REFRACTIVE DISPERSION OF OILS AND FATS.

PART I. DISPERSION OF GHEE AND VEGETABLE OILS.

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In view of the large number of products now being put on market as ghee substitute, the problem as to how one can best detect the adulteration has become a matter of great importance. Godbole (*Butter Fat,* 1930, p. 27) has suggested certain methods for detecting the adulteration of ghee. It is not our intention to discuss about all these methods in the present paper, but to refer only to the one which depends on the measurements of the refractive indices and dispersions of the samples and to see whether this method is feasible.

Godbole (*loc. cit.*) drew attention to the earlier observation made by Gruen (*Analysis Fette and Wasche,* vol. I, p. 127), that ghee unlike other oils or mixtures of oils shows characteristic violet colour fringes in a butyrorefractometer and suggested that the observation of the refractive index along with the coloured fringes would be of great help in pronouncing an opinion on the purity of the sample.

Hawley (*Current Science,* 1936, **4**, 815) raised a number of objections to the above method: (1) Godbole used an instrument intended for use with butterfat only and having a fixed dispersion correction, (2) in an improved type with adjustable dispersion correction no bands were observed either with ghee or a mixture of coconut oil and groundnut oil having the same index of refraction as ghee, and (3) in his opinion, it was a simple matter to prepare a mixture free from butterfat having not only the same refraction as genuine butterfat but also the same dispersion, colour fringes being merely a manifestation of dispersion.

It is true that with an instrument with adjustable dispersion correction no colour fringes should be seen but this does not explain why the use of a butyrorefractometer which has only a fixed dispersion correction be discarded if it is possible with the help of this instrument to differentiate between the genuine and the adulterated butterfat. The third objection raised by Hawley does not seem to have been based on proper evidence. Not that it is always impossible with a proper choice of substances to get a mixture having not only the same refractive index but also the same dispersion, but we have to take into account only such substances which are commonly used for adulteration. Neither Godbole nor Hawley has given any data regarding the actual dispersions of ghee (butterfat) or of oils which are commonly used for adulteration of ghee.

The refractive indices and dispersions of oils and butterfat were measured systematically first by Szala'ygi (*Biochem. Zts.*, 1914, 66, 173–176) and four years later by Fryer and Weston (*Analyst*, 1918, 311–317). The latter authors having paid more attention to the purity of the substances, their results are regarded as more reliable. Their object in carrying out this investigation was to find out whether it was possible with the help of the measurements of dispersion to detect the adulteration of one oil with the other and according to them, the results obtained were not of a great help except in differentiating broadly between the drying and the non-drying oils. The refractive indices and dispersions of a number of oils and butterfat were measured on a Pulfrich refractometer at 40° and the results were tabulated as n_D, $n_F - n_C$ and $\frac{n_D - 1}{n_F - n_C}$.

We plotted the refractive index for the D line against $n_F - n_C$ from the data of Fryer and Weston and found that the oils in general fall in three groups, *one* (Table I) showing the linear variation of dispersion with the refractive index, *two* (Table II) also showing linear relationship but having different slope, and *three* (Table III)

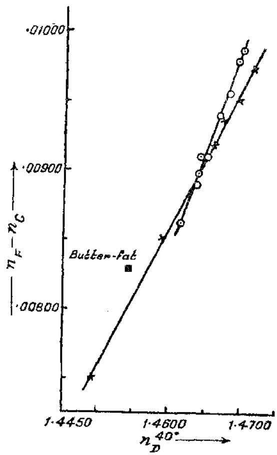

Fig. 1.

Vegetable Oils and Butterfat (Tables I, II and III) Fryer and Weston.

TABLE I.

$m = 0 \cdot 000097$.

