

$$v_1 = \left( \frac{s_1}{t} \right) t_1,$$

where  $t_1$  = the time of flow,

$s_1$  = the specific gravity of the liquid under consideration,  
and  $t$  = the time of flow of water under like conditions.

The specific gravities of the soap solutions of all the principal oils, as based on a large number of determinations, were found to approximate 1.07 (within  $\pm 0.005$ ), so that this figure may be substituted in place of  $s_1$  in the above expression. An extreme error of 0.005, due to this assumption, will merely affect  $v_1$  by 0.5 to 0.7.

The formula, therefore, reduces to

$$v_1 = kt_1,$$

where  $k$  is a constant for the particular apparatus employed. The value of  $v_1$  for pure, fresh olive oil of good quality is usually 165-185, for most other oils it is about 125-135.

In general, it is advisable to determine the viscosity of the soap solution while fresh, as it has been found that after standing several days the viscosity is sometimes increased and sometimes decreased.

In the hands of the writer, the time required for a determination by the present method is less than half that required by the method as described by Blasdale.

In conjunction with Dr. H. C. Sherman, at whose suggestion this investigation was undertaken, the modified method has been applied to a number of samples of olive, lard, and other fatty oils, in comparison with the "constants" by means of which such oils are usually judged. The results of this study will be given in a subsequent paper.

QUANTITATIVE LABORATORY,  
June, 1903.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA  
UNIVERSITY, No. 88.]

## THE VISCOSITY OF THE SOAP SOLUTION AS A FACTOR IN OIL ANALYSIS.

BY H. C. SHERMAN AND HERBERT ABRAHAM.

Received June 26, 1903.

AS PART of a comparative study, undertaken in this laboratory, of some of the so-called analytical constants, we have determined

the viscosities of solutions of the potassium soaps of several vegetable and a few animal oils. The method of making this viscosity test" and the principal conditions which influence the results have been fully described by one of us.<sup>1</sup> In the present paper, we give the figures obtained by the method as finally adopted, and compare them with some of the more commonly determined constants.

The specific gravities and iodine absorption (Hübl) figures were determined as in previous investigations.<sup>2</sup> The figure here called "Specific Maumené" is the rise of temperature produced on mixing 10 cc. of sulphuric acid with 50 grams of the oil, the result expressed in percentage of the rise shown by 50 grams of water under the same conditions.<sup>3</sup> The reaction was carried out in small, jacketed beakers, ordinary "C. P. concentrated" acid being used, except in cases where the reaction became too violent, when acid of about 89 per cent. was substituted, as noted below.

All of the olive oils tested were purchased from presumably reliable dealers in New York City and are believed to be pure, though some are cheap oils of rather poor quality. With the exception of No. 18, all of the samples of lard oil, cottonseed and maize, and the first sample of linseed were sent to us by the makers as pure typical specimens. The remaining samples were purchased from responsible dealers and are believed to be pure. The dates given in the table indicate the years in which the samples were obtained by us.

The results obtained are shown in the following table:

VISCOSITY FIGURES AND OTHER CONSTANTS OF SOME FATTY OILS.

No.	Description of oil.	Sp. gr. 15.5°.	Hübl figure.	Specific Maumené.	Viscosity figure.
1	Olive, "Lucca," 1903 .....	0.9144	79.7	88	168.4
2	Olive, "Marseille," 1903.....	0.9152	82.3	91	168.0
3	Olive, "Niece," 1903 .....	0.9156	81.5	88	174.6
4	Olive, "Bordeaux," 1903.....	0.9158	81.0	88	185.5
5	Olive, "Bordeaux," 1903.....	0.9160	81.6	88	185.7
6	Olive, "California," 1903 .....	0.9160	86.0	93	180.0
7	Olive, "Bordeaux," 1903.....	0.9162	80.6	87	174.4
8	Olive, "Marseille," 1903.....	0.9162	83.9	97	145.8
9	Olive, "Lucca," 1901 .....	0.9165	80.5	..	165.8
10	Olive, "Bordeaux," 1903.....	0.9165	84.5	100	151.9
11	Olive, unknown origin, 1899 ..	0.9170	84.5	100	153.7
12	Olive, unknown origin, 1903 ..	0.9171	81.5	89	168.0

<sup>1</sup> See the preceding paper.

<sup>2</sup> This Journal, 23, 168.

<sup>3</sup> This Journal, 24, 266-273.

VISCOSITY FIGURES AND OTHER CONSTANTS OF SOME FATTY OILS.—  
(Continued).

