Acknowledgment

The authors wish to express their appreciation to Kenneth M. Decossas for drawing the graphs shown in this paper.

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[Received June 4, 1951]

The Hydrogen Value—Refractivity Relationship of Unsaturated Fatty Acids of Natural Origin

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IN a previous paper (2) the authors have shown that a relationship exists between the refractive indices and the unsaturation value (iodine or hydrogenation value) of unsaturated fatty esters derived from cod liver oil, haddock liver oil, and sardine oil. When the refractive indices were plotted against the hydrogenation values, a straight line D_1H (Fig. 1) was obtained; this line remained unbroken until a point H, corresponding with the C_{22} hexaene acid, was reached, after which it continued in a new direction. The curve was directly applicable to pure individual esters as well as to unresolved fractions unless the latter contained components belonging to the different branches of the curve. It was stated that "whatever the precise significance of the hydrogen value/refractivity curve, the latter appears to offer direct and trustworthy empirical indication as to whether a product is an original component or only a secondary one."

Since the publication of this paper, some pure methyl esters of unsaturated fatty acids have been derived from natural materials of widely different origins. The experimental conditions under which they were prepared offer a good guarantee as to the original structure being conserved. Their constitution is well established, and they cover a wide range of unsaturation.

It is the purpose of this paper to show that the refractive indices published for these products as well as their unsaturation values also verify the line D_1H of the graph shown in Figure 1 (l.c.).

This line is defined by the co-ordinates of the two points D_1 and H:

$$D_1\begin{cases} n_D^{20} = 1.4589 \\ \text{H.V.} \times 100 = 120 \end{cases} \qquad H\begin{cases} n_D^{20} = 1.4930 \\ \text{H.V.} \times 100 = 355 \end{cases}$$

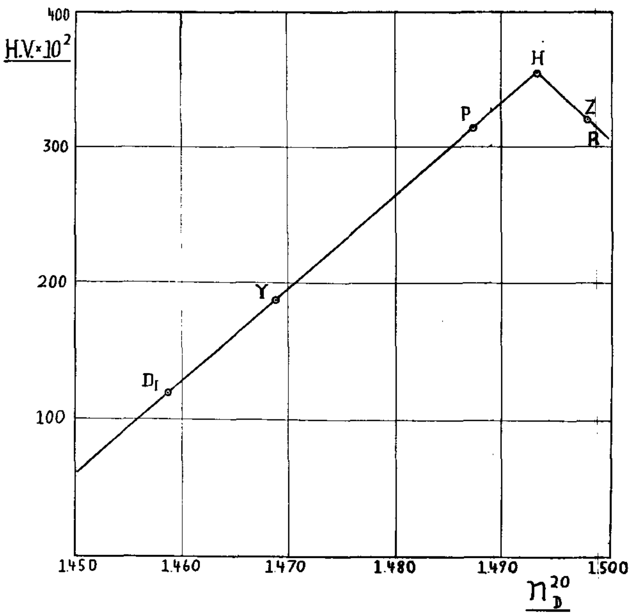

FIG. 1.

From the equation of this line the following empirical expression can be derived:

$$n_D^{20} = 1.44163 + \text{H.V.} \times 0.0145 \qquad \text{(I)}$$

In this expression H.V. represents the hydrogenation value (mg. of hydrogen necessary to saturate 1 g. of compound). The iodine value is linked to the hydrogenation value by the following simple relationship:

$$\text{H.V.} = \text{I.V.}\,\frac{1.008}{126.93} = \text{I.V.} \times 0.79414 \times 10^{-2} \qquad \text{(II)}$$

In Table I are listed a series of methyl esters, their origin, and method of isolation.

TABLE I

Source and Method of Isolation of Unsaturated Methyl Esters

Sample No.	Name — Methyl:	Source and Method of Isolation	Reference
1	Oleate (9-octadecenoate)	From olive oil by the fractional crystallization method.	(6)
2	Petroselinate (7-octadecenoate)	From coriander seed oil by fractional crystallization.	(1)
3	Linoleate (9, 12-octadecadienoate)	From tobacco seed oil by chromatographic separation on silicic acid.	(7)
3a	Linoleate (9, 12-octadecadienoate)	From cotton seed oil through debromination followed by molecular distillation.	(9)
3b	Linoleate (9, 12-octadecadienoate)	From cottonseed oil through the same process as 3a.	(6)
3c	Linoleate (9, 12-octadecadienoate)	From cottonseed oil by chromatographic separation on alumina.	(8)
4	Linolenate (9, 12, 15-octadecatrienoate)	From Linseed oil by chromatography on silicic acid.	(7)
4a	Linolenate (9, 12, 15-octadecatrienoate)	From Linseed oil by debromination followed by molecular distillation.	(9)
4b	Linolenate (9, 12, 15-octadecatrienoate)	From Linseed oil by the same method as 4a.	(6)
5	Arachidonate (6, 10, 14, 18-eicosatetraenoate)	From beef suprarenal gland lipids by fractional crystallization.	(4)
6	Docosahexaenoate	From cod liver oil, haddock liver oil, and sardine oil, by molecular distillation.	(3)

