significant effects upon the percentage of protein and of starch in the kernels were produced by shutting off the direct rays of sunlight from the plants during the last ten or twelve days of the ripening period. A careful study of the figures fails to reveal any exact relation between the decreased percentage of starch and the increased proportion of nitrogenous bodies. Hence it appears that the increase in the percentage of crude protein is not due simply to the failure of the plant to build up its normal amount of starch, but to some disturbance of the physiological processes caused by the absence of direct sunlight.

We plan to repeat this experiment during the coming season in considerably greater detail, and to extend the investigation to other grains and to vegetables which store up their reserve of carbohydrate food material in other forms than starch.

WASHINGTON STATE EXPERIMENT STATION,
Pullman, Wash., Feb. 28, 1907.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE].

RIPENING OF ORANGES[1]

BY W. D. BIGELOW AND H. C. GORE.

Received February 18th, 1907.

In order to obtain some general information regarding the changes in composition of fruit during its growth and ripening, we have found it necessary to so plan our work as to include the examination of varieties of fruit in which certain ingredients or complexes are present in considerable proportion. The error of determinations in proximate organic analyses is relatively so great, and the percentage of certain complexes in certain fruits and the percentage of some of the complexes in all fruits so small, that it is impossible to select a single fruit in which a sufficient number of determinations can be made to give an adequate idea of the changes that take place in fruit during its growing and ripening stages.

In the fruits thus far reported by us, the acid content has been so low that the determination of its rôle in the growth and ripening of the fruits is difficult. The majority of the fruits grown in temperate climates contain a relatively small amount of acid, and it is not an easy matter to select fruits in which the course of the formation and the disappearance of acid may be traced to advantage. Accordingly the orange was selected as a fruit relatively rich in acid. As was pointed out by us in our study of apples[2], fruits, especially in their green state, suffer changes in composition very rapidly after picking, and a serious error attends the study of the ripening of fruit which is grown at a distance of several days from

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[1] Read before the American Association for the Advancement of Science at New Orleans, December, 1905.

[2] U. S. Dept. Agr. Bur. Chem. Bull., 94, p. 51.

the place of its examination. In fact, satisfactory results can only be obtained when the fruit is taken immediately from the tree to the laboratory.

The oranges used in this study were grown in the Department greenhouse, and each sample was picked immediately before the examination was begun. At each picking the oranges of the tree were carefully sampled, fruit being taken from all portions of the tree, and the attempt was made to secure at the successive pickings samples that would represent correctly, successive stages in the ripening of the fruit.

No chemical work on the ripening of oranges is known to the writers except that of Berthelot and Buignet[1]. They worked on a sample of unripe oranges which were picked and then stored until ripe. No figures are given, but the authors note that analyses made before and after storage indicated an increase of sucrose on ripening, invert sugar remaining nearly constant. In no case do our results confirm those of these writers.

In Table I is given the composition of the fruit of the orange St. Michael, grown in the Department greenhouse. Samples were picked from the same tree at eight stages of their growth and submitted to analysis. Sub-samples from six of these samples were stored in the laboratory for periods varying from 16 to 31 days, and examined at the end of these periods of storage.

The analytical results show that during growth the skin and pulp increased steadily in weight per orange, the pulp increasing much more rapidly than the skins. The weight of solids[2] per orange in the skins increased gradually during growth. A slight loss in solids, however, took place on storage. Considerable desiccation took place on storage at room temperatures, particularly in the skins. This is shown by the higher percentages of solids found in the stored fruit.

In regard to the chemical changes taking place in the pulp, it will be noted that the percentage of acid decreased gradually from the beginning of the period of observation until the fruit was mature.

The percentage of total solids of the pulp of fruit remained almost constant until October 5th, after which a gradual increase occurred.

The percentage of the sugars in the pulp increased from the beginning to the end of the period of observation, the percentages of reducing sugar and of sucrose being nearly equal. The percentage of marc[3] decreased from the beginning. It would seem, therefore, as far as can be determined from the percentage composition of the pulp of the fruit, that the total amount of acid and marc are formed somewhat early in the develop-

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[1] Compt. rend., 51, 1094, (1860).

[2] Determined by drying at 100°.

[3] The term "marc" is used in its usual significance to designate the cell wall structures of the fruit, or the material insoluble in cold water.

ment of the fruit, while the sugars continue to be formed up to its full maturity.

TABLE I.

