Relation Between The Refractive Index And Iodine Number Of Raw Linseed Oil

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Though it is generally recognized that there are definite relations between the chemical and physical constants of aliphatic fatty acid oils and fats which are influenced in certain directions by differences in the chemical construction of the oils and fats, not much use has been made of the refractive index except as an aid in detection of adulteration and in classification. Various workers have observed that there is a close association between the refractive index and the iodine number. This should naturally follow from the theories of molecular refraction wherein unsaturation is considered an additive factor with respect to both of these constants.

Lund (1)* observed that the specific gravity, saponification number, refractive index and iodine number of the glycerides and their fatty acids may be mathematically correlated. The melting point could not be so closely linked with the other constants. He found that in equal mixtures of two fats the melting point, specific gravity, and refractive index were always the average for the two fats, which suggests that the constants for these mixtures of varying proportions follow a straight line relationship. Lund's expression for the mathematical relation between the refractive index ($n\frac{40°}{D}$) and the iodine number (I. No.) including the saponification number (S. No.) in the expression was:

$$n\frac{40°}{D} = 1.47020 - .000129 \text{ (S. No.)} + (.00009 \text{ to } .00011) \text{ (I. No.)}$$

Pickering and Cowlishaw (2) derived an expression taking into account both the saponification number and the acid number (A. No.),

$$n\frac{40°}{D} = 1.4643 - .000066 \text{ (S. No.)} - .0096 \left(\frac{\text{A. No.}}{\text{S. No.}}\right) + .0001171 \text{ (I. No.)},$$

and for linseed, soybean, cottonseed, and peanut oils having very low acid numbers and small variations in the saponification numbers presented the simple expression:

$$n\frac{40°}{D} = 1.4515 + .0001171 \text{ (I. No.)}$$

For hydrogenated cottonseed, linseed, arachis, sesame, and sardine oils, and bassia tallow, Tate and Pooley (3) found the relation:

$$n\frac{60°}{D} = 1.4468 + 1.03 \times 10^{-4} \text{ (I. No.)} + 7.3 \times 10^{-8} \text{ (I. No.)}^2$$

to have an accuracy of ± .0005 in refractive index.

From studies made on the triglycerides of aliphatic fatty acids, Backer (4) proposed the following empirical relation for the specific refraction (R).

$$100R = \left(\frac{n^2 - 1}{n^2 + 2} \times \frac{100}{d^t_4}\right) = 33.07 + .00075 \text{ (I. No.)} - .01375 \text{ (S. No.)} + .002 (t - 15).$$

The specific refraction is considered as being governed by the degree of unsaturation and the size of the molecule and may be best calculated by use of the formula of Lorenz and Lorentz from the refractive index and is independent of temperature.

Wolff (5) confirmed the relations experimentally established by Lund (1) on purely theoretical grounds, assuming only that the molecular refraction suffers no unusual exaltation. Starting with the number of CH_3, CH_2, CH and COOH groups and their molecular weight in a fatty acid, he derived the following expression which gives the relation for refractive index (n), density (d), acid number (A. No.) and iodine number (I. No.).

$$n = 1 + d\,(.5557 - .00022 \text{ A. No.} + .000035 \text{ I. No.})$$

Sudborough, Watson and Athawale (6) found the curves representing the relation between the refractive index and the iodine number for hydrogenated cottonseed, linseed, peanut, mahua, sesame, and sardine oils to lie very close together and may be represented by the equation

$$n\frac{60°}{D} = 1.4468 + 1.03 \times 10^{-4} \text{ (I. No.)} + 7.3 \times 10^{-8} \text{ (I. No.)}^2$$

having an accuracy of about 0.0005. The refractive indices at 60° C. of these oils when completely hardened were found to be practically identical at the value of 1.4468.

According to Cheneveau (7) the difficulties encountered in the practical application of the relation,

$$n = 1 + a + b \text{ I. No.},$$

in which a and b are constants, are due more particularly to incomplete knowledge of the refractive indices of the glycerides and of the glycerides themselves.

It is observed (1, 2, 4, 5) that the relations apply only to the fats containing fatty acids, saturated and unsaturated, liquid and solid, that belong to the general aliphatic series, and do not apply to those containing cyclic groups, hydroxy and isomeric acids, or double-bonds causing unusual exaltation of the refractive index.

The refractive index is lowered (1, 2) by free fatty acids or acidity and raised by oxidation and polymerization. Since the change caused by oxidation and polymerization is the greater the net result is that the refractive index rises on storage of the oil, particularly when stored in a warm, light place.

