

Melting-point .....	50°
Saponification number .....	196.2
Melting-point insoluble fatty acids .....	47.5°
Mean molecular weight insoluble fatty acids .....	278.2

The presence of fat, sluffed off from the walls of the intestinal tract, could not, therefore, explain the differences noted in Table III. The most satisfactory and plausible explanation of the facts is a difference in digestibility of the various constituents of the rice oil. The liquid unsaturated bodies are very largely absorbed in the process of digestion, as is shown by the marked decrease in the iodine number. The fatty acids of lowest molecular weight are also the easiest to assimilate; hence, the oil excreted in the feces consists largely of a residue of acids of high mean molecular weight and high melting-point. Reference was made, in the first section of this paper, to the probable presence in rice oil of such higher acids as arachidic, behenic, or lignoceric, and this supposition finds support in the character of the fatty acids in the oil from the feces, these having a mean molecular weight higher even than the molecular weight of arachidic acid (312).

Stearic acid, the highest saturated fatty acid in the animal body, has a molecular weight of 284, and saturated fatty acids of greater molecular weight than stearic are probably assimilated by the animal only to a limited extent.

In conclusion, the writer desires to express his indebtedness to Dr. W. C. Stubbs, under whose direction the work was carried on, for advice and encouragement.

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### OLIVE OILS AND OLIVE OIL SUBSTITUTES.

BY L. M. TOLMAN AND L. S. MUNSON.

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#### SOURCES OF THE OILS.

IN AN investigation of olive oils and their substitutes, a number of pure California and Italian olive oils were obtained and analyses of them made. The California oils were largely obtained from representative producers, with affidavits as to their purity. The Italian oils were received through agents in Italy. The collection of oils thus made contained samples from most of the oil-producing districts of both countries.

The varieties of olives used are given, to a certain extent, with California oils, but with the Italian oils it was impossible to obtain this information. The methods of analysis used were those given in the U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin 65, pp. 20-35.

#### FATTY ACIDS.

By liquid fatty acids are meant the acids, the lead soaps of which are insoluble in ether, and by the solid fatty acids, those the lead soaps of which are insoluble in ether. This method of separation, while not absolutely exact, gives a very close approximation of the amounts of saturated or solid fatty acids and unsaturated or liquid fatty acids. The iodine number of the liquid fatty acids was determined exactly as with the Hübl method on oils. Great care is necessary in drying the liquid fatty acids to prevent oxidation and in this work they were dried at about 70° C., in a current of coal gas.

#### TABLES OF ANALYSES.

In Table I are the analyses of thirty-eight samples of California olive oil and eighteen samples of Italian olive oil. These are mostly virgin or first-pressing oils, but a few oils have been included which cannot be classed as edible oils. These are not included in the average or maximum and minimum, but are given in order to show what widely varying results may be obtained with pure oils, and that the cause of these abnormal results would not be detected unless the determination of free acids was made. The amount of free acids present in an oil affects the specific gravity and index of refraction to a marked degree. Sample No. 22,619, with an index of refraction of 1.4672 and 44.40 per cent. of free acid, and No 673 with specific gravity of 0.9149 and 12.11 per cent. of free acids are examples of this fact. It seems very probable that some of the very low figures on these determinations, reported by various analysts, would be explained if the free acid had been determined.

#### DISCUSSION OF ANALYTICAL DATA.

An examination of Table I will show that on the high-grade oils there is only a very small variation in specific gravity and index of refraction for both the California and Italian oils. The wide range in Maumené figures means nothing, as different strengths of acid were used, but the specific temperature figures

TABLE I, PART I—PURE CALIFORNIA OLIVE OILS.

