being 10.50% (a gas rush is hard to prevent in the analysis, even after careful grinding of the specimen with fine copper oxide). The compound is very slightly soluble in benzene, more so in ether, most in methyl alcohol and even in this case cannot be said to be more than somewhat soluble in the hot solvent, hydrolysis taking place. It is colorless, melting with gas evolution at 155–156° (uncorr.). It forms a copper salt, drying emerald green and not decomposing under 240°. The silver salt darkens after separation. The benzoyl derivative forms from the sodium salt in water on shaking with an ether solution of benzoyl chloride; it is soluble in methyl alcohol, insoluble in water and melts at 150–151°. It seems to suffer the ordinary decomposition with sodium hydroxide with the formation of an oily and very stable isocyanate.

Summary

A discussion of the azide rearrangement and the possibilities of test of the univalent nitrogen hypothesis is presented. An attempt to arrange an experiment limiting the alternative formulations of the rearrangement is given and the preparation of some azides and a quinoline hydroximic acid is described.

NEW YORK CITY

[CONTRIBUTION NO. 3 FROM THE CHEMICAL RESEARCH LABORATORY OF THE UNITED FRUIT COMPANY]

QUANTITATIVE CHANGES IN THE CHLOROPLAST PIGMENTS IN THE PEEL OF BANANAS DURING RIPENING[1]

BY HARRY VON LOESECKE

RECEIVED NOVEMBER 30, 1928 PUBLISHED AUGUST 7, 1929

Introduction

The purpose of this investigation was to gain some knowledge of the changes which the pigments in banana peel undergo during the process of ripening of the fruit, and the cause of the yellow color. It is a well-known fact that during maturation the fruit changes in color from green to yellow, but no quantitative data seem ever to have been collected indicating the relation of these pigments in the peel of the banana to one another during ripening.

The three pigments estimated were chlorophyll (a + b), xanthophylls and carotin. These are not the only pigments present, as during the process of separation there were indications of flavones and anthocyanins. These latter pigments are present in the cell sap, while chlorophyll, xanthophylls and carotin are present only in the specialized portions of the protoplasm known as plastids.

Method of Investigation

Each determination (Table I) represents the peel from three fingers and these fingers were taken from three separate hands on a specially

[1] This is one of a series of investigations carried out by the Research Department of the United Fruit Company, to be published in scientific journals.

selected stem.[2] The fruit was of one variety[3] and was ripened under controlled conditions as to temperature and humidity in specially constructed rooms.

The fruit was peeled, the pulp side of the peel scraped free from pulp, the peel cut into small pieces and ground in a mortar with sand. It was practically impossible to macerate green peel fine enough to remove all of the pigment, and even after repeated extractions the peel still showed very faint traces of green. Ripe peel could be mashed to a fine pulp and extraction was apparently complete.

Quantitative determinations of total sugars (calculated as invert sugar) were made on the pulp of the fruit from which the peel was taken.

The peel, prepared as above, was extracted in the cold with 30% aqueous acetone to remove gums and flavones. The chloroplast pigments were then extracted with pure acetone after the method of Schertz.[4] After the chlorophylls had been extracted and saponified to chlorophyllins, they were determined colorimetrically using a solution of chlorophyllins prepared from pure chlorophylls as a standard.

Xanthophylls and carotin, after extraction and separation from the chlorophylls, were determined colorimetrically using a solution of Naphthol Yellow as a standard for the former, and Naphthol Yellow and Orange G as a standard for the latter, after the method of Sprague.[5] It was found impossible to compare xanthophylls and carotin with these dyes by artificial light.

Results

The results of the determinations are given in Table I. The age of the fruit *from the time it was discharged from the boat* is given in the first column. In the second column chlorophylls are indicated, in the third xanthophylls, in the fourth carotin and the fifth total yellow pigments (carotin plus xanthophylls). All results are expressed in milligrams of pigment per kilogram of fresh peel.

The sixth column represents percentage of total sugar (as invert) in the pulp of the fruit from which the peel was taken. From researches extending over a period of two years during which more than six thousand determinations of total sugar in the pulp of the fruit were made, it has been established that total sugar is the best criterion of the ripeness of the fruit.