Experimental

In order to determine and make practical use of the relation between the refractive index and the iodine number (Wijs) of raw linseed oil consideration was first given to procedures for grinding and pressing the oil from the seed and filtering and storing the oil after expression.

The seed was ground with six by six inch (40 corrugations per inch) roller mill. The rolls were run at 400 to 600 revolutions per minute and set close enough to pull a piece of medium carbon paper from the hand. The oil was pressed from the meal with a laboratory hydraulic press. A small amount of filter aid was mixed with the oil and the oil filtered by suction through an asbestos mat in a Gooch crucible supported by a bell jar and collected in small bottles. The samples were stored under refrigeration.

For rapid routine work in quantity, cold pressing was too slow and

*Figures in parentheses refer to literature citations.

tedious. A warm pressing procedure was adopted in which the meal was heated without stirring in a beaker suspended in a steam bath for not more than 20 minutes and then pressed. The hot plates of the press between which the pressing cylinder was placed were maintained at a temperature between 60° and 70° C. A 2¼ inch test cylinder was used and not more than 75 grams of the meal pressed at a time.

In practice the flaxseed contained usually less than 8 per cent moisture. As the seed was not tempered with moisture, before or after grinding, to increase the oil yield a relatively moisture-free oil was obtained.

The iodine number was determined by the Wijs method observing all precautions of the official procedure and allowing one hour for reaction. Carbon tetrachloride was used as the oil solvent. The refractive index was determined by use of an Abbe refractometer, keeping the prisms as near to 25° C. as possible and using a correction factor of .00037 for each degree divergence. The average of ten readings was taken as the final value.

Comparative results (Table I) for the two methods of pressing the oil from the meal show that in the large majority of 26 samples that the difference in the iodine numbers (Wijs) and the refractive indices were within reasonable experimental error.

TABLE 1—COMPARISON OF IODINE NUMBERS (WIJS) AND REFRACTIVE INDICES (25° C.) OF COLD AND WARM PRESSED LINSEED OIL

	Iodine Number (Wijs)			Refractive Index (25° C.)		
Sample	Cold Pressed	Difference	Warm Pressed	Cold Pressed	Difference	Warm Pressed
1	187.2	+0.6	186.6	1.47967	.00012+	1.47979
2	183.7	+0.1	183.6	1.47912	.00011+	1.47923
3	182.5	+1.1	181.4	1.47917	+.00002	1.47915
4	182.5	0.7+	183.2	1.47929	+.00005	1.47924
5	180.6	1.1+	181.7	1.47900	.00008+	1.47908
6	180.5	0.5+	181.0	1.47889	.00024+	1.47913
7	179.6	0.7+	180.3	1.47879	.00016+	1.47895
8	179.0	+1.4	177.6	1.47844	+.00005	1.47839
9	178.9	0.0	178.9	1.47874	.00026+	1.47900
10	178.0	+1.7	176.3	1.47826	.00018+	1.47844
11	177.8	1.2+	179.0	1.47857	.00005+	1.47862
12	176.5	0.1+	176.6	1.47839	.00010+	1.47849
13	176.4	+0.4	176.0	1.47834	.00000	1.47834
14	176.2	0.0	176.2	1.47826	.00004+	1.47830
15	175.6	+1.0	174.6	1.47812	.00018+	1.47830
16	174.8	0.8+	175.6	1.47814	.00002+	1.47816
17	174.0	0.2+	174.2	1.47807	.00004+	1.47811
18	173.6	+1.2	172.4	1.47798	.00001+	1.47799
19	173.6	+0.6	173.0	1.47800	+.00007	1.47793
20	170.3	+0.8	169.5	1.47757	+.00010	1.47747
21	170.0	+0.8	169.2	1.47748	.00000	1.47748
22	169.1	+0.7	168.4	1.47742	+.00004	1.47738
23	168.6	+1.2	167.4	1.47723	.00014+	1.47737
24	167.6	+ .4	167.2	1.47717	.00002+	1.47719
25	167.0	1.5+	168.5	1.47725	.00020+	1.47745
26	165.0	1.3+	166.3	1.47716	.00007+	1.47723
Average	175.7	.77[1]	175.6	1.47825	.000090[1]	1.47832

[1]Without regard to sign.

Tests on oil from the first and last flow from the cake showed no appreciable differences. This probably results from the fineness of grinding of the seed.

During the course of experimental work on flaxseed from climatic study and breeding work a large number of samples of oil have been examined. Table 2 gives a sum-

TABLE 2—DISTRIBUTION OF SAMPLES OF LINSEED OIL AND RANGE IN AND AVERAGE OF THEIR REFRACTIVE INDICES ACCORDING TO THEIR IODINE NUMBERS (WIJS).