Serial No.	Variety and locality.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maumené number.	Specific temperature reaction.	H&Ml number.	Iodine number of liquid fatty acids.	saponification number.	Melting-point of fatty acids, °C.	Solid fatty acids, Per cent.	Free fatty acids as oleic. Per cent.
23,692	Mission olive, Chico .....	0.9168	68.5	1.4713	...	....	85.6	96.6	191.2	22.6	5.12	0.95
23,463	" " Concord.....	0.9164	68.4	1.4712	48.0	106.6	85.6	91.5	191.9	21.3	4.92	0.79
22,713	" " Santa Barbara .....	.....	68.7	1.4715	...	....	85.3	94.9	191.1	22.4	5.11	0.73
22,714	" " " " <sup>1</sup> .....	.....	68.5	1.4713	...	....	84.6	...	191.5	22.4	3.87	1.26
22,715	" " " " <sup>2</sup> .....	.....	68.2	1.4711	...	....	84.7	...	191.3	20.5	2.02	2.73
23,458	" " " " .....	0.9169	68.7	1.4715	48.4	107.5	88.2	94.9	191.4	23.5	4.42	0.73
838	" " San Diego.....	0.9169	69.2	1.4718	49.5	108.5	86.2	...	190.6	24.0	6.15	1.07
839	" " " " .....	0.9171	69.2	1.4718	48.4	106.0	89.0	...	189.9	21.2	4.94	3.51
840	" " " " .....	0.9169	68.9	1.4716	48.2	105.7	86.3	...	189.4	24.0	5.94	1.09
23,457	" " Santa Clara.....	0.9166	68.3	1.4711	47.0	104.4	86.2	91.2	191.6	21.1	3.39	0.97
832	" " " " .....	0.9173	68.8	1.4715	47.6	100.1	84.9	...	189.3	20.5	5.40	0.85
834	" " " " .....	0.9168	68.8	1.4715	46.2	97.2	84.5	...	189.3	19.4	6.03	0.34
23,605	" " Santa Barbara .....	0.9171	68.5	1.4713	47.1	104.2	88.5	94.5	191.5	20.2	2.43	1.54
798	" " " " .....	0.9177	68.8	1.4715	51.0	107.3	89.7	...	190.0	19.2	...	0.63
795	" " " " .....	0.9177	69.0	1.4717	50.0	105.2	89.7	...	189.8	19.8	4.73	0.75
796	" " " " .....	0.9177	68.8	1.4715	52.1	109.7	89.8	...	189.9	19.2	4.69	0.61
797	" " " " .....	0.9177	68.8	1.4715	50.2	105.6	89.8	...	189.7	19.6	5.44	0.63
22,617	Redding picholine olive, Berkeley <sup>3</sup>	.....	67.3	1.4706	...	....	78.5	...	194.4	30.2	...	0.36
23,462	picholine olive, Oroville ..	0.9162	66.9	1.4703	43.0	95.5	79.9	91.7	192.2	31.0	10.91	0.79

<sup>1</sup> Second pressing.<sup>2</sup> Common grade of oil for lubricating.<sup>3</sup> Made in 1893.

TABLE I, PART I (Continued)—PURE CALIFORNIA OLIVE OILS.