Analyses of St. Michael Oranges, 1905 — Analysis of Pulp

Condition	Date	Weight per Orange grams	Skins pct.	Pulp pct.	Seeds pct.	Solids in Skins pct.	Solids in Skins grams per Orange	Solids pct.	Acid as Citric pct.	Reducing Sugar as Invert pct.	Total Sugar as Invert pct.	Polarizations Direct degrees V	Polarizations Invert Degrees V	Sucrose by Reduction pct.	Sucrose by Polarization pct.	Marc pct.	Total Determined[1] pct.
Fresh	July 31 '05	68.2	33.5	64.6	1.9	21.8	4.98	11.83	2.66	1.47	2.95	+ .4°	—1.32°at28°	1.41	1.34	4.08	9.62
"	Aug. 23 '05	86.7	27.1	70.4	2.5	21.3	5.00	11.57	2.05	2.35	4.32	+ .6	—1.65 at 30	1.77	1.80	——	——
Stored	Sept. 19 '05	65.5	16.85	81.16	1.99	43.4	4.79	13.20	2.23	3.57	4.83	— .2	—1.43 at 30	1.20	.97	4.16	11.16
Fresh	" 19 '05	98.9	23.02	74.66	2.32	22.7	5.17	11.95	1.88	2.83	5.51	+1.3	—1.76 at 30	2.55	2.41	2.60	9.86
Stored	Oct. 5 '05	83.4	17.62	80.36	2.02	30.95	4.55	12.59	1.88	3.47	5.38	+ .3	— 1.72 at 24	1.81	1.55	2.92	10.08
Fresh	" " "	104.8	22.51	75.43	2.07	23.06	5.44	11.78	1.71	2.89	5.79	+1.2	—2.14 at 24	2.75	2.57	2.47	9.82
Stored	" 23 '05	90.5	17.35	80.15	2.50	34.93	5.48	12.68	1.79	4.25	6.38	+ .75	—2.1 at 21	2.02	2.19	2.73	10.79
Fresh	" 30 '05	128.4	24.52	73.48	2.00	22.88	7.20	12.03	1.40	3.67	6.87	——	—2.2 at 22	3.04	——	2.02	10.13[2]
Stored	Nov. 27 '05	100.9	14.10	83.40	2.50	43.00	6.12	13.71	1.46	4.49	7.43	+1.4	—2.4 at 21.5	2.79	2.90	2.73	11.47
Fresh	" 14 '05	132.6	22.71	75.56	1.73	24.7	7.44	12.28	1.39	3.86	7.52	+2.2	—2.4 at 20	3.48	3.49	1.86	10.59
Stored	Dec. 15 '05	107.7	14.02	83.94	2.04	43.4	6.55	14.55	1.38	4.77	8.08	+1.4	—2.4 at 24	3.14	2.92	2.89	12.18
Fresh	" " "	138.3	25.22	73.05	1.73	24.8	8.65	13.96	1.26	4.44	8.64	+2.3	—2.7 at 24	3.99	3.85	2.07	11.76[3]
Stored	Jan. 11 '06	107.7	17.08	80.88	2.04	38.6	7.10	14.29	1.15	5.13	9.00	+2.4	—2.3 at 24	3.68	3.61	2.40	12.36
Fresh	" " "	124.1	30.82	67.67	1.51	22.9	8.76	14.33	1.04	5.43	9.03	+2.75	—2.3 at 24	3.42	3.88	2.06	11.95

[1] Ash and nitrogen are not included in the total determined constituents.

[2] Ash, 0.43.

[3] Ash, 0.43, N, 0.16.

The changes of the sub-samples during their storage are of interest and confirm on the whole our previous observations with other fruits. The increase in percentage of total solids is of course due to the desiccation of fruit during storage. The increase in percentage of reducing sugar, and the corresponding decrease in the percentage of sucrose indicate the transformation of sucrose to reducing sugar. It will be noted that in all cases the sucrose decreases in proportion to the increase in reducing sugar, the latter, however, being somewhat greater than the former. This last fact resulting in the increase of the percentage of total sugars present is doubtless due to the desiccation of the fruit.

The results of the oranges from a second tree, are given in Table II[1]. Seven samples were taken at different periods, and sub-samples from four of these were stored for a number of days in the laboratory.

The results shown in Table II confirm in every essential detail those of Table I. The apparent decrease in the percentage of total solids from August 1st to September 19th can probably be explained by a slight error in sampling. The difficulty of securing a sample which correctly represents the average fruit on the tree is readily understood. On the whole, however, the results indicate that the samples were satisfactory.

With this variety of fruit, as with the one already described, the percentage of acid and of marc decreased throughout the period of observation. The percentage of total sugar, calculated as invert, increased throughout, and the total sugar was about evenly divided into sucrose and invert sugar. Here, again, on storage the percentage of reducing sugar increased in proportion to the decrease of the sucrose.