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In Table II are listed the I.V. and refractivities published for the same samples; their H.V. calculated from the I.V. using relation (II). In two cases (Samples 3 and 4) the refractivities were given for 25°C., and it was necessary to extrapolate for 20°C., using the known increment: 0.00038/degree (6, 10).

TABLE II

Comparison Between Actual and Calculated Refractive Indices n_D^{20} of the Samples of Methyl Esters Listed in Table I

No.	I.V.	H.V.	n_D^{20}		Deviation
			Calculated	Actual	
1	86	68	1.4515	1.4517	—0.0002
2	86	68	1.4515	1.4508	+0.0007
3	173	137	1.4615	1.4611	+0.0004
3a	173	137	1.4615	1.4613	—0.0002
3b	173	137	1.4615	1.4616	+0.0001
3c	173	137	1.4615	1.4613	—0.0002
4	260	207	1.4716	1.4726	—0.0010
4a	260	207	1.4716	1.4709	+0.0007
4b	260	207	1.4716	1.4711	+0.0005
5	319	253.5	1.4784	1.4798	—0.0014
6	445	355	1.4930	1.4930	+0.0000

Table II shows moreover the values of n_D^{20} calculated by expression (I). The calculated values show little deviation from the experimental one.

There remains little doubt that the relationship expressed by relation I indicates definite structural characteristics common to all the esters examined; any material which does not follow this rule must be structurally different or must contain appreciable amounts of structurally different material. This latter type of material would be represented by points falling below the line D_1H, and these must include the points situated on the HR branch of the curve shown on Fig. 1.

The new evidence strongly supports the views expressed previously and confers an enhanced interest on the hydrogenation value/refractivity relationship of naturally occurring unsaturated fatty acids.

It is very likely that similar relationships exist between the unsaturation values and the refractive indices of other esters of the unsaturated, naturally occurring fatty acids. These would include the glycerides or mixtures of glycerides.

It is interesting to note in this connection that empirical relationships between I.V. and refractive indices have been found for samples of oils of natural origin (5), but these are not to be confused with the relationship described by the present paper. The relationship for natural oils varies with the type of oil and is only applicable within narrow limits. The presence of variable proportions of saturated constituents accounts for this behavior.

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[Received June 11, 1951]

Lye-Dipping for the Removal of Objectionable Skin Color From Various Grades of Shelled Spanish Peanuts

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MUCH interest has been shown in the production of solvent-extracted meals and light-colored proteins from peanuts (2, 3) for nutritional and industrial applications. By their presence red peanut skins discolor meals, and the pigments in such skins impart a dark brown color to protein during processing. These color difficulties may be avoided by using white-skinned peanuts (5), but their availability is limited. Light-colored proteins may be produced by controlling the pH at which they are precipitated (7), and still lighter proteins (cream color) may be produced by treating the kernels with a dilute solution of sodium hydroxide for removal of objectionable skin color (3, 4).

Pilot-plant work on peanut kernels and oil and protein losses, using the sodium hydroxide treatment on 100-g. portions of kernels, have been reported by Burnett (3). The present paper reports on the application of the sodium hydroxide treatment, commonly referred to as lye dipping, to large amounts of the three commercial grades of shelled Spanish peanuts. Data are given on oil and protein losses of these kernels after treatment, and on the protein solubility of materials from various steps involved in the preparation of solvent-extracted meal from the original shelled kernels. Information is included on the color of proteins prepared from meals produced by solvent extraction of treated kernels.

Materials

Commercial U. S. No. 1 shelled Spanish peanuts were used in an initial series of tests of several dilute sodium hydroxide treatments. Upon completion of these tests another lot of U. S. No. 1 plus lots of U. S. No. 2 and oil mill stock shelled Spanish peanuts were evaluated using a common method of lye treatment. Spanish peanuts were used in both series since this type is the most widely distributed in this country.

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