Serial No.	Variety and locality.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maumené number.	Specific temperature reaction.	Hübli number.	Iodine number of liquid fatty acids.	Saponification number.	Melting-point of fatty acids, °C.	Solid fatty acids, per cent.	Free fatty acids as oleic. Per cent.
23,461	Picholine olive, Guerneville.....	0.9162	67.5	1.4707	45.0	100.0	83.0	92.4	192.0	28.0	7.62	1.07
22,619	Manzanillo olive, Berkeley <sup>1,2</sup> .....	.....	62.0 <sup>3</sup>	1.4672	...	....	79.6	...	191.8	24.5	...	41.40
23,456	Italian varieties olive, Santa Clara .	0.9169	68.3	1.4711	47.7	106.0	84.3	93.4	191.9	23.4	7.23	0.53
831	" " " " " "	0.9168	68.8	1.4715	46.6	98.1	85.2	...	189.3	20.6	...	0.61
833	" " " " " "	0.9170	68.8	1.4715	48.0	101.0	84.8	...	189.8	20.2	6.55	0.65
506	Mixed varieties olive, Los Angeles	0.9174	68.5	1.4713	38.0	98.9	84.4	...	193.1	22.4	...	0.71
836	" " " " " "	0.9174	68.8	1.4715	48.2	105.7	86.0	...	190.7	24.8	...	2.51
837	" " " " " "	0.9167	68.4	1.4713	45.0	98.6	84.2	...	190.3	23.6	5.16	0.51
835	" " " " " "	0.9167	68.2	1.4711	44.8	98.2	82.7	...	190.4	26.0	6.19	0.96
21,091	" " " Cloverdale .	0.9167	68.8	1.4715	45.3	94.5	81.9	...	190.0	26.6	12.96	1.42
3,460	" " " Yolo .....	0.9167	68.2	1.4711	47.0	104.0	85.7	93.8	190.4	23.4	6.24	2.24
22,618	Mixed olives, Berkeley <sup>2</sup> .....	.....	67.5	1.4707	...	....	83.7	...	192.5	20.7	...	8.21
23,124	" " Redlands .....	0.9171	68.2	1.4711	45.5	...	83.7	92.5	193.3	25.4	6.20	0.47
841	" " " .....	0.9168	68.8	1.4715	47.1	98.3	86.9	...	189.4	21.6	8.61	0.20
842	" " " .....	0.9168	68.7	1.4715	46.8	97.7	87.2	...	189.5	21.4	7.52	0.21
843	" " " .....	0.9169	68.6	1.4714	45.6	95.2	85.1	...	189.6	22.8	4.33	0.28
23,459	" " Napa .....	0.9162	67.7	1.4709	45.5	101.2	82.9	90.3	191.6	25.0	5.69	1.72
673	" " " <sup>3</sup> .....	0.9149 <sup>3</sup>	66.4	1.4699	45.5	95.0	83.3	...	189.5	21.6	7.58	12.11
23,649	" " Oroville .....	0.9164	68.0	1.4710	43.5	96.6	83.4	88.9	192.1	22.6	...	1.43

<sup>1</sup> Poor quality.

<sup>2</sup> Not included in the average on account of high percentage free acid.

<sup>3</sup> Second pressing.

TABLE I, PART II.—PURE ITALIAN OLIVE OILS.

Serial No.	Locality.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maumené number.	Specific temperature reaction.	Hübl number.	Iodine number of liquid fatty acids.	Saponification value.	Melting-point of fatty acids, °C.	Solid fatty acids. Per cent.	Free fatty acids as oleic. Per cent.
580	Bari .....	0.9177	67.9	1.4709	39.6	103.1	81.8	...	191.7	28.5	...	...
933	Puglia .....	0.9158	67.7	1.4708	43.5	95.6	80.4	94.8	192.0	26.2	16.47	1.02
960	Bari .....	0.9159	67.6	1.4707	44.7	101.8	80.9	96.0	191.4	26.6	16.87	0.80
961	Bitonti .....	0.9162	67.6	1.4707	43.5	95.6	80.8	96.5	191.7	27.3	13.67	0.69
935	Puglia .....	0.9162	67.7	1.4708	44.2	97.1	80.5	95.1	191.9	29.3	15.20	1.03
936	" .....	0.9155	67.7	1.4708	44.8	98.4	81.8	96.2	191.5	26.2	11.07	2.79
962	Bari .....	0.9159	67.6	1.4707	43.5	99.1	81.2	96.5	191.8	27.9	17.72	0.62
931	Toscana <sup>1</sup> .....	0.9166	67.6	1.4707	44.4	97.4	80.7	89.8	189.6	25.8	5.01	0.82
932	Lucca .....	0.9167	67.5	1.4707	44.4	97.4	80.5	...	190.1	25.2	8.67	0.80
958	" .....	0.9158	68.0	1.4710	48.0	102.3	81.8	90.6	190.4	22.9	6.04	0.79
959	" .....	0.9164	68.0	1.4710	46.2	98.4	81.5	92.0	190.5	23.9	7.95	0.63
934	Genoa .....	0.9159	67.6	1.4707	42.5	96.8	81.1	92.4	190.6	24.5	8.60	0.92
952	Liguria .....	0.9160	68.0	1.4710	45.0	97.9	81.4	90.5	190.1	21.6	7.38	0.61
953	" .....	0.9161	67.3	1.4705	47.0	100.0	79.2	90.8	191.3	24.9	9.76	1.18
954	" .....	0.9180	68.5	1.4713	48.3	103.0	86.1	97.5	190.5	25.0	7.76	2.55
955	" .....	0.9157	67.8	1.4709	44.2	97.1	82.6	94.8	190.8	23.5	8.93	1.09
957	" .....	0.9166	68.0	1.4710	45.0	97.9	82.1	91.1	189.7	21.6	5.53	1.90
956	Aburzi .....	0.9164	68.3	1.4712	49.1	104.7	84.5	98.4	190.7	28.5	13.51	0.57
	California oils {	Average ..	0.9168	68.2	1.4711	46.8	101.6	85.1	190.6	22.5	...	0.85
	{	Maximum	0.9180	69.2	1.4718	52.1	109.7	89.8	194.6	31.0	12.96	3.51
	{	Minimum	0.9162	66.9	1.4703	38.0	94.5	88.9	189.3	19.2	2.02	0.20
	Italian oils... {	Average ..	0.9163	67.8	1.4709	44.9	99.1	81.5	94.0	...	25.4	...
	{	Maximum	0.9180	68.5	1.4713	49.1	104.7	86.1	192.0	29.3	17.72	2.79
	{	Minimum	0.9155	67.3	1.4703	39.6	95.6	79.2	189.6	21.6	5.01	0.57