Oil	n_D	$n_F - n_C$	$-$ C
Coconut	1·44924	·00751	0·036066
Lard	1·45928	·00851	0·036040
Arachis (Groundnut) ..	1·46431	·00898	0·036058
Cotton	1·46535	·00910	0·036039
Whale	1·46630	·00918	0·036051
Rape	1·46770	·00936	0·036007
Sunflower	1·47211	·00973	0·036064
Almond	1·46403	·00890	0·036111
Walrus	1·47023	·00950	0·036112
			0·036069

TABLE II.

$m = 0 \cdot 000140$.

Oil	n_D	$n_F - n_C$	$-$ C
Walnut	1·47054	·00985	0·056026
Poppy	1·46984	·00978	0·055998
Shark Liver	1·46849	·00955	0·056039
Maize	1·46711	·00938	0·056016
Cotton	1·46535	·00910	0·056049
Almond	1·46403	·00890	0·056064
Arachis (Groundnut) ..	1·46431	·00898	0·056023
Olive	1·46184	·00862	0·056038
Peach Kernel ..	1·46439	·00910	0·055918
			0·056018

TABLE III.

Substance	n_D	$n_F - n_C$
Butterfat	1·45427	0·00830
Cacao butter	1·45724	0·00812
Castor Oil	1·47194	0·00897
Hemp ,, ...	1·47404	0·00980
Linseed ,, ...	1·47379	0·01032
Niger ,, ...	1·46968	0·00935
Sesame ,, ...	1·46650	0·00908
Palm Kernel Oil ..	1·45034	0·00812
Menhaden ,, ..	1·47361	0·00979
Sperm ,, ..	1·45814	0·00864

showing irregular variations of dispersion, in which the constants ot butterfat may also be included. The results are shown graphically in Fig. 1.

The straight line relationship in the two cases mentioned above can be expressed by the equation

$$n_F - n_C = m\,(n_D - 1) - C,$$

where m is the slope of the curve, *i.e.*, the change of $n_F - n_C$ for a a change of 0.00100 in the refractive index, and C is a constant and is equal to the value of $n_F - n_C$ when $n_D = 1$. The Tables I and II show the values of m and C so calculated.

The Arachis (groundnut), cotton seed and almond oils have dispersions which fall near the intersection of the two straight lines representing Tables I and II. It is difficult to say to which of the groups, I or II, these three oils belong.

The oils given in Table III are not those which are used for adulteration.

The refractive index and dispersion of butterfat is given in Table III. The butterfat does not either belong to the group of oils given in Table I which gives a dispersion of 0.00799 on the basis that C = −0.036069, or to the second group, the dispersion of which is 0.00744, the corresponding value of C being −0.05602. The measured dispersion of butterfat is 0.00830, which is much above the values calculated above. From these results it is clear that the dispersion of butterfat is much higher than that of the oils.

Now an isolated point on the curve showing the refractive dispersion of butterfat cannot tell us as to whether it belongs to either set of oils which have specified values for m and C. We have, therefore, measured the refractive indices and dispersions of a number of samples of genuine ghee with a view to find out how the two constants vary with each other. Measurements were also made with a few vegetable oils and the results are presented in the light of the discussion given previously.

EXPERIMENTAL.

The refractive indices were measured for the mercury green and violet lines on a Pulfrich refractometer at 40°C. The dispersions were calculated from the angular deviations measured on the screw scale of the refractometer. The mercury green and violet were chosen because the characteristic colour bands for ghee were in the violet region and also because the dispersion at these wave-lengths was greater, and hence it was considered to be a better guide in differentiating between ghee and the oils.

The samples of the genuine ghee were obtained from three sources, *viz.*, Jersey cow, Sindhi cow and buffalo, and were kindly supplied by the Imperial Dairy Farm, Bangalore.

The results are given in Tables IV and V.

