinary thermometer dipped in the oil bath).
Time: 8 hours.

Product: (After hot filtration through a filter paper into a clean, dry, glass-stoppered bottle) solid, fairly hard at room temperature, snow white in color, vegetable smell disappeared, rather a butter-like smell was perceptible, it had a very pleasant taste. It was labeled A₁ - HYDROG. ARACHIS OIL.

A₂ - HYDROG. ARACHIS OIL was produced from the same original oil under the same conditions except temperature was 130-190°C. and time 6 hours.

Exp. II

Sample: B - ARACHIS OIL of very bright, quite intense yellow color and vegetable smell.
Catalyst: Exactly as in Exp. I.
Pressure: 1.1 atmospheres.
Temperature: 125-130°C. (measured as in Exper. I)
Time: 7.5 hours.
Product: Liquid at room temperature completely decolorized and partly deodorized. It was labeled B₁-HYDROGEN. ARACHIS OIL.

A new batch of the catalyst was added to B₁ (after drawing out a small sample to reserve for examination, cf. infra.) and hydrogenation resumed at:

Pressure: 1.1 atmospheres.
Temperature: 155-160°C. (measured as before)
Time: 6 hours.
Product: (after filtration etc.) solid at room temperature, perfectly white in color, odor was as that of A₁ of Exper. I. It was labeled B₂-HYDROGEN. ARACHIS OIL.

Exper. III

Sample: B-COTTON SEED OIL, light greenish-yellow in color with a penetrating unpleasant smell.
Catalyst: As in Exper. I, except it was cooled in an atmosphere of dry CO₂.
Pressure: Atmospheric
Temperature: 180-185°C. (measured as before)
Time: 6 hours
Product: (after filtration etc.) solid at room temperature, cream-like in color, partially deodorized. It was labeled B-HYDROGEN. COTTON SEED OIL.

Exper. IV

Samples: A-OLIVE OIL, bright intense-green in color, with characteristic pleasant vegetable smell. A-SOJABBEAN OIL, light red in color, smelling benzine with an unpleasant vegetable odor.
Catalyst: Exactly as in Exper. III
Pressure: Atmospheric
Temperature: 185-190°C.
Time: 6 hours
Product: (after filtration etc.)- A-HYDROGEN. OLIVE OIL, very hard with unpleasant smell, color was lightly dirty greenish. A-HYDROGEN. SOJABBEAN OIL, liquid, color became lighter red, completely deodorized acquiring a smell like A₁ of Exper. I.
Composition of the Labeled Oils:

The Iodine value and the Thiocyanogen value were determined for each of the twelve labeled oils (five originals, and seven differently hydrogenated) so that an appreciation of the conditions and products becomes possible. Further, assuming the perfect application (at least in case where no unsaturation higher than linoleic is present) of Kaufman's formula, the compositions of Arachis, olive and cotton seed oils were calculated. The following table gives the results:

<table>
<thead>
<tr>
<th>Label</th>
<th>Iodine Value</th>
<th>Thiocyanogen Value</th>
<th>Oleic &amp; Isoleic Glycer.</th>
<th>Linoleic Glycer.</th>
<th>Saturated Glycerides</th>
</tr>
</thead>
<tbody>
<tr>
<td>A - Arachis oil</td>
<td>92.34</td>
<td>72.38</td>
<td>60.91</td>
<td>23.03</td>
<td>16.06</td>
</tr>
<tr>
<td>A1 - Hydrog. Arach. oil</td>
<td>71.18</td>
<td>69.11</td>
<td>77.90</td>
<td>2.39</td>
<td>19.71</td>
</tr>
<tr>
<td>A2 - Hydrg. Arach. oil</td>
<td>75.85</td>
<td>69.22</td>
<td>72.73</td>
<td>7.65</td>
<td>19.62</td>
</tr>
<tr>
<td>B - Arachis oil</td>
<td>91.99</td>
<td>89.20</td>
<td>53.46</td>
<td>26.53</td>
<td>20.01</td>
</tr>
<tr>
<td>B1 - Hydr. Arach. oil</td>
<td>90.50</td>
<td>76.16</td>
<td>66.50</td>
<td>11.15</td>
<td>22.80</td>
</tr>
<tr>
<td>B2 - &quot; &quot; &quot;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B - Cottonseed oil</td>
<td>106.76</td>
<td>74.35</td>
<td>48.73</td>
<td>37.40</td>
<td>15.97</td>
</tr>
<tr>
<td>B - Hydr. Cotton seed oil</td>
<td>73.40</td>
<td>66.65</td>
<td>69.60</td>
<td>7.79</td>
<td>22.61</td>
</tr>
<tr>
<td>A - Olive oil</td>
<td>84.66</td>
<td>78.37</td>
<td>83.75</td>
<td>7.26</td>
<td>8.99</td>
</tr>
<tr>
<td>A - Hydr. Olive oil</td>
<td>58.40</td>
<td>58.66</td>
<td>67.86</td>
<td>0</td>
<td>32.14</td>
</tr>
<tr>
<td>A - Sojabaen oil</td>
<td>121.41</td>
<td>86.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A - Hydrg. Sojabaen oil</td>
<td>111.82</td>
<td>84.82</td>
<td>67.18</td>
<td>31.16</td>
<td>1.66</td>
</tr>
</tbody>
</table>

