Nomographs for Calculating the Fatty Acid Composition of Oils and Fats from Iodine Values and Either Extinction Coefficients or Thiocyanogen Values

K. ANANTH NARAYAN [1] and B. S. KULKARNI,[2] Department of Chemical Technology, Osmania University, Hyderabad, India

THE use of alignment charts for a variety of routine calculations has recently become so widespread in the chemical engineering practice that nomography may be considered as a unit operation by itself. In the field of oils and fats however the use of such alignment charts is comparatively rare since very few nomographs dealing with oils and fats are available in the literature. The following few nomographs pertaining to fats may be mentioned as noteworthy: a) nomograph by Wan and Ho for observed and actual iodine values of tung oil (6); b) nomograph by Illarionov and Torchinskii (3) for iodine values and refractive indices at different temperatures; c) nomograph by Kaufmann for hydrogen iodine values and hydrogen P-V-T relations at room conditions (4); d) nomograph by Suomalainen and Archimo (5) for quantitative relations of lower molecular weight fatty acids in binary mixtures of fatty acids; e) nomograph by Hussain and Dollear (2) for calculation of fatty acid composition on the basis of iodine and thiocyanogen values.

The determination of fatty acid or fatty glyceride composition is a routine operation frequently required in analytical and process calculations. Since fatty acid composition can be easily determined on the basis of the algebraic relationships between the composition and the iodine and thiocyanogen values, it is easily amenable to illustration on an alignment chart. This chart has recently been made available by Hussain and Dollear (2), which still does not directly give the composition of the individual components of the fatty acid mixture. With the latest introduction of spectroscopic methods in fat analysis, more reliance is being placed on the ultraviolet absorption data than on the purely chemical methods like thiocyanogen value, insoluble bromide value, etc., for accurate determinations of linolenic and linoleic acids. The relationship between the fatty acid composition, the ultraviolet absorption data, and the iodine value are equally amenable to a plot on an alignment chart.

In this communication an attempt has been made to present three alignment charts for the determination of percentage of fatty acid composition in a fatty acid mixture on the basis of

1(A). Extinction coefficients at 233 millimicrons and iodine values;
1(B). Iodine values and thiocyanogen values when linolenic acid is absent; and
2. Extinction coefficients at 268 and 233 millimicrons and iodine values when linolenic acid is present.

In the first two charts use is made of triangular co-ordinates to give directly the ternary fatty acid composition. The use of triangular diagrams in nomography may mark a radical departure from the usual rectangular structure of alignment charts, and these charts incorporating triangular co-ordinates are probably the first of their kind in nomography.

[1] Present address: Department of Food Technology, University of Illinois, Urbana, Ill.

[2] Present address: Southern Regional Research Laboratory, New Orleans, La.

1(A) Nomograph for Calculation of Fatty Acid Composition from Extinction Coefficient at 233 mμ and Iodine Value When Linolenic Acid Is Absent

For this case the following algebraic equations are available for calculation of the fatty acid composition:

% linoleic acid,

$$x = \frac{K_{233}}{92.1} \times 100 \qquad \text{(I)}$$

Where K_{233} is the observed extinction coefficient at 233 mμ and 92.1 is the standard value of extinction coefficient for pure linoleic acid, determined by Brice and Swain (1) by alkali-isomerizing linoleic acid at 180°C. for 25 minutes, using the ethylene glycol-air technique.

% oleic acid,

$$y = \frac{100\,\text{I.V.} - 181.0_x}{89.87} \qquad \text{(II)}$$

Where I.V. is the iodine value.

The extinction coefficients considered here are those that do not require any background absorption or preconjugation corrections. Extinction coefficient is taken to mean D/LC, where D is the optical density of the solution, L the cell width, and C the concentration in gms./1,000 ml. Suitable modification of the scale may be made if standard extinction coefficients are used. In the equations mentioned above, all values are on the mixed fatty acid basis, but if values are available on a glyceride basis, suitable modifications may be made, assuming that the fatty acids, together with the unsaponifiable matter, comprises approximately 95.4% of the oil or fat.

Now in order to construct a triangular diagram for directly reading the fatty acid composition, it is possible to construct on an alignment chart a constant extinction coefficient line and a constant iodine value line, which will intersect on the triangular diagram to give the ternary fatty acid composition. For this purpose the following property of a triangular diagram has been used.

