Summary

1. A study of the addition of hydrogen iodide to ethylenic compounds which are capable of forming "normal" and "abnormal" addition products with hydrogen bromide (depending on the "peroxide" content of the reactant mixture) has shown that only the "normal" product of addition is formed, even in the presence of peroxides.
2. The normal addition of hydrogen iodide is assumed to be due to the reducing action of this halogen acid on organic peroxides.
3. It is noteworthy that "peroxides" even though they do not affect the direction of addition of hydrogen iodide to unsaturated compounds, increase the velocity of addition, and in the case of allyl bromide allow the isolation of an addition product, which without added peroxides is formed to a slight extent only.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DEPAUW UNIVERSITY]

An Examination of the Fatty Oil from Pumpkin Seed. The Constitution of Linoleic Acid

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Since our knowledge regarding the fatty oil from the common pumpkin seed is derived almost solely from the early work of Power and Salway,[1] it appeared desirable to reinvestigate this material using the more modern methods available.

The pumpkin seed[2] was found to contain 9.6% moisture and 36.6% of an ether extractable oil whose physical and chemical characteristics, as determined by standard methods, were as given in Table I.

TABLE I

PHYSICAL AND CHEMICAL CHARACTERISTICS OF PUMPKIN SEED OIL

Specific gravity (20°/4°)	0.9159
Refractive index (Abbe 20°)	1.4737
Iodine number (Hanus)	116.8
Saponification value	174.2
Mean molecular weight saturated acids	269.0
Mean molecular weight unsaturated acids	289.2
Iodine number unsaturated acids	138.2
Iodine number saturated acids	9.6
Unsaturated acids (basis of oil) (corrected %)	76.3
Saturated acids (basis of oil) (corrected %)	11.4
Unsaponifiable matter, %	1.58
Reichert-Meissl number	1.5
Acetyl value[3]	2.76
Acid value	12.49

Unsaturated Acids

Preparation of Methyl Esters.—The unsaturated acids were separated by the lead salt–ether method. Their methyl esters were prepared and distilled at 4.5 mm. pressure. The boiling range of 175–180° indicated that the mixture contained acids with the same number of carbon atoms. The mean molecular weight further indicated 18 carbon atom acids.

Bromination.—The unsaturated acids were brominated using the method of Eibner and Muggenthaler,[4] 3.0042 g. of the unsaturated acids yielded 2.0316 g. of the tetrabromide (m. p. 114°). This corresponds to 0.9482 g. of linoleic acid or 31.5% of the acids brominated. Since the iodine number (138.2) of the unsaturated acids indicated the presence of 52.9% of linoleic acid, there must have been present the so-called beta-linoleic acid, the tetrabromide of which is soluble in petroleum ether. No hexabromide was produced, which indicated the absence of linolenic acid.

Ozonolysis.—Ninety grams of the methyl esters was treated with ozone using the method of Riebsomer and Johnson[5] and the resulting methyl esters from this process fractionally distilled in vacuum using a modified Claisen flask, with the following results. With the pressure at 24 mm.: fraction (1) b. p. 54–58°, weight 4.5 g.; fraction (2) b. p. 58–103°, weight 2.8 g.; fraction (3) b. p. 103–106°, weight 8.3 g. Remainder of distillation was at 5 mm.: fraction (4) b. p. 70–117°, weight 4.8 g.; fraction (5) b. p. 117–123°, weight 25.0 g.; fraction (6) b. p. 123–175°, weight 1.0 g. Undistillable, 9.0 g.

Fractions (2), (4) and (6) were obviously intermediates and were not investigated.

Fraction (1) as obtained above contained caproic acid together with a small amount of material not acidic in nature. The entire fraction was saponified and the potassium salt solution extracted with ether to remove the impurity. Treatment of the potassium salt with hydrochloric acid produced the acid, which was distilled. The neutral equivalent for the acid was 117.7. For pure caproic acid this figure is 116.1. The anilide was prepared and melted at 95–95.5°, and a mixed melting point with the anilide of known caproic acid was 95.5–96° (m. p. of known anilide 96°). From these data the presence of caproic acid was inferred.

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(1) Power and Salway, THIS JOURNAL, **32**, 346 (1910).

(2) Obtained from Carroon and Company, Fowler, Indiana.

(3) Lewkowitsch, *J. Soc. Chem. Ind.*, **16**, 503 (1897).

(4) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th ed., Vol. I, p. 585, 1921.

(5) Riebsomer and Johnson, THIS JOURNAL, **55**, 3352 (1933).