TABLE IV.

m = 0·000097 *change in* $n_{436} - n_{546}$ *for a change of* **0·00100** *in the refractive index for* Hg_{546} *line.*

Oil	n_{546}	n_{436}	$n_{436} - n_{546}$	− C
Olive	1·46445	1·47363	·00918	0·035872
Arachis (Groundnut) ..	1·46625	1·47561	·00936	0·035866
Saf-flower	1·47159	1·48146	·00987	0·035869
			Mean ..	0·035869

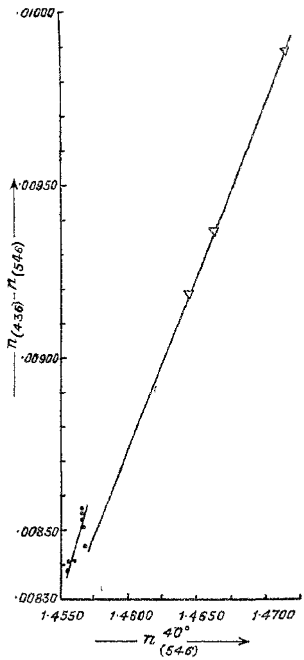

FIG. 2.

Vegetable Oils and Butterfat.
(Tables IV and V) Authors.
△—△ Oils
•—• Butterfat

On plotting these results (Fig. 2) as refractive index for green line against dispersion, *i.e.*, the difference in the refractive indices for the green and the violet line, it will be seen that these oils fall exactly on a straight line, while seven out of the eight samples of ghee which have been analysed fall away from this line, the dispersion being much higher than what it would have been for an oil having the same refractive index.

TABLE V.

m = 0·00015 *change in* $n_{436} - n_{546}$ *for a change of* 0·00100 *in the refractive index for* Hg_{546} *line.*

Ghees		n_{546}	n_{436}	$n_{436} - n_{546}$	$-$ C
Jersey Cow	1	1·45690	1·46537	0·00845	0·060085
	2	1·45670	1·46518	0·00853	0·059975
Sindhi Cow	1	1·45569	1·46399	0·00838	0·059974
	2	1·45569	1·46409	0·00841	0·059944
	3	1·45599	1·46439	0·00841	0·059988
Buffalo	1	1·45670	1·46518	0·00856	0·059945
	2	1·45660	1·46508	0·00851	0·059980
	3	1·45670	1·46527	0·00855	0·059944
				Mean ..	0·05996

The ghees among themselves form another straight line having a different slope. The straight line relation in the two cases can be represented by the equation which has already been given from which the values for C can be calculated, the slope of the curve being known. m in this case represents the change in the dispersion $(n_{436} - n_{546})$ for a unit change in the refractive index for the green line while C is the dispersion when the refractive index is 1. These results are given in Tables IV and V.

The slope of the line for the oils is 0.000097 for a change of 0.00100 in the refractive index which is the same as for the group of oils given in Table I. The slope of the line for ghees is 0.000150 for an equal variation in the refractive index.

The values for C which we may call the 'dispersion constant' are $-$ 0.03587 and $-$0.05996 respectively which are sufficiently wide for accurate measurements.

The essential difference in ghee and the coconut oil is the presence of butyric and caproic acid with a relatively large proportion of oleic acid as can be seen from Table VI in which the approximate proportions of fatty acids in some of the oils and ghee are given. [*Cf. Butterfat*: P. B. Holand and J. P. Buckley (*J. Agric. Res.*, 1918, **12**, 719), Violett (*J.S.C.I.*, 1890, 1157), Lewkowitsch, **2**, 820–21), Jamieson (*Vegetable Oils and Fats*, 109, 112, 138, 212 and 230), *Peanut Oil*: Hilditch and Vidyarthi (*J.S.C.I.*, 1927, **46**, 172T), Armstrong and Allen (*J.S.C.I.*, 1924, **43**, 216T), Midlton and Barry