To obtain an adequate conception of the changes in composition of the fruit during its growth it is necessary to compare the results of various analyses expressed on the basis of grams of each constituent per fruit.

In Figure I the composition of the St. Michael orange is expressed as grams per fruit.

The weights of acid and marc remained nearly constant during the growth of the fruit. These constituents therefore are formed early in the development of the fruit. The total solids increased uniformly throughout the period of observation[2] as did also the sucrose and reducing sugar, the respective weights of these sugars remaining identical throughout the period of observation.

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[1] Note by Mr. Wm. A. Taylor, Pomologist in charge of Field Investigations, U. S. Department of Agriculture: "The fruit reported on in Table II was from a tree which has long stood in the Department orange house under the label name "dulcis Braziliensis." It is a navel orange, closely resembling the Bahia or Washington navel, but not considered identical with that variety".

[2] Unfortunately the crop was picked before our sample of Jan. 11 was taken. The few oranges left on the tree were probably not representative, and while their percentage composition is included in Table I, the results are not given in the chart.

TABLE II.

Analyses of Naval[1] Oranges, 1905.

Analyses of Pulp.

												Polarization		Sucrose by			
Condition	Date	Weight per Orange grams	Skins per cent.	Pulp per cent.	Seeds per ct.	Solids in Skins per ct.	Solids in Skins grams per Orange	Solids per ct.	Acid as citric per ct.	Reducing Sugar as Invert per ct.	Total Sugar as Invert per ct.	Direct Degrees V	Invert Degrees V	Reduction per ct.	Polarization per ct.	Marc. per cent.	Total[2] Determined pr ct.
Fresh	Aug. 1 '05	80.2	35.2	64.8	none	18.8	5.31	11.82	1.99	1.98	4.04	+ .21	—1.43 at 28°	1.96	1.43	4.18	10.11
“	“ 23 '05	99.6	29.9	70.1	“	20.2	6.02	11.71	1.61	2.63	5.28	+1.15	—1.87 at 30°	2.30	2.42	....	....
“	Sept. 19 '05	116.2	25.6	74.4	“	20.7	6.16	11.02	1.45	2.65	5.48	+1.55	—1.87 at 30°	2.69	2.69	2.45	9.24
Stored	Oct. 5 '05	105.9	18.42	81.58	“	29.30	5.72	11.55	1.30	3.38	5.74	+ .6	—2.31 at 24°	2.24	2.24	2.65	9.57
Fresh	“ “ “	136.7	21.66	78.34	“	22.50	6.66	11.70	1.08	3.24	6.55	+1.6	—2.2 at 24°	3.14	2.92	1.88	9.34
Stored	“ 23 “	119.5	18.38	81.62	“	28.74	6.31	12.84	1.09	3.99	6.87	+1.35	—2.1 at 21°	2.74	2.65	2.45	10.27
Fresh	“ 30 “	156.1	21.36	78.64	“	22.45	7.48	11.62	.96	3.55	7.25	......	—2.1 at 22°	3.52	......	2.05	10.07[3]
Stored	Nov. 27 '05	124.9	14.30	85.70	“	37.80	6.75	12.60	.96	4.36	7.85	+1.7	—2.5 at 21.5°	3.32	3.20	2.04	10.68
Fresh	“ 14 '05	158.1	23.96	76.10	“	24.80	9.39	12.46	1.03	4.07	8.07	+2.3	—2.75 at 20°	3.80	3.83	1.85	10.75
Stored	Dec. 15 '05	119.5	15.27	84.73	“	39.7	7.25	13.35	.90	4.71	8.56	+1.8	—2.8 at 24°	3.63	3.54	2.44	11.71
Fresh	“ “ “	148.1	26.16	73.84	“	24.5	9.49	13.76	.89	4.78	9.38	+2.5	—3.1 at 24°	4.37	4.31	1.86	11.90[4]

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[1] See note page 770.

[2] Ash and nitrogen are not included in the total determined constituents.

[3] Ash, 0.33.

[4] Ash, 0.38; N, 0.18.

