intervals during the first eight and one-half hours of the hydrolysis.

2. Corresponding non-mercaptalated hydrolyzed celluloses were prepared under exactly similar conditions, except that the ethyl mercaptan was omitted.

3. Sulfur analytical data indicated that the average degrees of polymerization of the mercaptalated products varied from 190 glucose units after 270 minutes to approximately 100 glucose units after 510 minutes.

4. The degrees of polymerization calculated, according to the formula of Kraemer and Lansing, from the cuprammonium viscosity data for the corresponding non-mercaptalated hydrolyzed celluloses were consistently higher than those calculated from the sulfur analytical data, and varied from 260 glucose units after 270 minutes to 174 glucose units after 510 minutes.

5. The mercaptalated hydrolyzed celluloses showed low but definite copper numbers, varying from 0.5 to 1.3. The non-mercaptalated celluloses had copper numbers increasing in value with increasing time of hydrolysis, and ranging from 5.3 to 8.1.

COLUMBUS, OHIO RECEIVED OCTOBER 8, 1938

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALIFORNIA FRUIT GROWERS EXCHANGE]

The Bitter Constituents of Navel and Valencia Oranges

BY RALPH H. HIGBY

The production of oranges in California is largely of two varieties, the Valencia, a seeded summer orange, and the Washington Navel, a seedless winter ripening variety. The Valencia and Navel are equally good for general use but the juice from this latter variety is not used extensively for canning or for the manufacture of other juice products because of the bitter taste and astringency which develops in the juice when it is allowed to stand exposed to air, or when it is pasteurized. The degree of bitterness is largely dependent upon the maturity of the fruit, most pronounced in early season, but usually disappearing entirely with warm weather in March and April. Bitterness is found also in the juice of unripe Valencia oranges, but never in fruit of this variety which has reached commercial maturity.

Although the presence of a bitter constituent in the edible portion of the Navel orange has long been recognized, no record of its isolation or identification has appeared in the literature. Naringin, the bitter glucoside of grapefruit has long been known, it is commercially available and its properties and structure are fairly well established.

The bitter substances of citrus seeds have also been investigated rather extensively. As early as 1841, Bernay[1] isolated a strongly bitter substance from the seeds of several varieties of citrus (*C. Aurantium Risso*, *C. Limonum Risso*, and *C. Bigardia Loisl.*) which he named limonin and erroneously thought to be an alkaloid. Since that time, various other workers, C. Schmidt,[2] Paternò and Oglialoro,[3] and Peters and Frerich,[4] have prepared this substance and made some study of its properties. In a recent publication, Koller and Czerny[5] have reported the results of a rather comprehensive investigation of limonin, from orange seeds, and have announced the isolation of a second bitter substance, from the same source, which they have named isolimonin. Shortly thereafter Feist and Schulte[6] separated what was thought to be a third bitter substance from lemon seeds, calling it citrolimonin. Similarity in equivalent weight and specific optical rotation have led Koller and Czerny[7] to believe that limonin and citrolimonin are identical despite a considerable discrepancy in the reported melting point.

As one part of a research program directed toward the commercial utilization of Navel orange juice, a study has been made of the bitter constituents of the orange, particularly those contained in the edible portion. Bitter crystalline substances have been extracted from the pulp of the Navel orange, and from both pulp and seeds of the Valencia orange. These substances have

---

[1] Bernay, *Ann.*, **40**, 317 (1841),

[2] C. Schmidt, *ibid.*, **51**, 388 (1844).

[3] Paternò and Oglialoro, *Ber.*, **12**, 685 (1879).

[4] Peters and Frerich, *Arch. Pharm.*, **240**, 661 (1902).

[5] C. Koller and H. Czerny, *Monatsh.*, **67**, 248–268 (1936).

[6] K. Feist and H. Schulte, *Ber.*, **69**, 1322 (1936).

[7] C. Koller and H. Czerny, *Monatsh.*, **70**, 26–29 (1937).

been purified and many of their properties determined.

Experimental

Isolation and Properties of the Bitter Principle of the Navel Orange.—By shaking out portions of bitter Navel orange juice with relatively immiscible solvents it was found that the bitter constituent could be extracted in benzene, toluene, butyl or amyl alcohol, butyl or isopropyl acetate or chloroform. It was not extracted by petroleum ether, gasoline or limonene. In most cases the carotenoid pigment was extracted with the bitter. Since petroleum ether readily dissolves the pigment, extraction in benzene, and treatment with petroleum ether offered a suitable means of separation.