(*Fats: Natural and Synthetic,* 107), Coconut Oil: Elsdon (*Analys* 1913, **38**, 8), Armstrong, Allen and Moore (*J.S.C.I.*, 1925, **44**, 63T and Stokoe (*Analyst,* 1924, **49**, 577), Palm Kernel Oil: Armstron and Allen (*J.S.C.I.*, 1924, **42**, 207T), Armstrong, Allen and Moor (*J.S.C.I.*, 1925, **44**, 143T), Palm Oil: Hilditch and Jones (*J.S.C.I* 1930, **49**, 363T), Jamieson and McKinney (*Oil and Fat Ind.*, 192[illegible] **6**, No. 6, 15), Hemp Oil: Kaufmann and Juschkuvetsch (*Z. Angei Chem.*, 1930, **43**, 90), Sesame Oil: Jamieson and Baughman (*J. Amer Chem. Soc.*, 1924, **46**, 775).]

Palm kernel oil and coconut oil which are largely used in adul teration of ghee are similar to each other in composition in regar to the lower acids, with a lower proportion of oleic acid. The othe oils are composed mainly of oleic, linoleic, stearic and palmitic acids.

TABLE VI.

Acid	78·5° n_C	58·8° $n_F - n_C$	m	Ghee	Coconut Oil	Peanut Oil	Palm Kernel	Sesame	Hemp
Butyric	1·37550	·00610	·000022	5·5	..	..	..	..	..
Caproic	1·39174	·00646	·000022	1·5	0·2	..	..	..	..
Caprylic	1·40426	·00672	·000022	1·0	7·0	..	3	..	..
Capric	..	..	..	2·0	7·0	..	5	..	..
Lauric	1·41749	·00725	·000014	7·0	50·0	..	50	..	..
Myristic	..	..	..	22·0	18·0	..	16	..	..
Palmitic	1·42719	·00739	·000014	20·0	6·0	7·5	7	7·3	..
Stearic	1·42924	..	·000014	11·0	3·0	4·0	2	4·4	..
Oleic	1·43752	·00854	·000140	30·0	8·0	55·0	17	46·0	12
Linoleic	..	..	·000140	..	1·0	23·0	1	35·0	50
Linolenic	1·4458	..	·000140	..	..	..	..	..	23
Lignoceric	..	..	..	..	..	3·0	..	tr	..
Arachidic	..	..	..	..	..	3·5	..	0·4	..

The dispersion data of the individual glycerides are not available in the literature. We have therefore started a systematic research on the physical properties of pure triglycerides. The dispersion data for some of the *fatty acids* (International Critical Tables VII, *Eijkman Rec. Trav. Chim.*, 1893, **12**,157) are given in the above Table (VI),

(Fig. 3), all the values having been reduced to 78.5°, taking 0.00035 and 0.00002 as the temperature coefficient of refractive index and dispersive power, $\frac{n_F - n_C}{n_D - 1}$ (Fryer and Weston, *loc. cit.*) respectively.

The values of the slope (m) in the dispersion refractive index curve for these acids calculated as before are given in the third column.

Assuming that the glycerides of the fatty acids will have the corresponding properties of the latter, the dispersion will be proportional to the refractive index and an addition of saturated acid to unsaturated acids will change the refractive index to a greater extent than what it can contribute towards the change in dispersion.

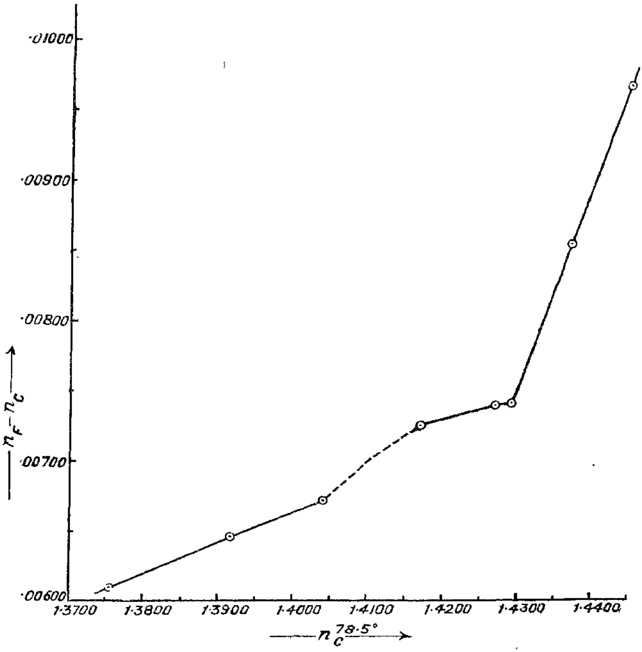

Fig. 3.