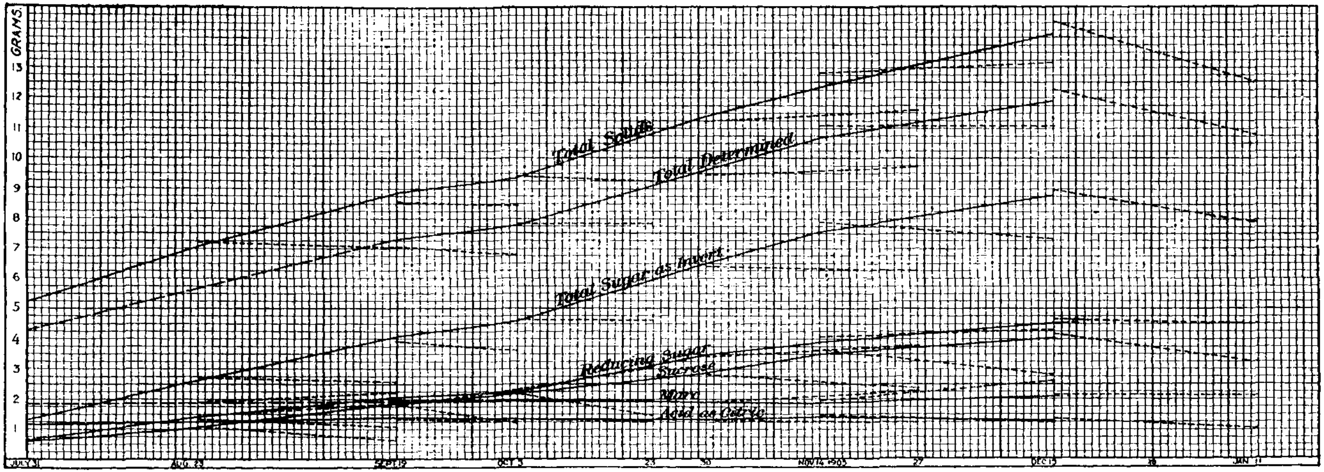

FIG I. Showing the changes in composition during growth of St. Michael oranges. Basis of grams per fruit.

During the storage there was a slight loss in acid and in sugar. This is confirmatory of similar results obtained with apples[1] and peaches[2], and is probably due to the decomposition of acid and sugar in the respiration of the fruit. Notwithstanding the loss in sugar there is a considerable gain in the weight of reducing sugar during the periods of storage. This is due to hydrolyzation of sucrose, the loss in weight of which is greater than that of total solids. Reducing sugar is therefore formed more rapidly than it is utilized for respiration. Storing also appears to cause slight loss in acid.

The results of the examination of the oranges from the second tree confirm the results obtained with the first variety. These results, however, as expressed in Figure 2 are not quite as regular as those with the former variety. This can probably be explained by our possible failure to obtain as uniform samples of this variety as of the other which has already been commented on. The curves representing the respective weights of acid, marc, total sugars, sucrose, and reducing sugar, at different stages of the growth of the orange, confirm in every particular those found in the study of the St. Michael orange.

The samples picked on October 5th were entirely green in color except for a few yellow spots where the orange had been attacked by insects, On storing, the samples turned yellow and on October 23rd, the date of their examination, the storage samples had assumed the full color of ripe oranges. The samples picked on October 30th were about half colored and, as in the previous case, the storage samples turned yellow. The samples picked on November 14th were almost entirely yellow, some specimens, however, being slightly green. From their appearance it was evident that the samples were not completely ripe. The samples picked on December 15th were of full rich orange color, and the majority of the fruits separated easily from the trees. In the study of apples previously noted[3], we called attention to the fact that the more immature a fruit on picking the more rapid the changes that tended toward its ripening. In the orange we find the same tendency in the case of the sugars but to a considerably less degree. This is an interesting point since it indicates that the orange may be examined at a greater distance from the place of its growth than is true of the apple.

CONCLUSIONS.

The pulp and skin increase during growth, the pulp increasing much more rapidly than the skin. In regard to the changes in the pulp, the acid of the fruit and the cell-wall tissue, or marc, are formed early in the life history of the fruit and remain nearly unchanged in quantity during

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[1] U. S. Dept. Agr. Bur. Chem. Bull. 94, p. 42.

[2] Ibid, Bull. 97, p. 23.

[3] loc. cit.