<sup>1</sup> First grade.

<sup>2</sup> Second grade.

do not show such a wide variation. The average for California oils is a little higher, due probably to the higher iodine value of the oils examined. The reason for including the figures given by the Maumené test is that the specific temperature figures are affected to a certain degree by the strength of the acid, as was shown by the work of Sherman, Danziger and Kohnstamm.<sup>1</sup> This will account for the somewhat lower specific temperature numbers obtained by De Negri and Fabris,<sup>2</sup> and Milliau, Bertainchand and Malet<sup>3</sup> on French and Algerian oils, as they used an acid which gives a rise of temperature with water of about 36° to 37° C., while the acid used in this work gives a rise of from 45° to 46° C.

The variation found in the Hübl numbers of the oils is very wide and the same is true with the iodine figures on the liquid fatty acids. The variation in the Hübl figures is, to a considerable extent, controlled by the amount of solid fatty acids present, but is also affected by the composition of the liquid fatty acids, as the wide variation in the iodine absorption of these acids shows. The Italian oils are not very different from the California oils in this particular, and this work is confirmed by De Negri and Fabris<sup>4</sup> in their recent extensive work on Italian oils.

These results make it evident that the iodine absorption alone can have little value in determining the purity of an oil, as all but very gross adulteration can be covered up by this range of from 78.5 to 89.8 for the Hübl figures. The average for the Hübl figures on the oils examined is higher for the California oils than for Italian oils, but from all the figures available on pure oils there is not so wide a difference. De Negri and Fabris<sup>4</sup> found an average of 83.7. In fifty-seven samples of commercial Italian olive oil, imported into this country, in which no adulteration was detected, the average figure was 80.5.

The melting-point of the fatty acids—the point where the acids in a capillary tube became clear—also showed wide variation and a very close relation to the percentage of solid fatty acids, as would be expected. These oils were all tested qualitatively for cottonseed, peanut and other seed oils, with negative results in all cases.

<sup>1</sup> This Journal, 24, 266.

<sup>2</sup> "Ann. Lab. chim. Cent. delle Gab.," Vol. I, Gli Olii, Part I.

<sup>3</sup> "Rap. sur les Huiles D'Olive de Tunisie," 1900.

