5 per cent. solution of potassium nitrate added, the mixture evaporated to dryness and ignited, at first gently, then under a blast-lamp, until the residue is white. It is then dissolved in hydrochloric acid, evaporated to dryness, and heated for some time in an air-bath to render silica insoluble. The residue is taken up in water with the addition of a little acid, filtered, and the sulphuric acid precipitated with barium chloride, etc., in the usual way.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 61].

ON THE RELATION OF THE HEAT OF COMBUSTION TO THE SPECIFIC GRAVITY IN FATTY OILS.

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FROM data given in a previous paper[1] it was inferred that among the common fatty oils there exists a certain definite relation between the heat of combustion and the specific gravity. Thus, comparing such typical oils as those of linseed, poppyseed, maize, cottonseed, sesame, almond, and olive, we find that the decrease in drying properties is accompanied by a decrease in specific gravity and a nearly proportional increase in the calorific power, so that the product of these two values shows comparatively little variation. It also seemed probable from the examination of a few samples which were known to have been oxidized by exposure, that such oxidation reduces the heat of combustion to nearly the same extent that it increases the specific gravity. We are now able to give additional data in support of each of these inferences.

The determinations of specific gravity and of heat of combustion have been made by the methods described in our previous paper and we are again indebted to Professor Atwater, for the privilege of doing a considerable part of the work in the laboratories of Wesleyan University. The heats of combustion given in the tables below are those obtained at constant volume; *i. e.*, the results actually shown by the calorimeter. The corresponding values for combustion at constant pressure may be calculated as already explained.[2]

Table A shows the specific gravities and heats of combustion

[1] This Journal, **23**, 164.
[2] *Ibid*, **23**, 167.

of the fatty oils thus far examined which were either fresh or had been well protected from the air, so that no considerable oxidation is believed to have taken place. The last two columns give respectively the product obtained by multiplying, and the quotient obtained by dividing the heat of combustion (in large calories per gram) by the specific gravity. A few non-fatty oils are added at the end of the table.

TABLE A.—RELATION OF SPECIFIC GRAVITY TO HEAT OF COMBUSTION IN FATTY OILS WHEN FRESH.

Lab. No.	Variety of oil.	Sp. gr. $\frac{15.5°}{15.5°}$.	Calories per gram.	Calories × sp. gr.	Calories ÷ sp. gr.
2052	Raw linseed, I	0.934	9.364	8.74	10.03
2070	Raw linseed, II	0.938	9.379	8.80	10.00
2122	Raw linseed, IV	0.933	9.381	8.75	10.05
Aver.	Raw linseeds	0.935	9.375	8.77	10.03
2073	Boiled linseed, I	0.934	9.394	8.77	10.06
2127	Boiled linseed, II	0.935	9.349	8.74	10.00
Aver.	Boiled linseeds[1]	0.935	9.372	8.76	10.02
2069	Poppyseed	0.926	9.382	8.69	10.13
2056	Maize oil, I	0.924	9.413	8.71	10.19
2066	Maize oil, II	0.926	9.436	8.74	10.19
2092	Maize oil, III (dark)	0.926	9.419	8.72	10.17
Aver.	Maize oils	0.925	9.423	8.72	10.19
2063	Sesame	0.924	9.395	8.68	10.17
2053	Cottonseed, I	0.920	9.396	8.64	10.21
2054	Cottonseed, II	0.921	9.401	8.66	10.21
2055	Cottonseed, III	0.923	9.390	8.67	10.17
2089	Cottonseed, IV (dark)	0.927	9.397	8.71	10.14
Aver.	Cottonseed oils	0.923	9.396	8.67	10.18
2102	Rape, I	0.920	9.489	8.73	10.31
2065	Rape, II	0.920	9.462	8.71	10.29
Aver.	Rape oils	0.920	9.476	8.72	10.30
2061	Peanut (arachis)	0.917	9.412	8.63	10.26
2064	Almond	0.919	9.454	8.69	10.29
2058	Olive, I	0.917	9.457	8.67	10.31
2093	Olive, II	0.916	9.451	8.66	10.32
Aver.	Olive oils	0.917	9.454	8.67	10.31
2091	Castor	0.967	8.863	8.57	9.17
2062	Castor	0.964	8.835	8.52	9.16
Aver.	Castor oils	0.966	8.849	8.55	9.16
2076	Menhaden	0.935	9.360	8.75	10.01

[1] Only boiled linseed oils of low specific gravity are here included. Data of other samples are given in Table B. It was recently found that the figures given for boiled linseed oil in our previous paper were incorrect. Through an error the heat of combustion was determined on a sample different from that in which determinations of specific gravity, iodine absorption, and acidity had been made.