III. DISCUSSION OF RESULTS

Concerning pressure it is seen that a 0.1 atmosphere increase in Experiment III had no effect at all in increasing the rate of hydrogenation. The best comparison that could be made is between Ag and B2-Hydrog. Arachis oils. In their production from almost the same original oil all conditions were made equivalent except pressure and temperature. A2 has a lower iodine value than B2. This indicates that the reaction is more sensitive to temperature than pressure changes in the neighbourhood of those conditions. The comparison between A1 and B2 - Hydrog. Arachis Oils is even more convincing. However Sabatier\(^1\) states that usually pressures of advantage are from 2 to 15 atmospheres.\(^2\)

Concerning temperature, the writer feels justified in stating that 160\(^\circ\)C. appeared as a critical temperature for any detectable speed of the hydrogenation reaction as carried in the above-described experiments. However, going up above 185\(^\circ\)C. seemed to mark a rapid increase in the rate of the reaction (Comp. A1 and A2-Hydrogen. Arachis oils.)

Concerning the catalyst it is regrettable to state that it was always reduced at temperatures much higher (dull-red) than the ones stated by many authorities to be optimum for high activity (450\(^\circ\)C. for 5.\(\frac{1}{5}\)(H,Adkins). Yet it did quite a good work. However, cooling in an atmosphere of carbon dioxide rather than in a hydrogen atmosphere, for subsequent protection from the poisoning action of the atmosphere, had no perceptible effect to the writer's best observation. This might mean two things: either there is no poisoning effect exerted by the atmosphere, or that there is such an effect but escaped detection due to the low level of catalyst activity (from reduction at high temperatures) or, and to the very short time the hydrogen-cooled catalyst was exposed to the atmosphere. Sabatier\(^5\) supports the first meaning in a footnote where he states: "the exact comparative experiments of Willstatter and Waldschmidtleiz go for towards proving that nickel is entirely inactive unless it contains some oxygen." It is fitting here to note that many investigators\(^4\) agree that the most active catalyst is the suboxide of nickel such as Ni\(_2\)O and not free metal.

---

The case of sojabeans oil in Exper. IV is indeed worth noticing. It might stand as a definite case of catalyst poisoning with benzine. Whereas sojabeans oil is expected to register a greater drop in its iodine value, relatively to the other oils used, it only dropped from 121.41 to 111.82. Here also this fact must be interpreted very cautiously. With due reservations it might be explained either as a poisoning case where one or more components of the benzine mixture acted as a poison (especially if it contained Sulphur which is quite likely to be present); or as an instance of selective hydrogenation where hydrogen went preferentially to saturate whatever olefins, etc... happened to be in the mixture. However, from the writer's own experience the second possibility seems improbable.

Considerations on the Reaction's Character:

The significance of the figures in the last three columns of Table VIII might very well bring us to some tentative conclusions regarding the mechanism of hydrogenation reactions when nickel is the catalyst. Three facts are quite obvious.

1. There is always an increase in column III for the figures of hydrogenated oil (except in case of olive oil, cf. infra) over those of the original ones in the same column.

2. This increase is derived from the larger part of the decrease in the corresponding figures of column IV.

3. In column V there is always an increase (a relatively slight one) in the figures for hydrogenated oils over those for the original ones in the same column.

With some reservation it appears quite certain that the selectivity of the reaction is a prominent character. The question of whether it is the only character, or whether it is the dominant character (if other characters exist) always or at some stage or level of the reaction is very difficult to meet satisfactorily with the relatively meagre experimental evidence at hand. However, this at least can be asserted that this observed selectivity is not an absolute, strict one; for to do so, the figure for a certain oil (while it is being hydrogenated) in column IV must become nil before any increase is noticed for its figure in column V. These two experimentally assered truths about the character of this reaction can be reconciled in the following statement (pending further support of experimental evidence): Down to a certain minimum concentration of a selected component, its rate of hydrogenation is independent of its concentration in the
mixture and thus in that region of concentration the reaction is not unimolecular in character for all practical purposes. Beyond that minimum concentration the rate might so slow down that another component (oleic, say) seems to enter into reaction in a noticeable manner (this is best observed in comparing A-Hydrog. Olive, and B-Hydrog. cotton seed oils with A1, A2 and B2-Hydrog. Arachis oil). Stated concisely, the hydrogenation reaction here studied is an unimolecular reaction showing in the regions of high concentrations an undoubted selectivity (this latter character is thought to be related to, or wholly springs from, the nature of the catalyst). The accompanying curves show more clearly what is meant by the above, tentative conclusions.

