II. THE PREPARATION AND PROPERTIES OF PURIFIED OLEIC ACID AND SOME OF ITS SALTS.

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NOTWITHSTANDING the large amount of work which has been done on the chemistry of oleic acid the published methods for preparing it leave much to be desired. The descriptions given of the compound itself inspire so little confidence that even the most recent edition of the Handbook of Lewkowitsch [1921] quotes melting points for oleic acid varying from 6.5° to 16° , although Kirschner's conclusion [1912] that the acid is dimorphous, is accepted. Edmed [1898] by recrystallisation of Kahlbaum's oleic acid from alcohol obtained a sample of the acid which was stated to melt at $13-15^{\circ}$. Partington [1911] by crystallising another specimen obtained from Kahlbaum, and probably one of inferior grade, could not obtain a product melting higher than 6.5° ; Kirschner [1912] by following much the same procedure obtained samples of the acid which showed dimorphism and therefore two different melting points. The present authors originally hoped to devise an improved method for the estimation of oleic acid in mixtures such as are obtained by hydrolysis of natural fats and oils, but soon found that it would be necessary to study the question of preparing and characterising pure oleic acid almost *ab initio*.

During the course of their studies, now extending over some years, the authors have been forced to retrace their steps many times, but they believe that they can now with advantage place some of their results on record and indicate with considerable confidence the probable margins of experimental error. Having tried nearly all the published devices for purifying oleic acid and numerous combinations and permutations of these and others, they have worked out a process by which oleic acid containing not more than 1 % of impurity can, with practice, be obtained with considerable certainty.

Separation of salts of higher fatty acids by recrystallisation.

The authors have latterly confined their experiments to the acids obtained by hydrolysis of olive oil, in which it is known that palmitic acid is the main saturated constituent. It is not intended to discuss this point in the present paper, but it may be stated that the authors have never detected the presence

of any saturated acid higher than palmitic acid in samples of oleic acid made from olive oil by the process recommended, so that stearic acid, for example, if present in the crude acid, was mainly eliminated as lead salt in the first stages of purification. In addition to oleic acid, palmitic acid and any acids which are easily eliminated owing to the sparing solubility of their lead salts, there are present linolic acid and perhaps others still more highly unsaturated. [Compare Hehner and Mitchell, 1896.]

Various metallic salts of oleic acid, linolic acid and palmitic acid with barium, lead, lithium and sodium have been examined by the present authors especially with regard to their suitability for the purpose of separating the acids from one another. It is unnecessary to go into the large mass of experimental detail and it will be sufficient to say that when a mixture of palmitic acid and oleic acid was converted into barium, lead, lithium or sodium salts and these were fractionated by crystallisation, the palmitate was invariably found in larger proportion in the solid than in the dissolved portions. This behaviour is quite consistent with solubility curves for solid solutions of certain types and renders it highly improbable that any recrystallisation process applied to these salts can yield pure oleates¹.

It has been suggested by C. W. Moore [1919] that the use of salts of bivalent metals for separating oleic acid from other acids is to be avoided owing to the possibility of double salts, such for example as barium oleo-linolate, being formed. The objection would doubtless hold good if barium oleo-linolate, for example, were less readily soluble than barium oleate, but as the mixed salts invariably, in the experience of the present authors, exhibit a much higher degree of solubility than the pure oleates, the difficulty is not a serious one from the theoretical point of view, and in actual practice the purification of barium oleate from barium linolate by recrystallisation is comparatively easy.

Properties of mixed lead salts of oleic and other fatty acids.

The separation of palmitic acid and other saturated fatty acids from oleic acid is as a rule effected by making use of the greater solubility of lead oleate as compared with palmitate, in ether, benzene or petroleum, usually the first. It is widely known that this method is imperfect but it is perhaps not generally realised that it is very rough indeed. The solubility of lead palmitate in ether, benzene and other solvents is not diminished as might be anticipated, but is in fact greatly increased by the presence of lead oleate, linolate, etc. Unless, therefore, care is exercised to remove, with the lead palmitate, a large proportion of the oleate itself, the oleic acid prepared by the lead salt process may contain 5 % or even more of palmitic acid. On freezing the solution, however, the lead oleate which then separates out carries down with it a large proportion of the remaining lead palmitate and finally an oleic acid can be

¹ The forms of the freezing point "curves" of mixtures of oleic and palmitic acid (compare Fig. 1, p. 15) also indicate that any complete purification of the former by a recrystallisation process applied to a mixture of the free acids would not be practicable.

isolated from the mother liquor which does not contain more than about 2 % of palmitic acid, which is the smallest proportion of palmitic acid which it has yet been found practicable to obtain in any sample of oleic acid purified by a process involving crystallisation only.