Number of samples	Iodine Number (Wijs)	Refractive Index 25° C. Range	Average
4	144	1.47417-1.47421	1.47420
1	145	....	1.47464
2	146	1.47462-1.47483	1.47472
3	147	1.47468-1.47496	1.47479
3	148	1.47477-1.47499	1.47489
5	149	1.47488-1.47504	1.47499
4	150	1.47489-1.47504	1.47500
3	151	1.47508-1.47519	1.47512
8	152	1.47508-1.47522	1.47515
5	153	1.47514-1.47526	1.47519
7	154	1.47525-1.47580	1.47553
13	155	1.47536-1.47587	1.47564
9	156	1.47554-1.47586	1.47572
15	157	1.47563-1.47622	1.47594
13	158	1.47579-1.47621	1.47598
28	159	1.47594-1.47647	1.47615
14	160	1.47600-1.47639	1.47619
12	161	1.47596-1.47644	1.47623
12	162	1.47629-1.47670	1.47648
17	163	1.47625-1.47689	1.47665
19	164	1.47632-1.47720	1.47677
25	165	1.47655-1.47700	1.47681
26	166	1.47664-1.47735	1.47699
39	167	1.47683-1.47737	1.47705
53	168	1.47689-1.47742	1.47711
47	169	1.47703-1.47775	1.47729
60	170	1.47700-1.47787	1.47730
50	171	1.47699-1.47795	1.47749
51	172	1.47719-1.47804	1.47762
46	173	1.47740-1.47812	1.47776
64	174	1.47744-1.47822	1.47788
52	175	1.47759-1.47842	1.47797
60	176	1.47777-1.47844	1.47808
58	177	1.47785-1.47856	1.47813
53	178	1.47800-1.47869	1.47824
63	179	1.47799-1.47885	1.47839
53	180	1.47818-1.47898	1.47857
67	181	1.47827-1.47915	1.47873
55	182	1.47844-1.47919	1.47884
51	183	1.47844-1.47929	1.47893
56	184	1.47858-1.47941	1.47902
44	185	1.47880-1.47939	1.47908
39	186	1.47899-1.47946	1.47919
37	187	1.47900-1.47967	1.47931
39	188	1.47907-1.47973	1.47942
24	189	1.47937-1.47984	1.47960
22	190	1.47933-1.47998	1.47966
15	191	1.47948-1.48009	1.47978
16	192	1.47955-1.48025	1.47999
8	193	1.47971-1.48032	1.48004
10	194	1.48003-1.48026	1.48012
3	195	1.48012-1.48026	1.48018
2	196	1.48046-1.48048	1.48047

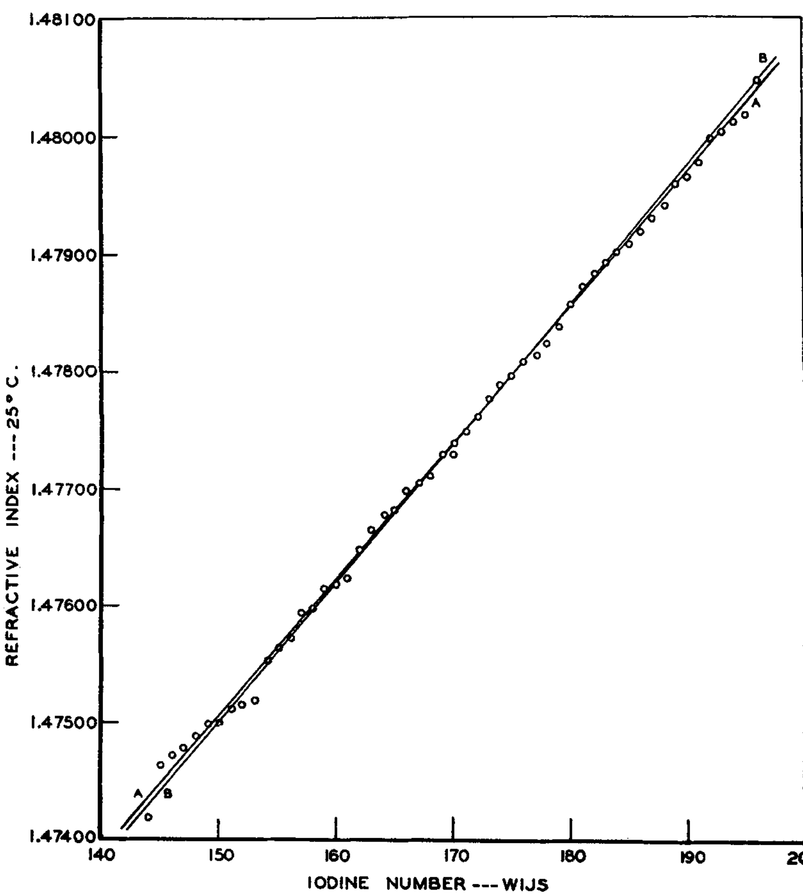

FIGURE 1.

mary of the data for 1485 samples varying in iodine number from 144 to 196 and in refractive index from 1.47420 to 1.48047.