In these curves the iodine and thiocyanogen values are plotted against the amount of linoleic acid glyceride at different stages of hydrogenation for three representative oils. It is interesting to note the relative position of the curves of the different oils. One could easily see that semi-drying oils would have such curves farther to the right while drying oils still further right. Also the distance between the initial points of the two curves for an oil gives a fair idea of the class it falls in etc...

Aside from the insight as to the place and class of an oil we observe (confining our attention to one oil) the following facts about the hydrogenation process:

1. The slopes of both curves appear to be (almost) equal in the solid uppermost portions.

2. Theoretically, the two curves meet at the abcissa (in the case of Arachis oil two of the experimental points were so near the abcissa that extrapolation to it became legitimate) and the point in which both curves meet may be hit happily in an experiment.

3. From a comparison of the initial points and the meeting point on abcissa it is graphically clear that the curves should contain some inflectional points.

4. The case of hydrogenated olive oil is such that the iodine and thiocyanogen values (both 53.4) lie on an unseen portion of the curve much below the value at which they are expected to meet (75.5). If this is true it prescribes a decrease in oleic and isoleic contents below their value in the original oil. This is confirmed experimentally (cf. Table VIII).

The probable conclusions from the above observations are:
Experimental Curves for
- Cottonseed Oil
- Arachis Oil
- Olive Oil

Iodine and Thioareneogen Values

Type Curves for
- A Type Oil
1. Only (practically) linoleic glyceride seems to be hydrogenated at the beginning to oleic and isomeric.

Thus the regions where both slopes are equal or almost so are the regions of high selectivity (latter is an accident due to catalyst) of the process. (It is intimated by someone that the 12-13 double bond is the one saturated.)

2. There is a maximum limit for the iodine value while it stays equal to the thiocyanogen value. This point marks the practical disappearance of linoleic acid. Below that point the one curve for both values might be thought to coincide with the abscissa and run till zero as a limit due to the saturation of the only double bond left - oleic and isomers.

3. When most of the component selectively reacting has disappeared, the unimolecular character of the reaction becomes noticeable. And thus the slopes of BC and B′C′ (in type curves) abruptly become very much different - the difference being a reflection of the difference in the concentration of the two components involved in the reaction. The points G and G′ (type curves) mark a further decrease in the rate of hydrogenation due to severe reduction in the concentration of both of the reacting components. From the magnitude of both slopes it is obvious that BC suffers a greater change.

4. After the meeting point of both curves the curve continues running along the X-Axis but infinitely higher than it. This one curve represents an infinite number of points each of which represents both an iodine and a thiocyanogen value (i.e. no linoleic glyceride). And as the curve proceeds to zero, the amount of oleic and isoleic glycerides also approaches zero. This is testified to experimentally in the case of hydrogenated olive oil (Table VIII).

To render these discussions and conclusions more comprehensible, the "Type Curves" were constructed. These curves are made categorical and exaggerated in order to emphasize the main features of the reaction in one of its stages. The shape, points and regions and their dependence on kind and nature of the catalyst, temperature and pressure, raise many exciting questions which only a more thorough future research can answer experimentally.

1. cf. Supra p. 49
Appendix

Changes in Analytical Values: ¹

Upon Hydrogenation:

Specific gravity increases approaching that of tri-
stearine - the latter being 1.0101 at 15°C., the melting
point increases; the iodine and thiocyanogen values
decrease - approaching zero as a limit, the index of refrac-
tion is strongly reduced, the saponification number does
not practically change, the contents of free fatty acids
change but little due to reduction of -COOH group. The
unsaponifiable matter practically suffers no change. The
acetyl value changes are quite noticeable; a reduction from
155-102 has been reported, it is intimated that the -OH
group is more or less broken down by the hydrogenation
process.

The effect on color tests is variable: Boudoiun's is
not influenced, Halphen's is not likely to be positive.

The cholesterols and phytosterols are not altered by
hydrogenation.

Tests for Hydrogenated Oils²

Different color tests and tests for special oils have
been recommended for the detection of hydrogenated oils.
However, because of the observed uncertainty of these color
tests and the narrow applicability of the special tests, the
test for nickel with dimethylglyoxime has been recommended
by Bomer and Leschly-Hansen as most reliable when positive.
When negative this test should be supplemented by some color
tests or a special test before the formulation of a safe
conclusion.

1. C. Ellis, Ind. Eng. Chem. 6, 117 (1914).
2. Allen's, pp. 48-52.
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3. Henry, Plantes & Huiles, Collection Armand Collin (Section d'Agriculture) No. 5.


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