It must be emphasised too, that the solubility of lead oleate, for example, in ether, varies considerably not only with the quantity of other salts present but apparently also with the quantity of alcohol and of water present and also with time. A clear solution of freshly precipitated, crude lead oleate in ether, if left for some days or weeks in a closely stoppered vessel, gradually deposits much of the salt in solid form and the deposit is then comparatively very sparingly soluble in ether. The cause of this phenomenon is obscure.

If a fresh ethereal solution of the mixed lead salts from olive oil be filtered at ordinary temperatures and then cooled, amorphous lead oleate mixed with palmitate tends to be deposited above -10° , but below that temperature the deposit tends to become crystalline and on warming to ordinary temperatures does not always wholly redissolve. The property which lead oleate has of becoming crystalline below -10° may be taken advantage of, if desired, to remove the bulk of the more highly unsaturated acids, as a preliminary in preparing oleic acid from olive oil, using ether as a solvent. In this case the ethereal solution remaining after the bulk of the palmitate has been separated by filtration at ordinary temperatures is slowly cooled to -15° with constant agitation, and as soon as the deposit has become granular¹ the whole may be filtered through a Buchner funnel with the aid of a pump; the physical condition of the crystalline deposit is so well fitted for rapid filtration that when using several hundred grams of ether the solid may be secured without difficulty or serious loss of solvent even if no special precautions are taken to cool the funnel beforehand. In this way the bulk of the lead salts of the more highly unsaturated acids may be removed and subsequent processes of purification to some extent facilitated.

Barium oleate.

Farnsteiner [1901] first drew attention to the fact that barium oleate, although nearly insoluble in hot benzene containing absolute ethyl alcohol, dissolves if a very little water is present, and comes out on cooling in lustrous needles or long laminae. He claimed that a method for the quantitative separation of oleic acid from more highly unsaturated fatty acids could be based on this, as the barium salts of these remained dissolved; this conclusion however was disputed by Lewkowitsch [1903] who stated that, in presence of these acids, barium oleate is soluble in the medium. The experience of the present authors agrees with that of Lewkowitsch, and in another paper data will be furnished which fully substantiate his statement. The barium salt of oleic acid may be made use of, however, for the isolation of highly purified oleic acid from a mixture which contains a large proportion of that acid—such as that from

¹ Repeated warming and cooling is sometimes necessary to obtain a granular material. **III**

olive oil. The authors find, however, that several great advantages are to be gained by substituting amyl alcohol for ethyl alcohol. When ethyl alcohol is used there is danger of the water, present or added, causing the alcohol to separate in diluted form as a distinct phase; with amyl alcohol on the other hand, if there is excess of water, it is the excess of water which remains as the separate phase and has no ill effect. Toluene was used in the later experiments rather than benzene as it is less volatile; the mixture of toluene and amyl alcohol is readily recovered with but little change in composition, by distillation in a current of steam, and used again as solvent. A moist mixture of equal volumes of toluene and amyl alcohol is recommended for rapid purification of barium oleate, but toluene with 10 % of amyl alcohol may be used.

Dry barium oleate is practically insoluble in benzene or toluene even on boiling. If a little of this salt is heated with either of these liquids in a test tube and a drop of water is added the powdery particles of the salt swell and soon the whole forms an opaque jelly and remains as a jelly when cool. On subsequent addition of one drop of amyl or ethyl alcohol and again heating, a thin, slightly opalescent solution is at once formed, and this on cooling deposits the salt in shimmering flat needles. The salt is soluble in a hot mixture of nearly dry amyl alcohol and benzene (or toluene) but on cooling comes down as a powder, which has no crystalline appearance unless a little water is first added.

The solubility of pure barium oleate in a moist mixture of equal volumes of amyl alcohol and benzene was found to be 0.219–0.224 g. per 100 cc. at 12°, determined about 12 hours after cooling a warm saturated solution to that temperature; it may be considerably less if the time of standing be prolonged. This, although small, is nearly fifteen times as large as that found by Farnsteiner for his solvent mixture of benzene and moist ethyl alcohol at 11° [1901]. This greater solubility extends to the other salts present in crude barium oleate, and the fact presents a definite practical advantage when the separation of barium linolate and similar salts from barium oleate is concerned, for these impurities in the oleate are in consequence more rapidly removed on recrystallisation¹. For rapid elimination of the salts of the more highly unsaturated acids the filtrations are best carried out within an hour or two of cooling to 12°, but it is even better to cool no lower than to 20° and filter at once.