[2] Banana terms are perhaps a little confusing to the uninitiated. A single banana is called a "finger;" the group of fingers, known to the laity as a "bunch," is called a "hand," each containing from 14 to 20 individual "fingers." The cluster of "hands" attached to the stalk is called a "stem."

[3] A variety of *Musa sapientum* known as Gros Michel. This is the yellow variety most common on fruit stands.

[4] Schertz, *Plant Physiology*, **3**, 211 (1928).

[5] Sprague, *Science*, **67**, 167 (1928).

Table I

Chlorophyll, Xanthophyll and Carotin in the Peel of Bananas

Expressed in milligrams per kilo of fresh peel

Days	Chlorophyll (a + b)	Xanthophyll	Carotin	Total yellow pigments	Total sugar (as invert) in pulp, %	Series no.
0	94.5	5.21	1.57	6.78	0.50	
2	15.5	5.45	1.90	7.35	1.64	
3	..	6.31	2.51	8.82	6.14	I
4	00.0	6.57	1.71	8.28	9.92	
0	102.9	7.34	2.05	9.39	0.40	
2	72.5	5.75	1.82	7.57	1.25	
3	48.7	5.91	2.27	8.18	2.24	II
4	29.0	5.70	2.87	8.57	4.54	
5	00.0	3.95	3.56	7.51	11.16	
0	51.7	6.61	1.54	8.15	0.58	
3	40.8	5.09	2.66	7.75	0.81	III
4	14.4	5.41	1.67	7.08	7.63	
0	83.4	5.92	3.66	9.58	0.98	
1	52.5	7.02	2.44	9.46	5.64	IV
0	70.1	7.21	1.22	8.43	0.93	
2	66.1	4.90	3.41	8.31	1.54	
3	14.1	5.15	3.39	8.54	6.52	V
5	00.0	5.00	3.69	8.61	8.25	

The last column, "Series," represents five different groups; in each group there are from two to five determinations depending upon the length of time the fruit was followed during ripening.

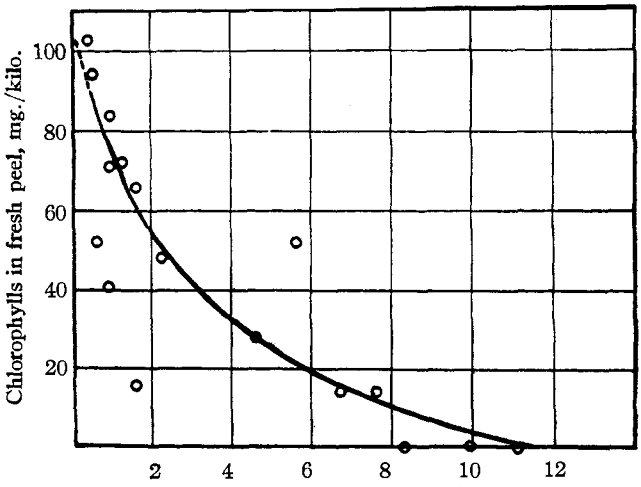

Fig. 1.—Relation of chlorophylls in banana peel to total sugar (as invert) in pulp.

It will be noticed that the total sugar in the pulp varies from 0.4% to nearly 1.0% at zero days (*i. e.*, at time of discharge from the boat). When picked from the tree the fruit contains less than 0.1% of total sugar as invert. Since the chlorophylls in the peel decrease rapidly at first with respect to sugar in the pulp, it follows that the peel of the fruit at the time of harvesting would contain more chlorophylls than at the time of discharge from the boat.

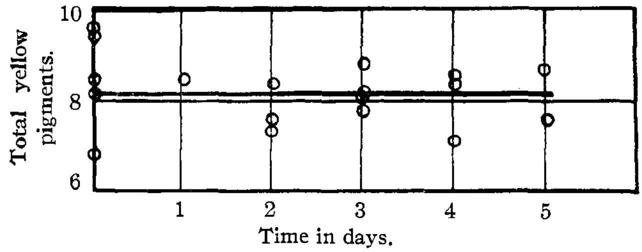

Fig. 2.—Total yellow pigments (xanthophyll and carotin) in banana peel with respect to time.