Consider a triangular diagram, ABC, (Figure 1), representing 100% linoleic acid at apex A, 100% oleic acid at apex B, and 100% saturated acids and unsaponifiables at apex C. The arm BA, in addition to representing the percentage composition of linoleic acid can also be made to read on the same axis extinction coefficients between 0 to 92.1, corresponding to the percentage composition of linoleic acid, according

TABLE I

Composition of Fatty Acid Mixtures Calculated from Equations I and II and from Nomograph Shown in Figure I

No.	Extinction coefficient at 233 mμ	Iodine value	Linoleic acid, %		Oleic acid, %		Saturated and Unsap., %	
			Calculated	Found	Calculated	Found	Calculated	Found
1	0	23.9	0	0	26.6	26.5	73.4	73.5
2	8.8	42.3	9.6	9.7	27.8	27.6	62.6	62.7
3	15.9	50.9	17.3	17.1	21.8	22.0	60.9	60.7
4	29.3	92.4	31.8	31.8	38.7	38.5	29.5	29.1
5	35.3	108.0	38.3	38.4	42.9	43.0	18.8	18.6
6	78.5	165.3	85.2	85.1	12.2	12.4	2.6	2.7

to equation (I). Similarly the arm CA, in addition to representing percentage composition, may be made to show the maximum and minimum possible iodine values of the mixture, *viz.*, between 0 and 181.0, 0 iodine value indicated at apex C, and 181.0 at apex A. For convenience of representation this iodine value scale is slightly shifted to A″C′, parallel to the arm AC. Since the saturated acids have 0 iodine value and the total iodine value of a mixture is made up by percentages of oleic and linoleic acids, only these two acids need be considered in the calculations. Now according to the property of the triangle it can be easily shown that in the fatty acid compositions indicated on any line such as BP joining the apex B (100% oleic) to any point on the side CA (0% oleic), for every unit change in percentage of oleic acid, either increase or decrease, there is a corresponding change in percentage linoleic acid by CP/CA units. In order that points on the line BP should represent compositions of constant iodine value, the point P must lie at 89.87 on the iodine value scale indicated along CA. Secondly any line parallel to BP will indicate fatty acid compositions of a constant iodine value. Therefore lines drawn parallel to BP from points on the iodine scale will represent on the triangular diagram *loci* of compositions having constant iodine values. The lines drawn from the extinction coefficient scale, A′B′ parallel to line BC, indicate *loci* of compositions having constant linoleic acid percentage or constant extinction coefficient.

The point of intersection of the constant iodine value line corresponding to the given iodine value with the constant extinction coefficient or constant linoleic percentage line, corresponding to the given extinction coefficient at 233 mμ, parallel to BC will fix up the desired fatty acid composition.

For the sake of convenience in easily drawing constant iodine value lines parallel to BP, another line B″C″ may be drawn passing through or near the apex B, parallel to the side AC and carrying markings exactly similar to those on A″C′, so that PB produced will mark 89.87 on the scale of B″C″.

The nomograph given in Figure 1 is constructed on the above considerations. Thus if the iodine value and the extinction coefficient at 233 mμ are given, the required fatty acid composition may be determined on the nomograph as follows.

Spot the iodine value (say 109.0) on the scale A″C′. Join the point to the corresponding point (marking 109.0) on scale B″C″, marking a constant iodine value (of 109.0) line. Now spot the extinction coefficient (say 35.0) on the scale A′B′ and draw the constant extinction coefficient line parallel to BC. The point of intersection of the constant iodine value line and the constant extinction coefficient line indicates the desired fatty acid composition (38% linoleic acid, 44.8% oleic acid, and 16.8% saturated acids).

1(B) Nomograph for Calculating Fatty Acid Composition from Iodine and Thiocyanogen Values When Linolenic Acid Is Absent

When the spectroscopic data are not available and high accuracy is not desired, the combination of iodine value and thiocyanogen value may be used to determine the fatty acid composition, using the following two equations:

$$181.0x + 89.87y = 100\ \text{I.V.} \quad \text{(III)}$$

$$96.7x + 89.3y = 100\ \text{T.V.} \quad \text{(IV)}$$

Where x and y are the percentages of linoleic and oleic acids and I.V. and T.V. are the iodine and thiocyanogen values respectively.