The process which the authors now use for preparing the most highly purified oleic acid is as follows.

ISOLATION OF OLEIC ACID FROM OLIVE OIL.

(With Edward Neville Mottram.)

Olive oil (400 g.) is heated on the steam-bath under a reflux condenser for 3½–4 hours with spirit (800 g.) and water (200 cc.) containing excess of sodium

¹ When Farnsteiner's mixed solvent is used for the latter purpose, it is almost impossible wholly to remove the more soluble barium salts by a limited number of crystallisations, unless the filtrations are carried out at temperatures not lower than 38–40°. L.

hydroxide. The whole is then cooled and its alkalinity nearly but not quite destroyed by addition of acetic acid, using phenolphthalein as indicator. A strong aqueous solution of lead acetate is slowly added while the whole is agitated, when a precipitate is formed and adheres to the walls of the containing vessel; the addition of lead acetate is discontinued when no further precipitation ensues. The supernatant liquid is poured off and worked up to recover alcohol, the lead precipitate is fairly well drained and then dissolved in toluene (1 litre) with the aid of a steam-bath. The toluene solution is now heated for some time with solid dehydrated lead acetate (50 g.)¹; this dissolves, but on cooling to ordinary temperature separates once more together with some 20 % of the whole quantity of the other lead salts originally present (crude lead "palmitate")².

After cooling the solution to ordinary temperatures and filtering from a residue of about 75–80 g. of insoluble lead salts, the clear toluene solution is shaken with excess of cold, dilute hydrochloric acid until no more lead chloride is formed on removing a portion of the upper solution and agitating with dilute hydrochloric acid. It is not difficult to separate the toluene solution of fatty acids from the aqueous layer in spite of the presence of finely divided lead chloride, and filtration through several layers of filter paper in a large Buchner funnel may be resorted to if necessary. The clear solution is subsequently agitated with water until quite free from hydrochloric acid, separated, and the solvent removed by distillation, finally under diminished pressure (15–20 mm.) on the water-bath.

The acids are now subjected to fractional distillation under a pressure not exceeding 2–3 mm.³ when the middle fractions are used to prepare the purest oleic acid, care being taken to reject a larger quantity of the earlier fractions than of the later ones, as the main impurity, which the operation is used to eliminate, is the relatively volatile palmitic acid⁴. The earlier portions of the

¹ The lead acetate is used to effect the complete conversion of any remaining sodium salts into lead salts and it also has the effect of clearing the toluene solution and rendering the crude lead "palmitate" easy to filter off. The excess is easily recovered by washing this crude lead "palmitate" with water.

² By means of a freezing mixture more lead salt, rich in palmitate, separates out, and the more of this which can be removed, the simpler does the subsequent removal of palmitic acid by fractional distillation become. The removal of 50 % of all the dissolved salts has yielded the best results, but in this case ether is much to be preferred to toluene as solvent. Some lead oleate, contaminated with much palmitate, may be obtained by extracting this crude lead "palmitate" with toluene, benzene or ether, and may be reconverted into free acid, and added to the next batch of oleic acid, before subjecting the latter to the lead salt separation process.

³ The authors used a very simple fractionating column 15 inches in length and about 1½ inches in diameter made by the "Scientific Glass-blowing Company, Manchester," which has proved very suitable for fractional distillations under reduced pressure, and was fused to the flask. The required reduction in pressure was attained by means of a mercury vapour pump of the Völler type in series with an ordinary Sprengel-Bunsen water pump.

⁴ The authors collected their distillates in the first fractionation in two main parts, in order of passing over, representing respectively about (I), one-third and (II) one-half of the total quantity of acid, a dark orange residue (III) representing rather more than one-sixth of the

distillate set to a nearly solid mass (mixed crystals of oleic and palmitic acid) on cooling and it is of interest to observe that the authors did not discover any solid saturated fatty acids in the least volatile portions of the material although, when the lead salt separation as a preliminary was omitted, such acids separated out from the residue in the flask¹.