Lab. No.	Variety of oil.	Sp. gr. $\frac{15.5^\circ}{15.5^\circ}$.	Calories per gram.	Calories × sp. gr.	Calories ÷ sp. gr.
2077	Menhaden	0.934	9.371	8.76	10.03
Aver.	Menhaden oils	0.935	9.366	8.76	10.02
2104	Cod-liver	0.926	9.434	8.74	10.19
1998	Cod-liver	0.927	9.437	8.75	10.18
Aver.	Cod-liver oils	0.927	9.436	8.75	10.18
2103	Seal oil	0.926	9.424	8.73	10.18
2084	Whale oil	0.924	9.473	8.75	10.25
2057	Lard oil, I	0.917	9.451	8.67	10.31
2060	Lard oil, II	0.919	9.447	8.68	10.28
Aver.	Lard oils	0.918	9.449	8.67	10.29
2080	Sperm oil	0.886	9.946	8.81	11.23
2081	Rosin oil	0.989	10.145	10.03	10.26
2098	Petroleum oil, I	0.881	10.797	9.51	12.26
2099	Petroleum oil, II	0.897	10.753	9.64	11.99
2100	Petroleum oil, III	0.905	10.682	9.67	11.80
Aver.	Petroleum oils	0.894	10.744	9.61	12.01
2143	Turpentine	0.862	10.800	9.31	12.52

Excepting the castor oils, which, of course, differ from all the others in containing a large proportion of ricinolein, the value obtained by multiplying the heat of combustion by the specific gravity shows very little variation as between oils of the same variety, while as between the different classes of oils this value decreases with the specific gravity, but to a less degree. The value obtained by dividing the heat of combustion by the specific gravity varies, of course, in the opposite direction and to a greater degree. Thus the difference between these two values increases as we pass from the oils of higher to those of lower specific gravity. These relations hold as well for the fatty oils of animal as for those of vegetable origin. The non-fatty oils, on the other hand, show quite different relations.

Table B shows the results obtained upon a number of commercial oils which had specific gravities higher than the corresponding fresh oils and which are believed to have been more or less oxidized by exposure to the air. In nearly all cases such exposure is known to have occurred. A sample of blown rapeseed oil is also included.

TABLE B.—RELATION OF SPECIFIC GRAVITY TO HEAT OF COMBUSTION IN "EXPOSED" FATTY OILS.

Lab. No.	Variety of oil.	Sp. gr. $\frac{15.5^\circ}{15.5^\circ}$.	Calories per gram.	Calories × sp. gr.	Calories ÷ sp. gr.
2082	Raw linseed, III	0.947	9.215	8.73	9.73
2123	Raw linseed, V	0.941	9.274	8.73	9.86
2124	Raw linseed, VI	0.952	9.099	8.66	9.56
Aver.	Raw linseeds	0.947	9.196	8.71	...
2072	Boiled linseed, III	0.949	9.191	8.72	9.69
2125	Boiled linseed, IV	0.951	9.152	8.70	9.62
2126	Boiled linseed, V	0.944	9.275	8.76	9.83
Aver.	Boiled linseeds	0.948	9.206	8.73	...
1999	Cottonseed, V (dark)	0.927	9.336	8.65	10.07
2087	Cottonseed, VI	0.929	9.323	8.66	10.04
2067	Cottonseed, VII (old)	0.941	9.168	8.63	9.74
Aver.	Cottonseed oils	0.932	9.276	8.65	...
2086	Rapeseed	0.926	9.412	8.72	10.16
2111	Blown rapeseed	0.974	8.805	8.58	9.04
2094	Almond	0.931	9.311	8.67	10.00
2085	Cod-liver	0.938	9.277	8.70	9.89
2059	Lard oil, III	0.924	9.372	8.66	10.14
2095	Lard oil, IV	0.922	9.394	8.66	10.19
Aver.	Lard oils	0.923	9.383	8.66	....

In this table the figures in the last column are, of course, lower than the corresponding figures in Table A and are quite variable, being dependent upon the extent to which the samples had become oxidized. The values obtained by multiplying the heat of combustion by the specific gravity are very little different from the corresponding values in Table A; in other words, the effect of exposure was to cause an increase in specific gravity and a nearly equal decrease in heat of combustion.