A rectangular nomograph for this purpose has already been given by Hussain and Dollear (2). As an improvement on their chart which incorporates a triangular diagram for directly reading the fatty acid composition, a nomograph constructed on the principles discussed previously can now be easily constructed.

It will be seen from the previous discussion that the main principle underlying construction is to draw parallel lines, representing constant values of the two variables, across the triangular composition diagram so that the point of intersection of the constant variable lines will represent the desired composition.

In this case (Figure 2) the iodine value scales represented by the parallel lines A″C′ and A′B′ are drawn in exactly the same manner as was done in the previous case so that a line joining the corresponding points of the scales represents a constant iodine value line across the diagram. Now if the arm CA is made to represent a scale for thiocyanogen value with the minimum possible value of O at C, and the maximum

TABLE II

Composition of Fatty Acid Mixtures Calculated from Equations III and IV and from Nomograph Shown in Figure 2

No.	Iodine value	Thiocyanogen value	Linoleic acid, %		Oleic acid, %		Saturated and unsap., %	
			Calculated	Found	Calculated	Found	Calculated	Found
1	56.9	51.5	6.0	6.0	51.2	51.3	42.8	42.6
2	71.3	54.6	19.6	20.0	39.8	39.6	40.6	40.6
3	98.3	76.7	25.3	25.4	58.4	58.6	16.3	16.0
4	118.5	88.4	35.2	35.4	60.9	60.7	3.9	3.9
5	100.9	66.1	40.7	40.9	30.3	30.1	29.0	28.9
6	121.9	74.7	55.8	56.0	23.2	23.3	21.0	21.0