The fractions selected are now treated in the following manner. A mixture of equal volumes of toluene and amyl alcohol, weighing roughly ten times as much as the oleic acid to be worked up, is heated to water-bath temperature with a pinch of phenolphthalein and rather more powdered crystallised barium hydroxide than is required to neutralise the oleic acid. The oleic acid is added to the hot suspension, and the whole shaken. Barium oleate is formed very quickly and, when the whole appears permanently suffused with the colour of alkaline phenolphthalein, it is allowed to settle. The nearly clear supernatant liquid is poured off while still hot and allowed to cool, when the barium oleate separates, usually in beautifully crystalline form; it is filtered off, washed with toluene and drained.

For the purification of the barium oleate, the drained salt is recrystallised from about two-and-a-half times its weight of a hot mixture of amyl alcohol and toluene in equal volumes, with addition on each occasion of a few drops of water, the process being repeated until 100 g. of the filtrate (filtered after remaining in the cold for about twelve hours at about 12°) yields not more than 0.21 g. of residue on evaporation. From two to five recrystallisations are usually necessary and the salt should be washed with toluene on each occasion². The salt requires now only to be redissolved, separated from insoluble impurities by filtration, and finally freed from adherent solvent by exposure to air or in a vacuum (if desired, after washing with ether). About 90–100 g. of barium oleate containing 2 or 3 % of barium palmitate is thus obtained. Before conversion into free acid the salt must be freed entirely from all odour of amyl alcohol and then suspended in cold water containing

original quantity of acid remaining in the distilling flask. Fraction (II) was refractionated and the corresponding fraction of this worked up for the purest oleic acid. The fractions not used for conversion into barium salt will yield more good oleic acid by repeating the whole process *ab initio*.

On a large scale, with the incomparably more efficient fractionating columns available in technical work, middle fractions could no doubt be obtained in one operation even purer than those obtained by the authors in two operations and representing a much larger proportion of the crude acid distilled.

¹ It is very doubtful whether these contained stearic acid, which has been stated by some workers not to be present in oleic acid from olive oil. It may be that they are acids higher than stearic acid, in which case it may prove satisfactory on the large scale to omit the lead salt separation process and trust to the fractionating process alone to effect the removal of all saturated acids; in view of the conflicting statements before mentioned, however, and the comparison of the results actually obtained on the small scale with and without the lead salt separation process, the present authors are not yet prepared to recommend the omission.

² The purification of the barium oleate from the more soluble barium salts is effected in a smaller number of recrystallisations if the temperature is not allowed to fall too low and if the filtrations are carried out as soon as possible after the selected temperature has been reached. A temperature of 20° is suitable, but if too high, clogging of the filter may occur.

a slight excess of 10 % hydrochloric acid. In the course of some hours, with frequent shaking, much salt is decomposed and if the whole be filtered through a layer of filter paper with the aid of a pump any unchanged salt may be recovered. The oily layer in the filtrate is separated and shaken repeatedly with dilute hydrochloric acid and then with water until free from barium. This mode of working, if somewhat tedious, prevents any contamination of the oleic acid with solvents or contained impurities.

The washed oleic acid is collected and after being freed from water as far as possible by mechanical means is transferred to a distilling flask, dried in a vacuum with the aid of very gentle warmth and fractionated under a pressure of not more than 2–3 mm. The great bulk distils almost constantly, usually between 170° and 175° when using a Völlmer glass mercury vapour-jet pump in series with a Sprengel water pump. About 53 g. are obtained from 100 g. of fractionated oleic acid (crude).

The bulk of the distillate should set readily, on cooling below 11°, to an ice-like mass, the thermometer rising to and remaining practically constant at not lower than 12° and sometimes as high as 12·8°¹.

Oleic acid obtained by the authors when using the above process of purification contains about 2 % of palmitic acid, which reduces its setting point by only about 0·5°. It also contains, however, small quantities of other impurities of unknown character, which are probably products of decomposition of oleic acid by heat and which further affect its setting point by several tenths of a degree; these may for the most part be removed however by draining on porous earthenware, in a vacuum, at 8–10°, while the palmitic acid cannot be so removed.

Properties of oleic acid.

Oleic acid, as Kirschner [1912] has shown, is dimorphous. This dimorphism is exhibited only by moderately pure oleic acid, and is often manifested during solidification, by the setting in of a slow rise in temperature at some stage after the rapid rise after supercooling to the steady setting point of the low melting modification. A constant higher setting point never seems to be reached in practice, however, and this is doubtless because change from the first to the second solid modification is very slow.

In other cases the oleic acid sets to an icy mass and only after some hours displays the phenomenon shown so well in the photograph given in Kirschner's paper, namely, the development of white, opaque sub-spherical aggregates of minute needles, into which the whole is ultimately transformed.