<sup>4</sup> *Loc. cit.*

TABLE II.

Serial No.	Kind of oil.	Specific gravity at 15.5° C.	Butyro-refractometer reading at 15.5° C.	Index of refraction at 15.5° C.	Maumené number.	Specific temperature reaction.	Hübl number.	Iodine number of liquid fatty acids.	Saponification value.	Melting-point of fatty acids. °C.	Solid fatty acids. Per cent.	Free fatty acids as oleic. Per cent.
773	Cocoanut .....	0.9259	49.1	1.4587	21.0	44.0	8.58	31.9	259.5	25.2	65.90	0.11
494	Palm .....	0.9128	...	.....	...	...	53.0	99.0	201.0	49.2	...	19.53
22,433	Lard .....	0.9148	67.4	1.4706	47.8	106.2	75.9	94.0	195.7	33.2	18.90	0.75
23,606	" .....	0.9160	69.5	1.4720	46.5	103.3	69.7	95.8	197.7	38.4	26.68	0.28
499	Peanut <sup>1</sup> .....	0.9186	70.0	1.4723	46.5	129.1	87.8	...	191.8	34.3	...	0.40
772	" <sup>2</sup> .....	0.9188	71.3	1.4431	63.2	135.3	96.3	114.6	189.9	36.4	...	0.24
495	Mustard. Black mustard .....	0.9170	76.5	1.4762	68.2	189.4	105.8	...	176.0	21.5	4.03	0.38
770	Brown " .....	0.9184	76.2	1.4760	77.6	165.4	110.4	114.2	178.5	20.6	1.06	0.48
771	Black " .....	0.9193	76.5	1.4762	79.4	169.3	113.0	119.8	182.8	20.8	2.32	0.34
776	Yellow " .....	0.9147	74.5	1.4750	61.4	130.9	98.4	103.1	173.0	21.0	tr	0.13
496	Rape .....	0.9143	74.3	1.4749	54.9	152.5	92.7	101.5	174.7	21.9	1.02	0.63
775	" .....	0.9163	74.1	1.4748	63.6	135.6	101.3	105.1	176.6	20.5	tr	1.26
1,187	Almond .....	0.9186	70.9	1.4728	45.3	117.6	96.2	...	192.5	23.2	...	0.48
23,624	Sunflower .....	0.9201	72.7	1.4739	...	...	108.3	113.8	192.3	21.0	3.67	0.18
498	" .....	0.9205	72.1	1.4736	60.0	166.7	104.1	...	191.2	21.0	4.12	1.72
777	Maize .....	0.9253	77.5	1.4768	89.2	190.2	123.3	134.5	189.9	21.6	7.44	3.65
1,186	Cottonseed .....	0.9236	75.6	1.4757	67.1	174.3	110.9	...	198.5	38.0	...	2.17
1,159	" "butter oil" .....	0.9226	72.5	1.4738	66.4	172.9	103.8	143.0 <sup>3</sup>	197.1	35.5	22.90	0.07
1,160	" "summer white" ..	0.9226	72.3	1.4737	73.4	191.1	106.2	145.4 <sup>3</sup>	196.9	39.0	22.43	0.07
1,161	" "cooking oil" .....	0.9226	72.3	1.4737	66.2	172.4	104.8	145.7 <sup>3</sup>	196.0	39.6	23.60	0.04
774	Poppy .....	0.9244	77.8	1.4770	75.8	213.3	134.9	142.0	193.8	25.8	6.67	0.90
1,188	Linseed .....	0.9318	88.8	1.4831	...	...	179.5	...	191.7	19.2	3.88	0.40

<sup>1</sup> 3.78 per cent. arachidic acid, melting-point, 72.5° C.

<sup>2</sup> 4.12 per cent. arachidic acid, melting-point, 72.0° C.

<sup>3</sup> Iodine value calculated.