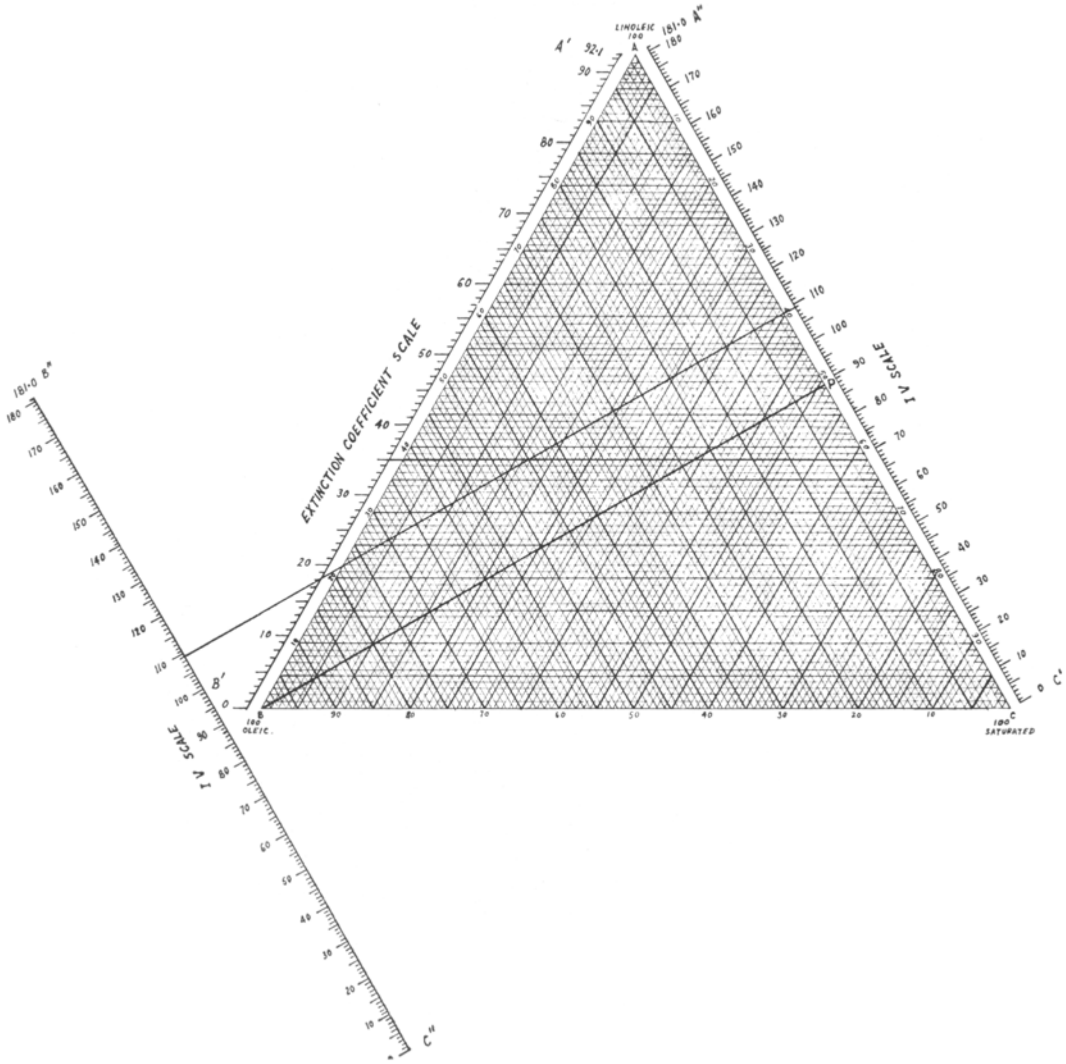

FIG. 1. Nomograph for calculating fatty acid composition from iodine values and extinction coefficients.

value of 96.7 at A, it will be clear by the property of the triangle that a line such as BT joining the apex B and a point T on the scale corresponding to a value of 89.3, will represent a constant thiocyanogen value. Also any line parallel to BT, drawn across the triangular diagram, will similarly indicate the *locus* of compositions of a constant thiocyanogen value. Two scales, NN′ and MM′, conveniently spaced, are drawn for the thiocyanogen values so that corresponding points on joining will give constant thiocyanogen value lines parallel to BT. Given the iodine value and the thiocyanogen value for a mixture, the point of intersection in the triangular diagram of the corresponding constant iodine value and thiocyanogen value lines will fix the desired composition.

The nomograph given in Figure 2 is constructed on the above principles. For determining the fatty acid composition from the iodine and thiocyanogen values, spot the iodine value (say 112.0) on scale A″C′ and spot the same value on the parallel scale A′B′. The line joining the two spots gives the constant iodine value line. Now similarly spot the thiocyanogen value (say 78.7) on the scale NN′ and the corresponding value on the parallel scale MM′. The line joining the two spots indicates the constant thiocyanogen value line. The point of intersection of these lines on the triangular diagram fixes the desired composition (39.2% linoleic acid, 45.6% oleic acid, 15.0% saturated and unsap.).

2. Nomograph for Determination of Fatty Acid Composition on the Basis of Extinction Coefficient at 268 mμ and at 233 mμ and the Iodine Value When Linolenic Acid Is Present

The nomograph for this system is given in the usual rectangular structure since the fatty acid mixture containing four components cannot be represented graphically as in the previous cases.

The algebraic equations for the calculation of the fatty acid composition are

% linolenic acid,

$$x = \frac{K_{268}}{50.7} \times 100 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (V)$$

Where K_{268} is the observed extinction coefficient at 268 mμ and 50.7 mμ the standard extinction coefficient for pure linolenic acid, alkali-isomerized at 180°C. for 25 minutes, using ethylene glycol air technique (1).

$$K_{233} = K_{T_{233}} - 1.215\,K_{268} \quad . \; . \; . \; . \; . \quad (VI)$$