About 22 kg. of immature Washington Navel oranges, picked November 1st, were peeled to remove the flavedo, and the peeled fruit ground in a food chopper. The mixture of albedo, pulp and juice was covered with thiophene-free benzene, stirred thoroughly and allowed to stand for sixteen hours at room temperature. The benzene and juice were separated from the pulp by pressing, and the benzene separated from the juice by decantation. The comparatively dry pulp was reëxtracted with benzene, the benzene fractions combined, washed with water to remove acid, and filtered. After concentration to a volume of about 500 ml., the bitter substance was precipitated by the addition of three volumes of petroleum ether. The amorphous precipitate was filtered off, dissolved in a mixture of equal parts of alcohol and benzene, evaporated to small volume, and allowed to crystallize. The crystals obtained were rather large colorless needles.

Several methods of purification were used.

1. Solution in acetone and precipitation by dilution with water produced shining square plates, melting at 240–242°[8] with evolution of gas.

2. Solution in dilute alcoholic alkali and precipitation by acidification with dilute hydrochloric acid produced colorless needles, m. p. 259–261° with decomposition.

3. Solution in hot alcohol and recrystallization by partial evaporation and cooling produced shining rhombic plates, m. p. 262–264° with decomposition.

The final purification of the bulk of the material was by successive application of all three methods in the order named. Variations in the melting point with method of crystallization may be due to the presence of water of crystallization, although this is not indicated by drying the material in air for sixteen hours at 105°.

The crystals resulting from this treatment were almost completely insoluble in water, slightly soluble in alcohol and benzene, moderately soluble in chloroform and easily soluble in acetone. The taste of these crystals is not bitter due to insolubility, but when dissolved in a little alcohol and diluted with water, the solution is approximately 75% as bitter as a similar solution of quinine sulfate.

Tests on the pure substance were negative for nitrogen, halogen, sulfur, and for phenol, aldehyde and ketone groups. A negative Molisch test showed that it was not a glucoside. It reduced Fehling's solution with boiling, and formed a yellow osazone, m. p. 221–225°, indicating carbonyl groups. A negative Zeisel test showed no alkoxyl groups, and failure to brominate indicated a probable absence of aliphatic double bonds. In neutral alcohol the bitter substance was non-acidic, and not titrable with a 0.1 *N* sodium hydroxide in the cold. Saponification with an excess of alkali in alcoholic solution gave a typical lactone titration.

The saponification values were obtained by dissolving the substance in 25 ml. of neutral alcohol, adding 10 ml. of 0.1004 *N* sodium hydroxide, refluxing on a hot-plate for two hours, and then titrating the excess alkali. The refluxing was then repeated with 5 ml. additional alkali to be sure the reaction was complete. A blank determination was run in parallel. Molecular weight was calculated as two equivalents. The molecular weight was also determined from depression of the melting point, using the method of Rast, as modified by Smith and Young.[9] Optical rotation of the pure compound was measured in a 200-mm. tube containing 0.2 g. of substance made up to 25 ml. with anhydrous acetone.

Anal. Calcd. for $C_{26}H_{30}O_8$: C, 66.35; H, 6.43; O, 27.22; mol. wt., 470. Found: C, 66.62; H, 6.24; O (by diff.), 27.14; equiv. wt. (by NaOH titration), 226, 227; mol. wt. (f. p. in camphor), 467, 477. *Optical rotation:* 0.2 g. in 25 ml. of acetone in 200 mm. tube, rotation −1.784°, giving specific rotation at 22° as −111.5°. Koller and Czerny report the following values for isolimonin from orange seeds—calcd. for $C_{23}H_{28}O_7$: C, 66.31; H, 6.78; mol. wt., 416. Found: C, 65.92, 66.25; H, 6.87, 6.83. The melting point was 264° in an evacuated tube.

Lacking further information, it is impossible to state definitely that our substance is identical with the isolimonin of Koller and Czerny, but the similarity of melting point makes this strongly probable. Our own data indicate that the substance is isomeric with limonin, having the same molecular weight and empirical formula. A higher carbon content is shown than that reported by them, corresponding with the formula $C_{26}H_{30}O_8$ which Feist and Schulte have suggested for citrolimonin. The compound contains two lactone groups.