No.	Description of oil.	Sp. gr. 15.5°.	Hübl figure.	Specific Maumené.	Viscosity figure.
13	Olive, unknown origin, 1901 ..	0.9177	86.1	106	157.9
14	Lard oil, first quality, 1903 ....	0.9165	72.1	92	135.0
15	Lard oil, second quality, 1903..	0.9181	74.2	99	133.1
16	Lard oil, third quality, 1903 ...	0.9187	63.9	79	126.9
17	Lard oil, best commercial, 1900	0.917	73.3	106	122.9
18	Lard oil, for lubricating, 1899 .	0.919	72.5	88	128.1
19	Almond, commercial, 1899 ....	0.919	98.1	114	167.8
20	Arachis, commercial peanut, 1899 .....	0.917	105.9	176	126.6
21	Castor, crystal, 1899 .....	0.964	86.9	94	126.6
22	Cotton, prime summer yellow, 1900 .....	0.920	102.8	161	127.9
23	Cotton, choice summer white, 1900 .....	0.923	105.2	171	126.6
24	Cotton, old sample .....	0.926	103.3	197 <sup>1</sup>	126.6
25	Rape, commercial, 1901 .....	0.920	107.4	144 <sup>1</sup>	125.6
26	Rape, unknown origin .....	0.920	108.6	...	125.7
27	Rape, unknown origin, old ....	0.926	99.3	...	124.7
28	Blown rape, commercial, 1901 .	0.974	56.6	...	123.2
29	Sesame, commercial, 1899 ....	0.924	105.3	158	139.2
30	Maize, from glucose works, 1900	0.924	117.2	174	126.6
31	Poppy, unknown origin .....	0.925	125.3	212 <sup>1</sup>	123.9
32	Linseed, from Dakota seed, 1900	0.934	180.1	300 <sup>1</sup>	126.6
33	Linseed, commercial, 1898.....	0.938	177.1	298 <sup>1</sup>	126.6

## COMPARISON OF VISCOSITY FIGURE WITH OTHER CONSTANTS.

The olive oils in the table are arranged in the order of their specific gravities and it will be seen that, with few exceptions, the increasing specific gravity is accompanied by increasing iodine absorption of Maumené figures, while the viscosity figure, as a rule, decreases. This may be shown by averaging separately the samples falling in the first and second halves as given in the table. The results are:

	Specific gravity.	Hübl figure.	Specific Maumené.	Viscosity.
Average, Nos. 1-7..	0.9156	81.8	89	176.7
Average, Nos. 8-13.	0.9168	83.5	98	157.2

The first group gives average figures which would indicate purity and high quality, and here the viscosity figures are high. The second group gives results which would be taken as indicating a lower quality of oil, and here the viscosity figures average much lower. It is interesting to note in this connection that five of the

Determined by the use of acid of about 89 per cent.

seven samples in the first group were commercially rated as extra high grade, and that four of the six samples in the second group were cheap oils.

Comparing samples Nos. 14, 15 and 16, lard oils of first, second and third quality from the same maker, it appears that here also the viscosity figure decreases with the quality of the oil, though the differences are too small to be of much significance.

Comparing olive oils with other oils, the only one of the latter examined by us which equals olive in its viscosity figure, is almond oil with a figure of 167.8. Next below comes sesame with a figure of 139.2. Blasdale<sup>1</sup> has already stated that almond equals, and sesame approaches, olive oil in this respect. We have, however, been unable to confirm his statement that rape oil gives a soap solution of as high viscosity as that of olive oil. The high result obtained by Blasdale may be due to the fact that he used a fixed amount, instead of a fixed excess, of alkali for saponification. This procedure would, of course, leave a larger amount of uncombined alkali in the case of rape than with the other oils, and this larger excess of alkali would increase the viscosity of the soap solution. We have not examined mustard-seed oil, which according to Blasdale yields a soap solution of very high viscosity.

All of the samples examined by us, other than olive, almond and sesame oil, showed viscosity figures between 122 and 135. It seems remarkable that this figure should show such slight variations between oils differing so markedly in other properties as, for example, lard, linseed and castor oils.

From the results obtained with castor and with blown rape-seed oils, it is evident that the viscosity of the soap solution is independent of the viscosity of the oil itself.

Our results fully confirm the conclusion, reached by Blasdale that the adulteration of olive oil with any other oil likely to be used for the purpose would result in a lowering of the viscosity figure. The following experiments were designed to determine whether the viscosity figure actually found in such a mixture would agree with that calculated from the constituents. Soap solutions of lard, cottonseed, and peanut oils were mixed in different proportions with those of olive oil and the viscosities determined with the following results:

<sup>1</sup> This Journal, 17, 940.