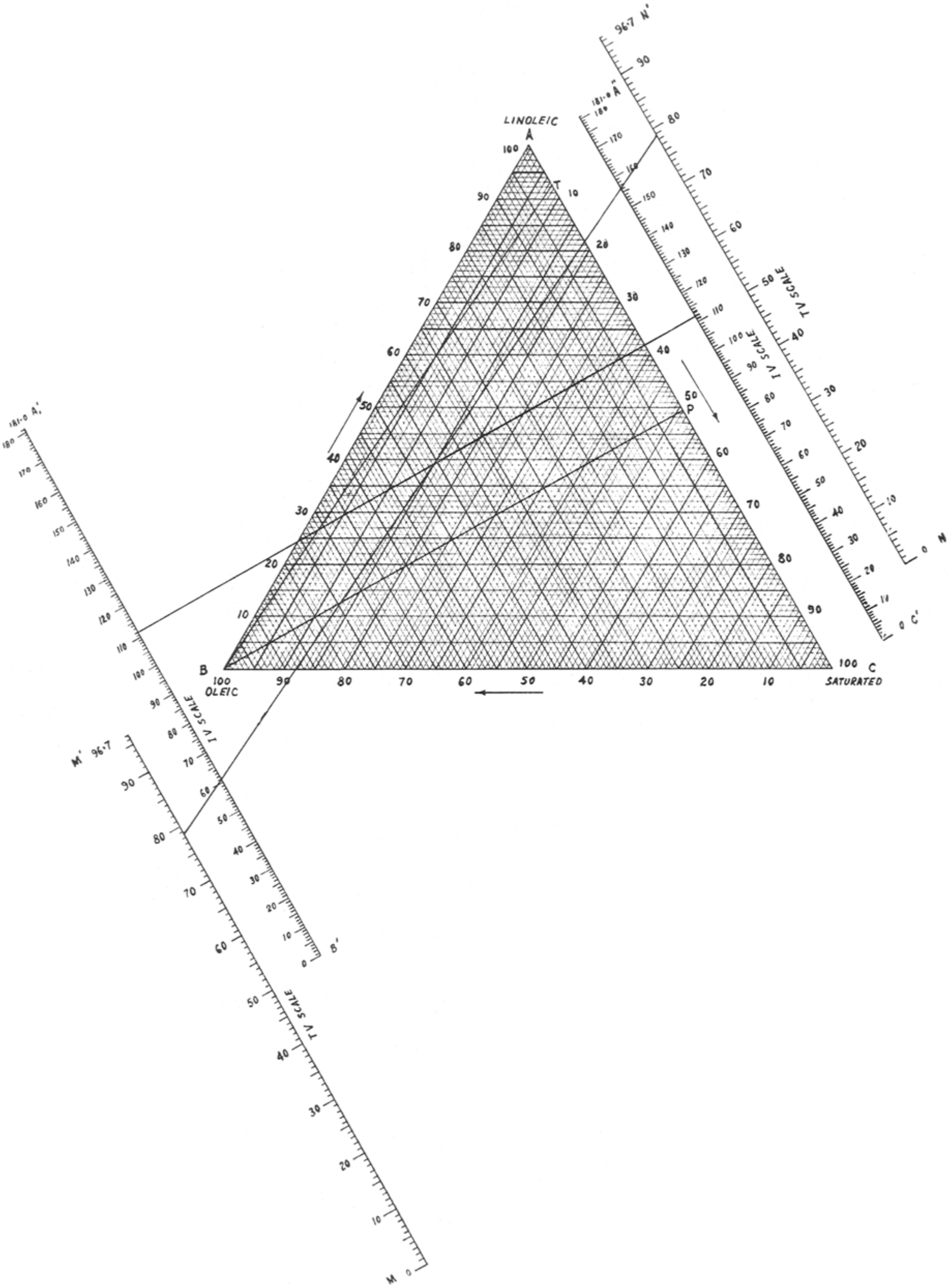

FIG. 2. Nomograph for calculating fatty acid composition from iodine and thiocyanogen values.

Where K_{233} is the extinction coefficient due to linoleic acid and K_{T233} is the total observed extinction coefficient at 233 mμ (due to both linolenic and linoleic).

% linoleic acid,

$$y = \frac{K_{233}}{92.1} \times 100 \quad \text{(VII)}$$

% oleic acid,

$$z = \frac{IV - (2.736x + 1.80y)}{0.8987} \quad \text{(VIII)}$$

Where IV is the iodine value of the mixed fatty acids.

