gave a value of 10.25 grams of urea nitrogen per 24 hours. The results of the hydrolysis-aeration method expressed as percentage of the Folin results varied from 99.45 to 101.94 per cent., the average being 100.43 per cent. The results of the Benedict-Gephart method expressed as percentage of the Folin results varied from 100.88 to 103.86 per cent., the average being 102.52 per cent.

Fourth, the hydrolysis-aeration method requires much less time and attention than does the Folin method and it does not require the expert manipulation and training necessary to get concordant results which the Folin method requires.

URBANA, ILL.

THE DEVELOPMENT OF FAT IN THE BLACK WALNUT (JUGLANS NIGRA).

BY F. M. M'CLENAHAN.

Received July 26, 1909.

There exists a recognized uncertainty as to the genesis of vegetable fats and their necessary progenitors. Especially is this true of the fats that occur in the seeds of plants.[1] With a view to shedding some light on this very interesting problem the following observations were made on the chemical development of the kernel of the black walnut during the summer of 1908. On account of the evenness of its development this nut is an ideal one for study. Different positions on the trees and even different trees in the locality did not show an appreciable difference of kernel development. By June 15th the nuts in the neighborhood of the laboratory had reached their full development of size. Thereafter the most significant changes were internal.

Studies were made on crops gathered June 15th, July 15th, July 29th, August 12th, and August 26th. At this last date the nut gave evidence of apparent ripeness, and college duties prevented further analytic study.

Crop of June 15th.—The hull of the nut seemed nearly mature in its structure. The shell had not yet developed its stony consistency, but could be cut easily with a knife. The kernel cavity and kernel capsule were fully developed in volume and form. The kernel, however, was a colorless limpid liquid, having a saline taste and an acid reaction with litmus. There was much tannin in the hull, in the canals of the undeveloped shell, and in the tissue of the kernel capsule, but none whatever in the liquid kernel.

The stem of a fresh nut was cut off close to the hull and the nut was soaked in fuchsine for three days. The fuchsine penetrated the hull and the canals of the shell progenitor, but in no degree was the kernel liquid tinted by it.

[1] See especially Jost's "Plant Physiology," Gibson, 1907, p. 176.

Two bushels of nuts were gathered in the crop of June 15th, from which were obtained 600 cc. of kernel liquid. Cuttings were made at right angles to the longitudinal axis of the nut and through the extremities of the four chambers of the kernel cell but not cutting the kernel capsule. By means of a fine pointed pipette the capsule was pierced and the liquid content was drawn off and drained on to a filter. It was observed as a regular phenomenon with the piercing of the capsule that there was an evident liquid pressure, which was able to eject the liquid for a distance of from one to two feet. The readiness of the liquid to become turbid compelled sterilization by boiling and addition of toluene.

Analysis of the Liquid Kernel.—Twenty-five cc. portions of the liquid kernel were pipetted into beakers and 75 cc. of 85 per cent. alcohol added. Immediately there was a white flocculent precipitate. After standing for some few hours there appeared small colorless bi-twinned, granular crystals of tetrahedral form. After filtering off the crystals and the associated flocculent residue upon ashless paper the deposit was ignited in platinum crucibles. The filtrate was set aside for later study. 0.1251 gram of crystals were obtained from 25 cc. of the liquid kernel.

Each ash residue was transferred to a beaker and was dissolved in boiling acetic acid. Boiling ammonium oxalate was added and the beaker was set aside for some hours to allow the precipitate to settle. It was finally filtered on weighed Gooch filters, dried at 100° for three hours and weighed as calcium oxalate. Previous qualitative tests revealed the absence of sodium, potassium, magnesium, nitrogen, sulphur and chlorine.

The analysis of the crystals gave Ca, 18.99, 19.09, 19.03; P, 4.37, 4.15, 4.18 per cent.

The phosphorus was estimated in the filtrate of the calcium oxalate precipitations by means of uranium nitrate titrations.

Qualitative tests were made in an effort to identify the nature of the acid group or groups in the crystalline compound. The weight of evidence seems to indicate the presence of the malic acid group, but this will be taken up more fully in a subsequent paper.

Qualitative tests of the alcoholic filtrate from the crystals indicated the presence of calcium, potassium, phosphorus and ammonia, and the absence of magnesium, chlorine, sulphur, cyanogen, sugar, starch, tannin, protein, pentosans, and dextrin. Both the crystals and the filtrate were acid to litmus.

The specific gravity of the liquid kernel obtained from the June 15th crop was 1.015 and the quantitative analyses giving its percentage composition are in the table below.

Crop of July 15th.—The kernels at this stage of their development were part liquid, part a jelly-like material, and part a firm, white solid. The three were treated as one and passed through a hashing machine, care being taken to have no trace of the capsule tissue present.