Fraction (3) was saponified and shown to be pelargonic acid: n^{20}_{D} 1.4325 (reported n^{20}_{D} 1.433); d^{20}_{4} 0.9079 (reported d^{20}_{4} 0.907); neut. equiv., 156.2 (calcd. 158.1); anilide, m. p. 56° (reported 57°).

The refractive index and density of fraction (5) were compared with dimethyl azelate: d^{20}_{4} 1.005, n^{20}_{D} 1.4361; dimethyl azelate d^{20}_{4} 1.005, n^{20}_{D} 1.436. The ester was saponified and azelaic acid was the product: neut. equiv. 94.5 (calcd. 94.1), m. p. 106.0° (reported 106.5°).

The presence of pelargonic and azelaic acids indicates that oleic acid was one of the unsaturated acids. Since the molecular proportion of azelaic acid was too great to have been associated with only the pelargonic acid in the original molecules, it must also have been a fragment of a molecule which gives azelaic and caproic acid upon ozonolysis. Since linoleic acid was the only unsaturated acid shown to be present with the oleic acid, it appears that caproic and azelaic acids must be the products of ozonolysis of linoleic acid. To obtain these results the formula for linoleic acid must be written as shown (I).

$$\text{(I)}\quad CH_3—(CH_2)_4—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—COOH$$

Malonic acid was not found in any of the products, so presumably it was decomposed completely during the ozonolysis process.

Structure (I) corroborates the finding of Haworth,[6] who oxidized linoleic acid with permanganate in acetone solution and obtained results similar to ours except that he was able to isolate malonic acid as well as caproic and azelaic.

On the other hand structure (I) does not agree with the one postulated by Takahashi,[7] who ozonized linoleic acid from soy bean and rice bran oils, and obtained butyric, glutaric and azelaic acids (rather the corresponding aldehydes) and assigned formula (II) to linoleic acid.

$$\text{(II)}\quad CH_3—(CH_2)_2—CH{=}CH—(CH_2)_3—CH{=}CH—(CH_2)_7—COOH$$

The iodine number of the unsaturated acids was 138.2, which makes possible the calculation of the percentages of oleic and linoleic acids.

	In unsatd. fraction	In oil % acid	% glyceride
Oleic acid	47.1	35.9	37.5
Linoleic acid	52.9	40.4	42.2
	100.0		

Saturated Acids.—The mean molecular weight of the saturated fraction as obtained from the lead salt–ether separation was 269.0. This lies between the values for palmitic and stearic acids and, therefore, indicated such a mixture. The methyl esters of 20 g. of the acids were prepared and fractionally distilled. The boiling range was from 155–190° at 3 mm. pressure. This boiling range also indicated a mixture of palmitic and stearic acids. The distillate was separated into five approximately equal fractions. The highest boiling fraction was saponified and the acid recrystallized from acetone. The highest melting acid obtained melted at 67.5–68°. This material when mixed with pure stearic acid (m. p. 68–69°) gave a m. p. of 68–69°. The neutral equivalent was 282.6. For pure stearic acid this figure is 284.2. Since no higher melting acid was obtained, it was concluded that no longer chain saturated acid than stearic was present.

The lower boiling fractions were saponified separately and converted into the acids. Every attempt to obtain pure palmitic acid from the lower boiling fractions by fractional crystallization from alcohol or acetone failed. Mixtures with a melting point of 56° could be obtained but further fractionation did not change the melting point. Mixed melting points with pure palmitic acid (m. p. 62°) and the mixture melting at 56°, melted at 60°. This indicated the presence of palmitic acid but was not conclusive.

Assuming the mixture to be palmitic and stearic acids and using the neutral equivalent of the mixture of saturated acids (269.0) calculation of the percentages of the saturated acids may be made as follows.

	In satd. fraction	In oil	
		% acid	% glyceride
Palmitic acid	54.3	6.2	6.50
Stearic acid	45.7	5.2	5.40
	100.0	11.4	

These percentages will be somewhat in error because no account has been taken of the small amount of unsaturated acids contaminating the saturated acids.

Summary

1. The physical and chemical characteristics of pumpkin seed oil have been determined.

2. The oil consists essentially of glycerides of oleic, linoleic, stearic and palmitic acids and a small amount of unsaponifiable matter.

3. Further evidence is presented to show that linoleic acid occurring in nature has the structure $CH_3—(CH_2)_4—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—COOH$.

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[6] Haworth, *J. Chem. Soc.*, **135**, 1456 (1929).

[7] Takahashi, *J. Chem. Soc. Japan*, **42**, 130 (1921).