In general the oils which had been exposed showed slightly more free acid than those in Table A. Hydrolysis of fat with liberation of fatty acid involves an absorption of water. To split off 1 per cent. of oleic acid, about 0.06 per cent. of moisture must be taken up. The oils examined contained very little free acid and for our purpose it is probably safe to neglect the small amounts of water involved. It may be noted, however, that any moisture thus taken up would lower the heat of combustion more than it would raise the specific gravity, thus decreasing the value of the product of these two factors; and it will be seen that such slight discrepancies as are found by a comparison of Tables A and B are always in this direction.

Sample No. 2067, an old cottonseed oil, shows such remarkable results that (as the history of the sample was not known) it seemed advisable to determine the elementary composition, in order to confirm the assumption that its peculiar properties were due to oxidation. It yielded, on analysis,

	Per cent.
Carbon	73.66
Hydrogen	11.34
Oxygen	15.00

Sample No. 2054, which was known to be fresh and was selected as being typical, yielded

	Per cent.
Carbon	76.65
Hydrogen	11.74
Oxygen	11.61

The increased percentage of oxygen found in the older sample is quite sufficient to account for the observed differences in specific gravity and heat of combustion; and while the elementary analyses are not in exact proportion to these differences, the agreement is perhaps as close as could be expected between samples produced by different methods at an interval of several years.[1]

Conclusions drawn from a comparison of the figures given in Table B, with those in Table A are open to objection inasmuch as the samples of "fresh" and of "exposed" oils of a given variety are not always from the same source, though the fact that the relations noted apply to each of the seven varieties included in the comparison makes it improbable that they are accidental.

In raw and boiled linseed oils, however, we have obtained sufficient oxidation by exposure in uncorked bottles for two to four months, to give positive confirmation of the inferences already drawn. Thus sample No. 2052, raw linseed oil, and sample No. 2072, boiled linseed oil, gave the following :

[1] A similar comparison was attempted in the case of the blown rape oil (No. 2111), No. 2102 being selected as a typical fresh sample for comparison. The latter yielded : Carbon, 76.23 per cent.; hydrogen, 11.52 per cent.; oxygen, 12.25 per cent. The blown oil yielded figures for carbon ranging from 71.22 to 73.00 per cent., and for hydrogen from 10.61 to 11.09 per cent. This would indicate that the extremely high viscosity of the sample prevented thorough mixing, in which case the determination of heat of combustion may also be less accurate than in the other samples. In general terms, however, it may be said that the increased percentage of oxygen in the blown oil corresponds approximately to the increase in specific gravity and decrease in heat of combustion.

	Sp. gr. at 15.5°.	Calories per gram.	Calories × sp. gr.
Raw linseed before exposure	0.934	9.364	8.74
Same after four months' exposure ...	0.942	9.288	8.75
Boiled linseed before exposure.......	0.949	9.191	8.72
Same after two months' exposure....	0.9595	9.078	8.71
Same after four months' exposure ...	0.968	8.963	8.68

The boiled linseed oil after four months' exposure was so thick that the determinations made upon it may be less accurate than in the other cases. Elementary analyses were made of the boiled linseed oil, before and after the two months' exposure, with the following results:

	Carbon.	Hydrogen.	Oxygen.
Before exposure	75.02	10.73	14.25
After exposure..................	74.15	10.70	15.15

Here the exposure, while raising the specific gravity 1.1 per cent. and lowering the heat of combustion 1.2 per cent., has lowered the combined percentages of carbon and hydrogen 1.1 per cent. of the amount originally present.

The simplest interpretation of these relations would be that the oil took up from the air an amount of oxygen equal to 1.1 per cent. of its original weight and that this oxygen was absorbed without appreciable increase of volume or loss of carbon or hydrogen. It seems probable also that each of the oils shown in Table B above had absorbed oxygen in the same manner.

A study of the quantitative relations of the changes produced by such oxidation in the usually determined "constants" is being carried on in this laboratory, and it is hoped that this may lead to more definite knowledge of the significance of these constants.

We believe that the data here given justify the following conclusions:

1. In fresh fatty oils the heat of combustion is a property quite as constant as the specific gravity, to which it bears a certain definite relation.

2. Oxidation resulting from exposure to air decreases the heat of combustion to practically the same extent that it increases the specific gravity. Hence it is to be inferred that the oxygen is taken up by direct addition and without essential change in the volume of the oil.

3. On account of its close quantitative relations to the specific gravity and ultimate composition, the heat of combustion is likely to prove a useful factor in the further study of the fatty oils.

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