Qualitative tests indicated the presence of protein, pentosans, and magnesium, but the absence of starch, sugar, and tannin. The percentage composition of this crop is given in the table below.

Crops of July 29th, August 12th and August 26th.—The crops subsequent to July 15th did not show any change in the nature of the kernel, except it was increasingly oily and more firm in texture. The proteins, pentosans, crude fiber and magnesium became more pronounced.

The following are the comparative analyses of the kernel crops gathered on the dates mentioned, and are the average percentages of duplicate and triplicate determinations.

THE NATURAL KERNEL.

Constituents.	June 15th.	July 15th.	July 29th.	August 12th.	August 26th.
Total solids	3.510	4.128	20.487	38.325	68.110
Ether extract	0.123	0.556	8.043	19.592	42.176
Crude fiber	...	0.526	6.495	11.755	(16.41)
Total nitrogen	0.182	0.290	0.818	0.892	1.044
Amino nitrogen	0.111	0.145	0.290	0.312	0.466
Protein nitrogen	0.071	0.145	0.528	0.580	0.578
Pentosans	...	present	0.775	0.758	0.940
Ash	(0.964)	0.502	1.336	1.321	1.570
Potassium	0.312	0.253	0.485	0.675	...
Calcium	0.266	0.048	0.072	0.071	0.044
Phosphorus	0.127	0.086	0.055	0.091	0.051
Magnesium	...	0.011	0.079	0.098	...
Sodium	...	...	...	...	...
Halides	...	...	...	...	...
Sugar	...	...	...	...	...
Tannins	...	...	...	...	...
Starch	...	...	...	...	...
Protein	...	slight	positive	positive	positive
Acidity	acid	acid	neutral	neutral	neutral

The above percentages were calculated from the wet weight of the hashed kernel. Below are given the percentages for the components of the dried residue, which are calculated from the above tables, taking the "total solids" as 100 per cent.

Constituents.	June 15th.	July 15th.	July 29th.	August 12th.	August 26th.
Total solids	100.00	100.00	100.00	100.00	100.00
Ether extract	3.54	13.44	39.26	51.12	61.92
Crude fiber	..	12.74	31.70	30.67	(24.09)
Total nitrogen	5.18	7.02	3.99	2.32	1.53
Amino nitrogen	3.16	3.51	1.41	0.81	0.69
Protein nitrogen	2.02	3.51	2.57	1.53	0.84
Pentosans	..	..	3.77	1.97	1.38
Ash	(27.46)	12.16	6.52	3.44	2.30
Potassium	8.88	6.13	2.36	1.78	..

Constituents.	June 15th.	July 15th.	July 29th.	August 12th.	August 26th.
Calcium	7.58	1.16	0.35	0.18	0.06
Phosphorus	3.61	2.08	0.27	0.23	0.07
Magnesium	..	0.26	0.38	0.25	..
Sodium	..	..	..	..	..
Halides	..	..	..	..	..
Sugar	..	..	..	..	..
Tannins	..	..	..	..	..
Starch	..	..	..	..	..
Protein	..	slight	positive	positive	positive
Acidity	acid	acid	neutral	neutral	neutral

Methods Employed.

Total Solids.—The kernels were carefully separated from the capsule and hashed to a fine pulp. Portions were weighed in weighed porcelain boats and dried at 100° in a current of hydrogen for four hours. The residues were taken as total solids.

Ether Extract.—The "total solids" residues were transferred to the extraction thimbles of a Soxhlet apparatus and extracted for five hours with ether as the medium.

Crude Fiber.—The crude fiber was determined by the conventional method.[1]

Amino Nitrogen.—Fresh portions of the hashed kernel were transferred to flasks, a sufficient amount of 10 per cent. potassium hydroxide was added and the evolved ammonia was distilled over into a known volume of 0.2 *N* standard hydrochloric acid. By the volumetric estimation of the neutralized acid the amino nitrogen was calculated, and the above percentages were calculated from the kernel weight taken.

Total Nitrogen was estimated by the Kjeldahl-Gunning method.

Protein Nitrogen was calculated as difference between the total and the amino nitrogen.

Pentosans.—The phloroglucinol method was employed in the estimation of the pentosans.[1]

Ash.—Careful ashing in platinum dishes.

Potassium.—Estimated as the chlorplatinate.

Calcium.—Estimated as the oxalate. The ash was weighed in portions of convenient amounts and dissolved in nitric acid. This acid solution was neutralized with ammonium hydroxide and reacidified with acetic acid. The acetic acid solution was raised to the boiling point and a hot solution of ammonium oxalate was added. The containing beaker was set aside for some hours to allow the precipitate to settle. Finally this was transferred to a weighed Gooch crucible, dried at 100°, weighed and calculated as calcium oxalate, $CaC_2O_4.H_2O$. The filtrate from the oxalate was reserved for the estimation of the phosphorus component.