% saturated acids, $s = 100 - (x + y + z)$ (IX)

TABLE III

Composition of Fatty Acid Mixtures Calculated from Equations V, VI, VII, VIII, and IX and from Nomograph Shown in Figure 3

No.	Ext. coefft. 268 mμ	Ext. coefft. 233 mμ	Iodine value	Linolenic acid, %		Linoleic acid, %		Oleic acid, %		Satd. acids & unsap., %	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1	29.4	57.2	209.1	58.0	58.0	23.3	23.3	9.3	9.4	9.4	9.3
2	14.96	54.0	164.8	29.5	29.4	38.9	39.0	15.2	14.2	16.4	17.4
3	20.7	28.7	124.2	40.8	40.9	3.9	4.0	6.2	5.8	49.1	49.3
4	39.7	57.7	237.9	78.3	78.6	10.3	10.8	5.6	5.6	5.8	5.0
5	7.6	81.2	182.6	15.0	15.1	78.2	78.5	0	0	6.8	6.4
6	10.0	39.9	131.6	19.8	19.8	30.2	30.3	25.3	25.0	24.7	24.9

On the basis of the above equations a nomograph can be easily constructed with the conventional methods of the *moduli* and the spacings. Therefore the construction of the nomograph and its use are described without elaborating on the calculations involved in its construction.

The alignment chart consists of five vertical scale lines on the same horizontal base (Figure 3). The scale AA′ is of convenient height, say 10 in., and carries scale markings from 0 to 50.7 for extinction coefficients at 268 mμ on the left side and scale markings from 0 to 100 for the corresponding linolenic acid percentage on the right hand side according to the equation (V). The scale line CC′ is also 10 in. high and spaced at any convenient distance from the scale line AA′ (say 5 in.). The line CC′ carries the common scale markings from 0 to 100, indicating both percentage of linoleic and percentage of oleic acid. The scale line BB′ carries the markings 0 to 92.1, indicating the extinction coefficient at 233 mμ. The spacing, the *modulus,* and the height of this line are calculated on the basis of equation (VI), namely, that the extinction at 233 mμ is additive for the extinction coefficients of the linolenic and linoleic acids. It will therefore be spaced at a distance of 2.996 in. from AA′ and will be 5.992 in. high. The line joining the point A, representing 0% linolenic at the point C′, representing 100% linoleic, will pass through B′, representing a 92.1 extinction coefficient at 233 mμ, corresponding to 100% linoleic acid. It will be clear that a line drawn through the given extinction coefficients at 268 mμ on AA′ and 233 mμ on BB′ will cut CC′ at a point giving the desired linoleic acid percentage.

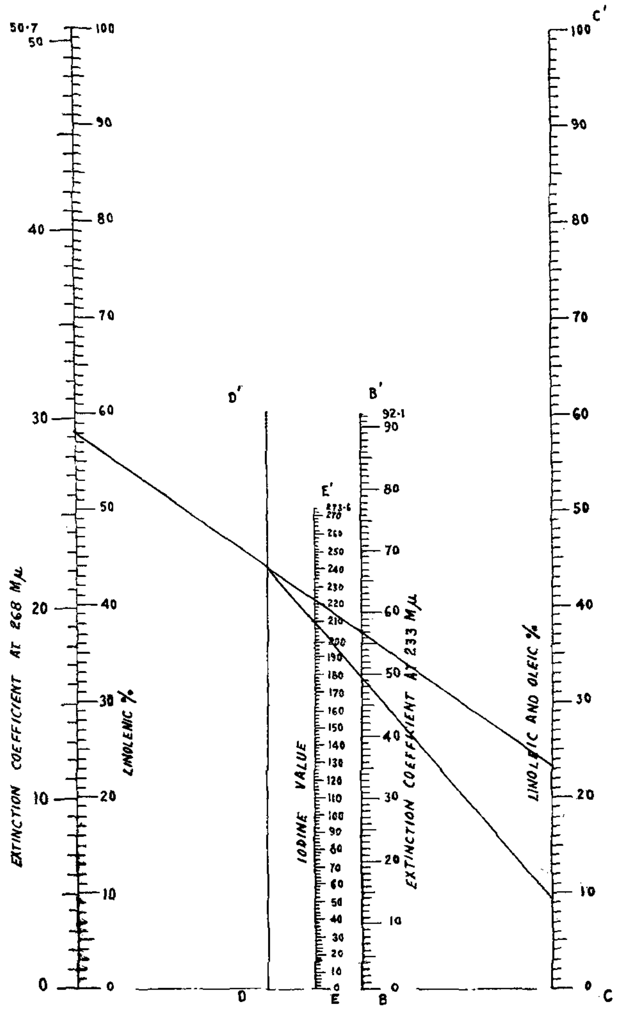

FIG. 3. Nomograph for calculating fatty acid composition from extinction coefficients at 268 and 233 mμ and iodine value.