MIXTURES OF SOAP SOLUTIONS OF OLIVE AND OTHER OILS.

Nature of soap solution.	Viscosity figure.	
	Found.	Calculated.
Olive oil .....	168.4	....
Lard oil .....	128.1	....
$\frac{3}{4}$ olive, $\frac{1}{4}$ lard oil .....	158.6	158.4
$\frac{1}{2}$ olive, $\frac{1}{2}$ lard oil .....	147.6	148.2
$\frac{1}{4}$ olive, $\frac{3}{4}$ lard oil .....	137.8	138.2
Peanut (arachis) oil .....	126.6	....
$\frac{3}{4}$ olive, $\frac{1}{4}$ peanut oil .....	143.6	158.0
$\frac{1}{2}$ olive, $\frac{1}{2}$ peanut oil .....	134.2	147.5
$\frac{1}{4}$ olive, $\frac{3}{4}$ peanut oil .....	129.0	137.1
Cottonseed oil .....	127.9	....
$\frac{9}{10}$ olive, $\frac{1}{10}$ cottonseed oil .....	152.0	164.4
$\frac{3}{4}$ olive, $\frac{1}{4}$ cottonseed oil .....	142.6	158.3
$\frac{1}{2}$ olive, $\frac{1}{2}$ cottonseed oil .....	132.1	148.2

From this table it appears that mixtures of olive and lard oils give practically the calculated results, while the viscosities of mixtures of olive with cottonseed or peanut oils are lower than would be calculated from the viscosities and proportions of the oils in the mixture. Hence the adulteration of olive with cottonseed or peanut oil produces a greater change in the viscosity figure than that which would have been predicted.

A somewhat similar, but more striking result was obtained from the examination of mixtures of soap solutions of pure fatty acids. Such mixtures also give viscosities lower than would be calculated. Three grams of lauric acid, treated in the same manner as described for fatty oils, gave a viscosity figure of 126.6, oleic acid gave a figure of 239.7, while stearic acid yielded a soap solution too viscous to be tested at ordinary temperatures. Yet large proportions of the oleate or stearate solution could be added to the laurate solution without appreciably increasing its viscosity.

INFLUENCE OF ATMOSPHERIC OXIDATION.

In view of the fact that even the so-called non-drying oils may undergo sufficient oxidation from simple exposure to air to affect seriously the "constants" usually determined in oil analysis,<sup>1</sup> it is of some importance to determine the effect of such oxidation upon the viscosity figure. Speaking generally, it appears that the effect of sufficiently prolonged exposure is to cause olive and almond oils to lose their characteristic high viscosity figures while those oils whose figures are lower are but little affected. A sample of olive oil exposed in an uncorked bottle for several months

<sup>1</sup> This Journal, 2, 711.

showed a loss of 7 units in the Hübl figure and of 25 units in the viscosity figure. An almond oil, similarly exposed for a longer time, decreased from 98.1 to 84.6 in the Hübl figure and from 167.8 to 123.8 in the viscosity figure. On the other hand, a sample of lard oil exposed until the Hübl figure fell from 73.3 to 66.7 showed no appreciable change in the viscosity figure; and in several samples of cottonseed, maize and linseed oils, in which atmospheric oxidation had caused losses of 10 to 40 units in the Hübl figures, the decrease in the viscosity figure was in no case greater than 4 units.

#### SUMMARY.

Olive and almond oils yield soap solutions of considerably greater viscosity than those obtained from the other more common fatty oils.

This "viscosity figure" is apparently higher in the better than in the poorer grades of olive oil.

The lowering of the viscosity figure by admixture of other oils furnishes an additional method for the detection of adulteration in olive and almond oils. As suggested by Blasdale, it will be especially useful for the detection of lard oil for which we have no specific test. The characteristic high viscosity figure of olive or of almond oil may be largely lost on sufficiently long exposure of the oil to air at ordinary temperature.

While the reason for the high figures shown by olive and almond oils cannot be stated, it appears probable that the explanation is to be found in the quantitative relations of the fatty acids present, rather than in the presence of any peculiar constituent, and that interesting results might be obtained from a study of the viscosities of the soap solutions of pure fatty acids and their mixtures.

QUANTITATIVE LABORATORY,  
June, 1903.

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[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION  
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### THE DETERMINATION OF COMMERCIAL GLUCOSE IN MOLASSES, SYRUPS, AND HONEY.

BY ALBERT E. LEACH.  
Received May 28, 1903.

THE importance of a ready method for the determination of so common an adulterant as commercial glucose is obvious. Several