[1] *U. S. Dept. of Agric., Bull.* 46, rev. ed.

Phosphorus.—The filtrate from the calcium oxalate was raised to the boiling point and standard uranium nitrate was run in until the end point was indicated by the coloration of test drops of potassium ferrocyanide.

Magnesium was estimated as the pyrophosphate. Portions of the dissolved ash were freed from calcium by the above method and to the filtrate was added sufficient sodium phosphate in ammoniacal solution to precipitate the magnesium, which was allowed to stand for some hours, filtered on a weighed Gooch crucible, dried, ignited and weighed as magnesium pyrophosphate.

The sodium, halides, tannins, starch, proteins and acidity were shown to be qualitatively absent except as otherwise noted in the table above.

Summary of Observations.

1. Starch, sugar and tannin were absent from the kernel at all periods of its development.

2. Fuchsine was not able to penetrate into the interior of the kernel capsule, although it would penetrate the other parts of the nut.

3. Tannin was markedly present in the hull and the tissue of the kernel capsule.

4. When the kernel was entirely a liquid (June 15th) there was a pronounced fluid pressure.

5. The first formation of the jelly-like kernel was on the interior surface of the capsule tissue. This gradually changed to a white solid, while the jelly-like formation retreated toward the center of the chamber of the capsule, replacing in turn the liquid and finally being itself replaced by the solid kernel.

6. The fats increase out of all proportion to the increase or decrease of other constituents.

Theoretical Conclusions.

Evidently the fat in the walnut is not formed from starch, sugar or tannin within the capsule of the kernel. The quantitative relation of the fats to the crude fiber, proteins and pentosans would not lead one to believe that the fats were formed from the decomposition products of these substances. The inability of the fuchsine to migrate to the interior of the capsule would lead one to doubt any direct circulatory connection of that chamber with the other parts of the nut. This conclusion is strengthened by the observed fluid pressure in the capsule. Again the very pronounced presence of tannin in the *tissue* of the capsule and none of it in the fluid within the capsule would favor the conclusion that the tannin may afford the material, from whose decomposition products are built up the fats, although these decomposition products are not transported to the interior of the capsule by means of ordinary fluid circulation. The early disappearance of acidity would indicate that at an early date in the nut's development the migration of free fatty acids into the capsule had ceased, if any such phenomenon had ever taken place. The successive steps in the metamorphosis of the kernel proceed from the interior surface of the capsule membrane. The fluid pressure is quite probably due to osmosis. May it not be that the interior cells of the capsule membrane cause the decomposition of tannin, produce metamorphic syntheses and allow the osmosis of these newly formed substances into the interior of the capsule? After the kernel had become solid the increase of fat went on, although there was no substantial change within the kernel in reference to the other components and there was no marked development of fat elsewhere in the nut than in the kernel. The most noticeable development aside from the fat was the tannin in the hull.

The author plans to study further this subject. He wishes to thank Prof. L. B. Mendel, of Yale University, for friendly criticism and advice.

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NEW BOOKS.

Grundriss der Kolloidchemie. By WO. OSTWALD. 525 pp., Steinkopff, Dresden, 1909. (Paper, M. 12; bound, M. 13.5.)

The author of this comprehensive work has apparently inherited the well-known powers of his father, and by this book and his editorship of the *Zeitschrift für Chemie und Industrie der Kolloide*, he seems to be standing in relation to colloid chemistry where Wilhelm Ostwald stood with respect to physical chemistry a decade ago. A thorough treatment of the subject is to be expected from a man in his position, and the reader is not disappointed. It is a surprise even to one who has followed the subject, to note that the author has read and used in this book not far from one thousand articles on the subject of colloids. No known part of the subject has been neglected, and the book is a much more exhaustive treatise than any other one on the subject. We hope an English translation will be made, as the subject and this treatment by Ostwald well warrant it. W. R. WHITNEY.

Problems and Questions in Chemistry. BY FRANKLIN TURNER JONES, University School, Cleveland, O. 46 pp. Published by the author, Price, 40 cents.

This little pamphlet contains 460 questions compiled from college entrance examination papers sent by Harvard, Sheffield, Princeton, Regents, Board, Case and Cornell. There are also 4 pages of hints on the solution of numerical problems and 295 incomplete equations stated in words. The value of such a compilation for teachers is evident. Its use by students would probably increase the examination evil about which so much has been written in England. Possibly, however, we are in more danger from lack of examinations in America. W. A. N.