Fatty Acids (Table VI).

Coconut oil contains lower saturated acids to a large extent but very little of the butyric and caproic acids while the percentage of oleic acid is also low. Palm kernel oil which resembles coconut oil in its composition, has a much higher dispersion obviously due to the higher percentage of oleic acid in this oil. The hemp and sesame oils have a slightly lower dispersion compared to their refractive indices. This is because these oils are composed mostly of oleic and linoleic acids with very little percentage of saturated acids.

The remarkably low refractive index of ghee is obviously due to lower fatty acids and the high dispersion to the relatively large proportions of oleic acid.

The refractive index and dispersion of ghee is $n_D = 1.45427$ and $n_F - n_C = 0.00830$ respectively. The only oils which have lower refractive indices than ghee are coconut and palm kernel oils, and are therefore convenient for adulteration purposes.

When two oils are mixed, the refractive index and the dispersion will vary linearly with the composition of the mixture. In Table VII, we have calculated (*i*) the quantities of various oils which when added to coconut oil will give a mixture having the same refractive index as ghee along with the corresponding dispersion and (*ii*) the quantities of various oils required to give the same dispersion as ghee along with the corresponding refractive index.

TABLE VII.

Oil mixed with coconut oil	n_D 1·4543		$n_F - n_C$ 0·00830	
	% Oil	$n_F - n_C$	% Oil	n_D
Groundnut	34	·00800	55	1·4576
Cotton	32	·00799	53	1·4576
Sun-flower	22	·00799	36	1·4576
Walnut	24	·00806	35	1·4582
Olive	41	·00796	71	1·4582
Hemp	21	·00799	35	1·4579
Linseed	21	·00806	28	1·4562

From these results it will be evident that it will be difficult to get a mixture of two vegetable oils which will have the same refractive index and also the dispersion as that for ghee. A mixture of palm kernel and groundnut oils in the ratio of 71 : 29 will give the same refractive index as that of ghee. But the dispersion is 0.00837, sufficiently different from that of ghee to be accurately measured on a Pulfrich Refractometer.

The difficulty of producing mixtures of vegetable oils with hydrogenated fat having the same refractive index and dispersion as ghee is still greater. The refractive index of groundnut oil at 40° C. is 1.4643 and that of completely hydrogenated oil calculated for 40° C. is 1.4549 which is 6 units higher than ghee (the corresponding dispersion being very much lower because of the lower oleic acid content of the oil).

It may be however pointed out that it is *possible* to prepare a *ternary* mixture of palm kernel oil, coconut oil and groundnut oil in the ratio of about 56: 14: 30, having the same refractive index and dispersion, but not the same consistency as ghee. Further work on the refractive dispersion of tallow hydrogenated fish oil and vegetable ghee (Vanaspathi) is in progress.

CONCLUSION.

1. The refractive dispersions of butterfats from different sources have been measured on a Pulfrich Refractometer and the dispersion constants are found to be sufficiently different from those of vegetable oils to account for the characteristic colour fringes on a simple type of butyrorefractometer.

It should be possible to detect adulteration of ghee by measurement of both refractive index and dispersion on a Pulfrich Refractometer using the green and violet lines of the mercury arc.

2. Mixtures of oils can be prepared to give the same refractive index as that of ghee, but it will be difficult to get the same dispersion, especially in view of the fact that oils of lower refractive index and consequently lower dispersion are usually employed for adulteration.

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