Knowing the linolenic and linoleic acid percentages, it is now necessary to construct scales to determine the percentage of oleic acid on the basis of iodine value. For this purpose a reference line DD′ is constructed, which is spaced at 1.991 in. from AA′ and of such height that the line joining points A′ and C pass through D′. Just as the line BB′ is additive for the extinction coefficients, the line DD′ is additive for the iodine equivalents

$$\left(\frac{\text{IV} \times \% \text{ fatty acid}}{100}\right)$$

of the linolenic and linoleic contents. In between DD′ and CC′, the iodine scale EE′ may now be placed at a distance of 0.4949 in. from DD′ and 5.0240 in. high, carrying the scale marking from 0 to 273.6, this being the iodine value of 100% linoleic acid. It will be clear from detailed calculations that a line from the point of intersection between DD′ and the line previously drawn across AA′, BB′, and CC′, to determine the linoleic acid percentage, to the point of given iodine value on the scale EE′, when extended to CC′, will *determine* the oleic acid percentage on the scale CC′.

The use of the nomograph can now be described. Spot the given extinction coefficient at 268 mμ (say 29.4) on line AA′, which will also give the linolenic acid percentage (58.0) on the same scale. Similarly spot the given extinction coefficient at 233 mμ (say 57.2) on BB′. Join the two, intersecting DD′, and extend to CC′, which will give the desired linoleic acid percentage (23.3). Now join the point of intersection on DD′ with the given iodine value (say 209.2), spotted on EE′, and extend to CC′, which will give the oleic percentage (9.3) on the right hand side.

It will be seen that this chart can also be used for determining the fatty acid composition when linolenic acid is absent, *i.e.*, for the case 1(A), previously described, provided that in all determinations the point A and the scale AA′, corresponding to 0% linolenic acid, is used in drawing the lines.

In Tables I, II, and III are given the calculated and observed values as read from the charts. The differences observed between the observed and calculated values are to be ascribed entirely to the limitations of manual skill in the drawing of the alignment charts and its convenient magnification. With accurately drawn scale markings and suitable magnification of the scales it is possible to secure reading accuracy very nearly approaching the mathematical accuracy behind construction of the chart.

Summary

Very few alignment charts are available which can be used for routine calculations in fat analysis and processing. Three alignment charts are presented in this communication for determining the fatty acid composition of a fatty acid mixture consisting variously of linolenic, linoleic, oleic, and saturated fatty acids or glycerides, incorporating for accuracy, data based on ultraviolet extinction coefficients. In two of the charts triangular diagrams have been used as a novel feature in nomography to give directly the fatty acid composition.

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Several Rare and Uncatalogued Oils of Ecuador

ROZIER D. OILAR, Consultant for Latin America, 1213 North Street, West Lafayette, Indiana

ONLY about three countries of South America have an exporting supply of native vegetable oils. Most of them are importers to a greater or lesser extent. All types of oil-bearing seeds and nuts are used in many of the other countries, and many have indigenous oil seeds that would be classed as rare and are little known in our well supplied countries and are, in general, uncatalogued.

This is the situation in Ecuador, which has but scant quantities of the usual oil seeds and must extend its supply by any and all seeds and nuts that will yield oils and fats. So we shall describe some of these oils and their nuts and seeds, adding a few which, although described by Jamieson *et al.*, are not commonly known but are of great importance.

In Manta, state of Manibi, Ecuador, in a new oil mill and refinery we produced oils from nuts and seeds of the following indigenous trees and plants, with their local name, family, and genera in that order:

Brazilargo of *Myristicaceae* family, genera not given, is a tree producing a roundish, slightly oval, thin-shelled seed with a kernel 1.5 by 2.5 cm. in size, its cross-section of white meats are speckled with brownish, chocolate-colored spots. There is a limited supply of this tree and nuts. The kernel contains some 60% of a very dark to blackish crude fat in its melted form, yellowish brown when solidified. On filtering, the color is more reddish brown and brownish yellow, respectively. It has a toasted flavor. The press room samples of crude have F.F.A. of 14 to 15% as oleic or 10% as lauric acid. The oil has a melting point (M.P.) of 46 to 47°C.