The highest melting point observed for the more stable form was 17·45°, the sample being one which, with an original setting point of 12·04°, had been left for some months during the winter. Another sample, with an original

¹ Several per cent. of palmitic acid do not greatly affect the melting point of oleic acid, but a high melting point is a fairly good guarantee that the more highly unsaturated acids and other impurities are absent.

setting point of 12.8° , was found to melt at 17° after remaining some days in the solid state.

The best samples of oleic acid made by the present authors, if slowly cooled while in the fluid condition, began to deposit crystals when the temperature had fallen to about some point between 12.3° and 12.8° and the temperature then rose quickly to a maximum, usually remaining then almost constant until the whole was nearly solid¹. It was very seldom that this supercooling was greater than $0.65-0.7^{\circ}$, but Kirschner was able to keep his oleic acid at 8° for some hours and could find no temperature of spontaneous crystallisation. Kirschner, however, prepared his oleic acid by the repeated partial solidification and centrifugalisation of Kahlbaum's purest preparation of oleic acid, some samples of which he found to deposit a solid which had the characters of elaidic acid; his acid was therefore apparently saturated with elaidic acid and may have contained other fatty acids capable of forming isomorphous mixtures with oleic acid without greatly affecting its melting point.

SOME FURTHER OBSERVATIONS ON THE PROPERTIES OF PURIFIED OLEIC ACID.

Mr Edwin Richardson has observed that when freshly distilled oleic acid contained in a glass vessel is exposed to diffused daylight for about twelve hours a small but definite depression of the setting point is often observed, amounting to about $0.07-0.1^{\circ}$. After this initial period further change is very slow and even when the acid is exposed to air, or when dry air is bubbled through it at ordinary temperatures for five hours, the setting point is lowered by only one or two hundredths of a degree. On the other hand, the setting point of a sample which had been left in a closely-stoppered glass bottle for about a year had fallen by about 1° .

Saturation of dry, purified oleic acid with water leads to a depression in the setting point of about 0.35° (mean of 4 concordant observations). Water is less soluble in oleic acid at 12° than at 25° , so that on cooling oleic acid saturated with water, considerable cloudiness is observed.

First setting points of mixtures of oleic and palmitic acids.

A weighed sample, usually amounting to 5-10 g. of each of numerous specimens of drained and undrained oleic acid prepared by processes not quite so efficient as the one above described, was placed in a thin glass tube which was surrounded by another which provided an air-space separating the former from the cooling bath of water. The bulb of the thermometer² was immersed

¹ This temperature is what hereafter is termed the "first setting point." When any marked change in temperature from the first setting point was observed, during the solidification of oleic acid containing less than 6 or 7 % of palmitic acid, it was a rise, due to the appearance of the second and higher melting modification.

² The temperatures given in this section were taken with a standardised thermometer capable of being read to 0.01° and are given to the nearest 0.05° .

in the acid, which was stirred with a platinum spiral. The rate of cooling in any series of observations was kept as nearly as possible constant and the first maximum temperature reached after solidification set in was recorded as the "first setting point," the observation being repeated until consistent results were obtained with a steady rate of cooling. Small weighed pellets of palmitic acid were added, dissolved by warming and stirring and new observations made.

Fig. 1.

The general character of the results obtained will readily be understood by reference to Fig. 1, which exhibits actual observations made with four different samples of fairly high grade oleic acid. The *percentage of palmitic acid* was in each case the weight of palmitic acid added divided by the total weight of material present. One of these, giving the points on *BPG*, was selected because it was practically free from secondary impurities; another, *CQH*, because it was the last sample examined and a specially large number of observations was made with it in order finally to decide whether a real break occurred. The other two, namely *DRJ* and *ESK*, illustrate the behaviour of somewhat less pure specimens. The descending branches (reading from left to right) of the setting point "curves" had a slope practically independent of the amount of impurity in the samples examined. The slope of descent was invariably nearly 0.25° for each additional 1% of palmitic acid. The steeper branches of "curves" actually traced in practice are

indicated by interrupted lines, as the slopes of these varied somewhat with the speed of cooling adopted and consequently were more or less fortuitous, but served to determine the approximate position of the "breaks."

The temperature at which the break occurs with each sample would of course always be the same if only oleic acid and palmitic acid were present. The fact that this break-temperature usually appears below 11.8° is due to very small quantities of oily secondary impurities; these are probably of low molecular weight and therefore very effective in depressing the melting point, but apparently with little influence on the iodine number or on the horizontal displacements of the "breaks" as these were scarcely altered after draining the acid; thus the undrained sample which gave the points on *ESK*, gave those on *DRJ* after draining.