Table II contains the results of analysis of a number of pure oils of various kinds, some of which were pressed in the laboratory and others were pressed under our supervision. The lard oils were obtained from Armour & Co., and cottonseed oils, except No. 1,186, from the American Cotton Oil Company. The lard oil No. 23,606 was a pure white product and free from lardy odor, except when heated. The peanut oils were cold-pressed from American nuts. The cocoanut oil was from fresh cocoanuts.

The mustard, rape and poppy oils were prepared from seeds which were identified by Miss Charles, of the Seed Laboratory of the U. S. Dept. of Agriculture, as follows:

770	Brown mustard	<i>Brassica Arvensis</i> (Charlock).
771	Black "	<i>Brassica Juncea</i> (Indian mustard).
776	Yellow "	<i>Sinapis Alba</i> (yellow mustard).
775	Rape seed	<i>Brassica Napus</i> .
774	Poppy seed	<i>Papaver somnifer</i> (opium poppy).

The other oils were prepared from commercial seeds or nuts and were cold-pressed. These oils, with the exception of linseed, are used as substitutes or adulterants of olive oil and were analyzed in order to obtain more complete data on American oils, there being very few published results on oils of this class.

The Maumené test was made on the oils having a high iodine number by using a weaker acid, as suggested by Sherman, Danziger and Kohnstamm.<sup>1</sup>

The relation between the solid fatty acids, the Hübl number and the iodine number of the liquid fatty acids should be noted. The mustard oils have a higher Hübl number than cottonseed-oil, but having only a small percentage of solid fatty acids, the true iodine number, as it is sometimes called, is only a little higher than the Hübl number, while the cottonseed-oils, with a large percentage of solid fatty acids, have a much higher iodine figure for the liquid fatty acids.

The relation of the iodine number of the liquid fatty acids to the drying properties of the oil is shown to the greatest extent in cottonseed and poppy oils. The iodine numbers of the liquid fatty acids of the two oils are practically the same and their drying properties are practically the same, but the Hübl number of poppy oil is 134.9 and cottonseed-oil 103-105. In this case, the Hübl number gives very little idea as to the drying capacity of the oil. This same relation holds true with other oils. Rape oils and cottonseed-

<sup>1</sup> This Journal, 24, 266.



oil with the same Hübl number have very different powers of absorbing oxygen.

The true iodine figure gives a much better idea of the nature of the unsaturated fatty acids present than the Hübl figure. Sample No. 23,606, with a Hübl number of 69.7, but containing 26.68 per cent. of solid fatty acids, has an iodine number of the liquid fatty acids of 95.8, which is practically the same as that given by olive oils, showing that the liquid portion of lard oil is very similar to the liquid portion of olive oil.

The Hübl figure depends largely on the method of making the oil, whether hot- or cold-pressed. The unsaturated fatty acids of the cocoanut oil are very different from those of the palm oil, the former having an iodine figure of 31 and the latter, of 99. This figure closely agrees with that of oleic acid, the unsaturated acid of lard and olive oils.

The iodine number of liquid fatty acids can be calculated from the iodine number of the oil and the per cent. of solid fatty acids, if one assumes that the total fatty acids in an oil is 95.5 per cent.

The total fatty acids less the solid fatty acids give the liquid fatty acids. From the following formula, the iodine number of the liquid fatty acids can be calculated:

$$A = \frac{I \ 100}{L}$$

A = Iodine number liquid fatty acids.

I = Hübl number.

L = Percentage liquid fatty acids.

The peanut oils Nos. 499 and 772 show quite a difference in iodine number, but it can be seen that a very large amount of either of these oils could be mixed with olive oil without changing any of the physical or chemical properties enough to certainly show its presence.

The only reliable test is the separation of the arachidic acid. These two samples had 3.78 and 4.12 per cent. of this acid present, which melted at from 72° to 72.5° C.

In all of these oils, even those taken fresh from the press, free fatty acids were found, showing that they must have existed as such in the seeds. The three samples of commercial cottonseed-oil contained only traces of free acid due to the process of refining, while sample No. 1,186, which had not been refined, but was fresh from the press, contained 2.17 per cent.