The mathematical relation between the two constants (Fig. 1) was calculated by the "Least Squares" method (8). The equation for the regression of the refractive index on the iodine number was

$$\text{(A)}\quad n_{D}^{25^\circ} = 1.45769 + .000115815 \text{ Iodine Number}$$

and the transposed equation for the regression of the iodine number on the refractive index

$$\text{(B)}\quad n_{D}^{25^\circ} = 1.45723 + .00011846 \text{ Iodine Number}$$

The correlation coefficient of the relation was .98874, having a probable error of ±.00039. The standard error of estimate of the refractive index was ±.0001718 and of the iodine number ± 1.4672.

Both relations are very close to the empirical short equation of Pickering and Cowlishaw (2) reduced to 25° C. conditions assuming that the temperature does not affect the increment of change.

Barring changes resulting from adverse conditions of storage of the flaxseed, the procedure developed for pressing the ground flaxseed and preparing and reading the oil samples gives reproductible and satisfactory estimation of the iodine number of raw linseed oil from the refractive index. The relation has been used for four years in evaluating the linseed oil quality of large numbers of samples from breeding trials and is considered sufficiently accurate for the purpose. Caution must be taken to prevent acidity and in particular, polymerization and oxidation of the raw linseed oil.

Summary

A procedure for obtaining linseed oil from flaxseed which gives reproductible results has been developed and the empirical relation between the refractive index and the iodine number (Wijs) of the oil so obtained has been calculated. This relation is thought sufficiently reliable for certain needs, where closest accuracy is not required.

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PATENTS FOR CHEMISTS*

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THIS is a discussion of certain points relating to patents of especial interest to a chemist rather than a lawyer.

A patent is in the nature of a contract between the inventor and the people of the United States. Its object is to promote invention, and for this purpose it secures to the inventor the sole right to use his invention for the term of seventeen years in return for his making a full disclosure of it to the public. The term of a patent cannot be extended beyond seventeen years except by a special act of Congress, which, of course, has been very rarely exercised.

While, in a sense, a patent gives a sort of monopoly to the inventor, it is not an ordinary monopoly in the sense of taking away from the public anything that the public previously enjoyed. On the contrary, it eventually gives to the public something it did not have before. For example, machine made shoe, vulcanized rubber, aluminum, machine weaving, and Bessemer steel, are a few of many examples of patented inventions which were exploited without oppression to the public, and reduced rather than increased the cost of living.

It should be noted that the government does not itself prevent others from using the patented invention, but merely gives to the inventor the right to protect himself. His recourse in case of infringement is through the courts and if he does not see fit to initiate court action to protect his invention, the government will not do so for him. Patents for really worth while inventions are very apt to be tested in court, so it is often said that no patent can be considered valid until it has been upheld in court. Unlitigated patents, however, may be just as valid and a mere threat of an infringement suit is often effective in stopping infringement and even in bringing in royalties. It is often cheaper or better policy for a possible infringer to take a license and pay a reasonable royalty than to get involved in expensive litigation. Patents and the rights under same are covered by numerous statute laws and also numerous court decisions which likewise have the effect of law, and while such laws and decisions cover almost every conceivable situation, they unfortunately often involve apparent conflicts which can only be interpreted by further resort to the courts.

In the hands of some individuals or firms patenting has degenerated to a sort of racket, so that reputable manufacturers are often compelled to resort in self-protection to patenting minor features of their processes or products that would not be considered worth patenting otherwise. On this subject of patent-racketing an eminent attorney recently wrote:

"Slight changes in chemical practice and improvements in the commercial purity of a product, or a decrease in its cost of production —things which would have passed unnoticed as ordinary steps of a day's labor 50 years ago—are now being patented and these patents exploited with a skill and daring that would have shamed the shrewd business tactics of the oil barons and the railroad kings of the gay 90's."

Questions often arise as to whether an invention should be kept secret or patented. Experience shows that secrecy is always

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