Consideration of the numerous results obtained makes it possible to conclude that the lower melting modification of pure oleic acid forms with palmitic acid a series of solid solutions, the liquidus "curve"¹ of which is given approximately by the line *AO* (Figs. 1 and 2). Beyond *O*, which corresponds with a total of 7.2 % of palmitic acid and a temperature of 11.8° , another series of solid solutions (liquidus = *OF'*)² appears which is doubtless that corresponding with the liquidus curve given by Carlinfanti and Levi-Malvano [1909]. The curve as shown by these authors is the one marked *BC* in Fig. 2, and is such as would be obtained by use of an oleic acid containing some 7 % of palmitic acid and also of other impurities, resulting altogether in a regular displacement of the true curve *AOC* towards the left. The approximate positions of the points on *OC* have been deduced by making regular proportional displacements of *BC* towards the right.

The lowest possible temperature for *O* (Fig. 1) was fixed by that of the break observed with the sample which gave the results indicated by the lines *BP* and *PG* (Fig. 1). This sample had been repeatedly remelted and redrained until its first setting point was constant at 12.95° ; it probably contained only minute traces of anything other than oleic and palmitic acids and its "iodine number" was 88.0, corresponding with a content of 2.2 % of palmitic acid.

The true percentage of palmitic acid in the pure eutectic, in other words the position of the point *O* with respect to the left-hand margin of the figure,

¹ These are termed "curves" although within the range of Fig. 1 they did not differ appreciably from straight lines.

² When the right-hand branches of the curves were worked out by observations of "first setting points" made with the usual speed of cooling adopted by the authors, namely about $0.2-1.0^{\circ}$ per minute, they had slopes roughly parallel with *OF*. This has a slope between that of the true liquidus curve and that of the solidus curve, but considerably nearer to the former. The true liquidus curve is given approximately by the full line *OF'*, which is nearly parallel with the curves which the authors obtained, by plotting the temperatures at which solid disappeared on warming or by plotting "first setting points" when an extremely low rate of cooling was adopted. The slope of *OF* agrees satisfactorily with that of the left-hand extremity of the liquidus curve found by Carlinfanti and Levi-Malvano [1909, p. 371]. In order to make these features clearer the short full line *OF''* has been added to the figure; this line indicates the slope (not of course the position) of the left-hand extremity of the solidus curve as given by Carlinfanti and Levi-Malvano.

was decided by reference to the preceding data for the specimen giving the "curve" *BPG*, taken in conjunction with data worked out with special care for a second sample of oleic acid which showed a break of 3.1 % of palmitic acid (added) and which had an "iodine number" of 86.00 (mean of three observations: 86.01, 86.09, 85.76)¹. The former places *O* at 6.8 % of palmitic acid and the latter at 7.55 %, and *O* has therefore been set about half-way between these points, namely at 7.2 %, with the reservation that this estimate may be inaccurate by 0.5 %.

Fig. 2.

The authors believe that any changes in the position of the "curves" *A*, *E*, *B* revealed by more accurate work in the future are not likely to do more than slightly raise the lines *AO* and *OF* (Fig. 1) parallel with themselves or

¹ The "iodine numbers" were determined by a modification of the familiar bromine absorption method which was found to give very consistent results. The authors were not wholly satisfied with the bare assumption that the low iodine numbers of the purified samples of acid were due to the presence of palmitic acid, and they therefore oxidised two different samples of acid with alkaline permanganate and isolated from the products that part of it which was soluble in petroleum and non-volatile in steam; it was found to be nearly pure palmitic acid.

Thus: Sample I. Iodine number, 86, corresponding with 95.55 % of oleic acid. Palmitic acid isolated and weighed 3.3 %, making a total 98.85 %.

Sample II. Iodine number 87.2, corresponding with 96.88 % of oleic acid. Palmitic acid isolated, 1.6 %, making a total of 98.48 %.

Taking into consideration the great practical difficulty of isolating the whole of the palmitic acid present in the samples, the authors believe that the results support their view that the "iodine numbers" were trustworthy to 1 part in 100 and that their best samples of oleic acid were free from all but traces of acids of more highly-unsaturated character.

displace them slightly to the right or left. The small square indicates what the authors consider to represent the probable limits of any future alterations in the position of the common point *O*.

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The authors have pleasure in stating that the work was undertaken at the suggestion of Mr John Allan, whom they have frequently consulted during its progress.

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