Caracolillo (Carcoli) of *Anacardiaceae* family and *Anacardium excelsum* genera, is a tree bearing a fruit with a seed that has a kernel 1 by 1.5 cm. in size, the cross-section of whose white meats is striated with chocolate color stripes. The kernels contain some 50% fat of reddish brown color in the melted form and yellowish brown in solidified form, quite similar to the Brazilargo oil. The Expeller sample tested F.F.A. of 11% as oleic, or 7.7% as lauric acid. The M.P. of fat is 47 to 48°C.

Chapil (Deopa) of *Palmae* family, genera not given, is a tree with a fruit similar to the Palm Real containing one edible coquito-like nut and is not very plentiful. It is known mainly for its wood. Few other data are available. The seed yields a liquid type of oil (only a slight amount of stearine at 18°C.), crude color around 25Y/20R Lovibond scale, with an agreeable flavor. The press room sample tests F.F.A. of 9.5% oleic acid. It is said the leaves of this tree carry a wool or fiber used by the natives for gun wads.

Guangara of *Myristicaceae* family and *Dial-yanthera gordoniaefolia* genera, is a tree, producing a roundish, thin-shelled brown nut 2 by 2.5 cm. in size, weight 3 gms., somewhat similar to the nutmeg. The cross-section shows light chocolate-colored meats. The nuts produce some 40% fat of dark brown color when melted and pale brownish yellow when solidified and refines to an unusual pinkish red oil or pinkish color when solidified. The Expeller samples test F.F.A. of 16% as oleic or 11% as lauric acid. The fat has a M.P. of 43 to 44°C.

There is some confusion as to the international botanical classification of Tangare (Figuarae) of *Meliaceae* family, *Carapa guianensis* genera, which is very probably the Andirobe of Brazil, listed by Jamieson as *C. tulucuna*. It is a tree whose seeds are 75% kernel with a solid, light chocolate-color cross-section, which, on drying, shrivel to an odd flattened shape like large candied figs and measure 3 by 5 cm., weigh up to 15 gm., yielding some 45% inedible fat of reddish color when melted and pale brown when solidified, with a bitter flavor. The F.F.A. from the press room is very high, 30-40%, and higher as oleic acid, but samples were not usually straight Tangare as the seed is usually mixed with meal of other seed for better pressing. The F.F.A. of a filtered sample was 51% as oleic or 36% as lauric acid. The fat has a M.P. of 38-39°C. Book data gives Saponification No. 198 to 200, Iodine No. 58 to 75, and Titre of Fatty Acids 35 to 37°C. (1).

Tagua (Cady) of *Palmae* family and *Pytelephas macrocarpa* genera (some say *P. acquatorialis*) is an unusual palm for its products. This tree bears a very large fruit, 25 by 40 cm. (10 by 15 inches) in size, which contains several large seeds enclosed in a pulp which, when dried like copra, is a pale brownish color and yields 35 to 38% semi-liquid type of edible oil. This crude oil is reddish yellow when melted and light golden yellow in solid form, is heavily stearinated at 20°C. but entirely melted at 29 to 30°C., and is quite similar to a high stearine natural cottonseed oil. It refines to around 35Y/7.6R on Lovibond scale and bleaches to 20Y/2.5R slightly greenish color. The flavor is normal, slightly bitter in the crude form. The F.F.A. from the press room tests 10 to 12% up to 20 to 30% as oleic acid and has a Sap. No. of 202 (2). This appears to be the first commercial production of Tagua oil since this tree is known for its seed or nuts which, when young and tender, are used as food but on maturity become the very hard Vegetable Ivory of commerce and are sold the world over for making buttons, novelties, marbles, and even billiard balls. These nuts are an important export article of Ecuador.

Palma Real of *Palmae* family and *Cocus butyriaceae* genera is not the Royal Palm *(roystonea regia)* or palm kernels *(claes guincensis)* listed by Jamieson as *Ynesis colenda*. These nuts