The amount of xanthophylls is always greater than the amount of carotin and the carotin to xanthophylls ratio changes at various stages during the ripening of the fruit.

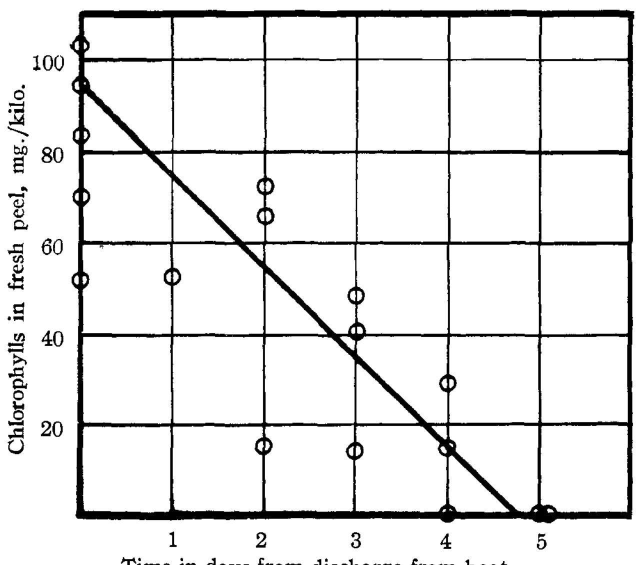

Fig. 3.—Decrease of chlorophylls in the peel of bananas during ripening in respect to time.

The total yellow pigments remain approximately constant throughout the maturation of the fruit (Fig. 2). In other words an unripe banana contains the same amount of total yellow pigments as a ripe banana, but in the case of the former the yellow color is masked by chlorophyll.

Acknowledgment

The writer wishes to express his appreciation to Dr. F. M. Schertz of the Bureau of Soils at Washington, D. C., for his kindness in supplying a sample of pure chlorophyll.

Conclusions

The pigments, chlorophyll (a + b), xanthophylls and carotin were determined in the peel of bananas. From the data obtained the following conclusions have been reached: the data indicate that the chlorophyll content of the peel ranges from 102.9 to 51.7 milligrams per kilogram of fresh peel in the unripe fruit at discharge from the boat and decreases as the fruit ripens. Chlorophylls decrease as a straight line function of time (Fig. 3). The total yellow pigments (xanthophyll plus carotin) remain approximately constant throughout the maturation of the fruit. The amount of xanthophylls is always greater than the amount of carotin, the range of the former being from about 5 to 7 milligrams per kilogram of fresh peel, while the range of the latter is from 1.5 to 3.5 milligrams per kilogram of fresh peel.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE POLARIMETRY SECTION OF THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

THE STRUCTURE OF ALPHA-METHYLXYLOSIDE[1]

BY F. P. PHELPS AND C. B. PURVES

RECEIVED JANUARY 21, 1929 PUBLISHED AUGUST 7, 1929

Crystalline trimethylxylose, derived from the corresponding β-methylglycoside, was the first member of the methylated monosaccharides to which an amylene oxide ring structure could be assigned with certainty,[2] and at the time the opinion was expressed that not only α- and β-methylxyloside, but possibly xylose itself, were similarly constituted. The intervening years, however, have brought to light several cases in which methylating agents, applied to a reducing sugar, have produced derivatives of more than one ring type and, in this connection, the behavior of galactose and arabinose may be cited.[3] Pryde, Hirst and Humphries have shown that in the case of these two sugars methylation with methyl sulfate and alkali undoubtedly gives at least two ring forms. In the case of xylose also this method gives an impure product, the rotation

[1] Publication approved by the Director of the Bureau of Standards.

[2] Hirst and Purves, *J. Chem. Soc.*, **123**, 1352 (1923).

[3] Pryde, Hirst and Humphries, *ibid.*, **127**, 348 (1925).