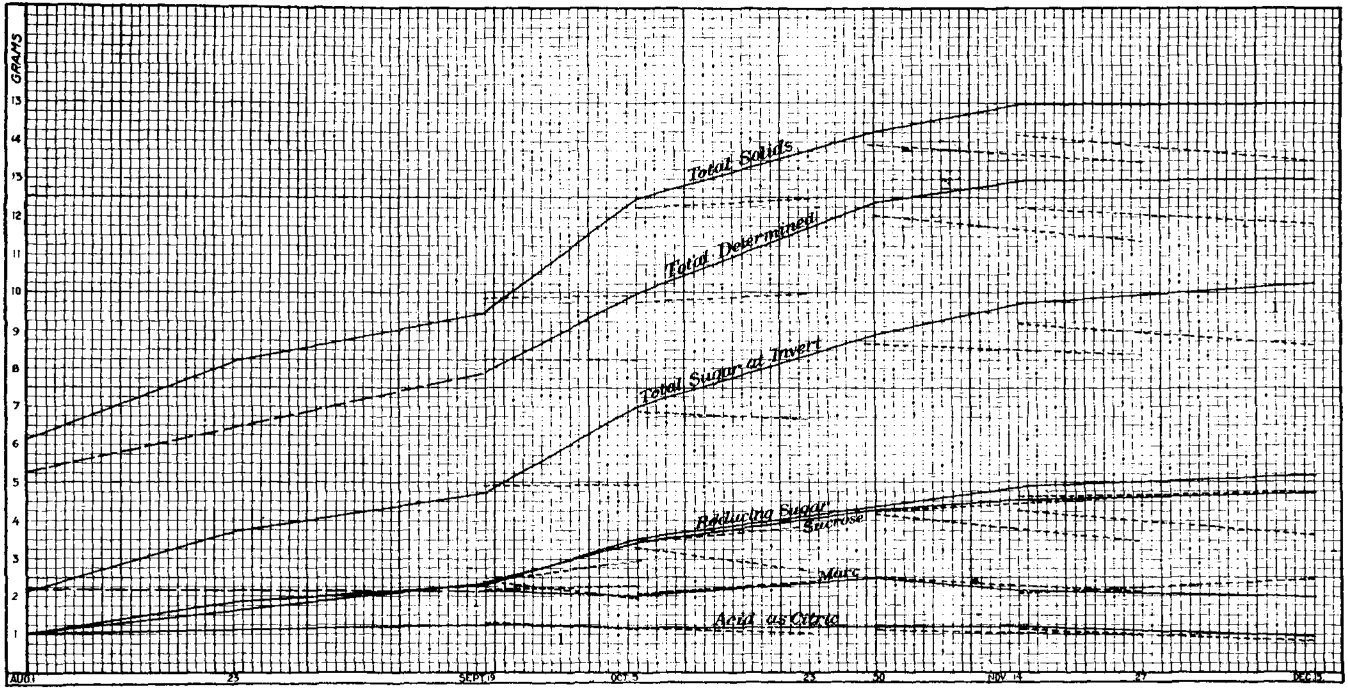

FIG. II. Showing the changes in composition during growth of navel oranges. Basis of grams per fruit.

the subsequent development. The sugars increase gradually during the growth of the orange, sucrose and reducing sugar existing in approximately equal quantity.

Storage of the fruit at room temperatures at all stages of its development results in slight loss of acid and of total sugar, a marked increase of reducing sugar, and a corresponding decrease of sucrose. The loss of acid and sugar noted above is to be explained as in the case of apples by the consumption of these substances as a result of the respiration of the fruit. The weight of marc remains practically constant, and the weight of acid appears to decrease slightly on storage during the various stages of the development of the orange.

ON THE ANALYSIS OF LIGNITIC AND SUB-BITUMINOUS COALS[1]

BY ALVIN J. COX

Received February 18, 1907

The directions for coal analysis recommended by the Committee appointed by the American Chemical Society,[2] which embody the salient points of the previous work on this subject are satisfactory for coking but not for certain non-coking coals, which were comparatively of insignificant value when the report of the Committee was made. These coals are now of sufficient importance to demand a method which will yield correct results in their analysis. The fact that the use of the directions recommended by the Committee gives uncertain results in the determination of volatile combustible matter in Philippine coals has already been published.[3]

These coals are deposits of the so-called black lignite and belong to the class which are usually spoken of under the name sub-bituminous, adopted by the United States Geological Survey. They are all non-coking. A few show incipient coking.

When the directions of the Committee are followed in the expulsion of volatile matter, their data indicate little if any mechanical loss for non-coking coals; on the contrary my results show a very large mechanical loss. It is not even necessary to have analytical data to prove that this loss is large. One can see the shower of incandescent carbon particles which are driven off during the first one or two minutes' heating.

The publication[4] above referred to in the discussion of certain analyses of Philippine coals says:

"The coal analyses were made according to the directions recommended by the Committee appointed by the American Chemical Society. In the

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[1] For the basis of this paper such results as are thought to be of general interest to coal investigators have been selected from an extended investigation of Philippine coals made in the Chemical Laboratory of the Bureau of Science, Manila.

[2] This Journal (1899) 21, 1116; The Coal and Metal Miners' Pocket Book 7th Ed. (1902), Scranton, Pa., 173.

[3] Cox. A. J., Phil. Jour. Science (1906) 1, 890.

[4] Ibid.