Location of the Bitter Constituent in the Fruit.—From the standpoint of commercial utilization, the location of the bitter principle in the fruit is of considerable importance. To determine this, a dissection was made of moderately green Navel oranges. Three types of tissue were carefully prepared. These were: (1) the albedo, free from flavedo, and the major veins, which lie next to the section covering; (2) center fibrovascular bundle and white material of the same nature surrounding the Navel, free from section covering; (3) section covering free from albedo.

These portions were extracted with acetone, most of the acetone boiled off, and the residue diluted with water. Slight dilution brought down a copious precipitation of hesperidin, which was filtered off, before more water was added for tasting. All three extractions were extremely bitter. It appears that the bitter principle occurs in the albedo, in the center bundle and in the veins of the carpellary membrane.

---

(8) All of the melting point determinations reported here were made in open tubes, using a 360° thermometer, calibrated for 70-mm. immersion, which had been checked and found correct at 285°.

(9) J. H. C. Smith and W. G. Young, *J. Biol. Chem.*, **75**, 289–298 (1927).

Since the juice from Navel oranges becomes bitter only after rupture of the cell structure, and then only after standing or heating, the existence of the bitter-forming substance in the juice itself is improbable. Tests were made in which the juice was extracted by burring, then screened immediately through a 70-mesh screen to remove broken cell tissue, and heated to 70° for fifteen minutes to develop the bitterness. Under these conditions the screened juice from immature fruit became slightly bitter, while samples containing pulp were intensely bitter. Apparently the momentary contact with the broken cell tissue was sufficient to extract some of the bitter-forming substance into the screened juice.

Since the juice was not bitter when first extracted, it is apparent that an easily water-soluble non-bitter parent substance must exist in the comparatively neutral albedo and section covering, which upon contact with the juice is extracted, and in this acid medium is then slowly converted to the intensely bitter lactone.

The acetone extraction of albedo from completely mature Navel oranges gave an extremely heavy yield of hesperidin, but no bitter substance. Hence, disappearance of the bitter substances in the fruit can be determined by acetone extraction of these portions. Until the pulp and albedo become free from bitterness, the immediate separation of pulp from the extracted juice is of primary importance in the production of non-bitter Navel juice.

Acid Hydrolysis of Navel Isolimonin.—One gram of the pure Navel isolimonin was dissolved in 50 ml. of acetone, 10 ml. of 6 *N* hydrochloric acid added and refluxed on the steam-bath for six hours. Lead carbonate was added to neutralize the acid, and the resulting precipitate filtered off. The acetone filtrate was evaporated to small volume, diluted with water and again heated. A crystalline precipitate came down, leaving an opalescent solution. The crystals were filtered off, and the filtrate allowed to stand. Overnight a white amorphous substance precipitated which was filtered off. Further evaporation of the filtrate and cooling gave nothing but a small additional quantity of the amorphous material.

This amorphous substance was purified by solution in benzene, and precipitation with petroleum ether, and several reprecipitations from hot water. From petroleum ether it separated in waxy lumps, and from ethyl ether by evaporation, it came out as a shining brittle brownish glass. This substance was readily soluble in alcohol and benzene, and moderately soluble in hot water, very slightly soluble in cold. From hot water it separated out upon cooling as cream colored, highly refractive globules, which, under the microscope, gave the water suspension the appearance of an oil in water emulsion. Water solutions were intensely bitter. It was distinctly more acidic than the other bitter substances, being partially titrable with 0.1 *N* sodium hydroxide in the cold. The substance recovered from water, after drying for two days at 45°, sintered with gas evolution at 139–140° to form a brownish wax, which melted at 175–177°. Titration gave an equivalent weight of 240. This figure and the melting point correspond exactly with those of hexahydrolimoninic acid, as reported by Koller and Czerny, who obtained this substance by the hydrogenation of limonin. The substance was found to be optically active, showing a specific rotation of −70° in acetone.

The crystalline substance was purified in the same manner as the Navel isolimonin. From hot alcohol it separated in colorless shining hexagonal leaflets, which melted at 292° with decomposition. From the appearance, crystalline structure, and high melting point, it was thought probable that this substance was limonin, as described by Koller and Czerny. Further identification is made in the following portion dealing with the bitter constituents of the Valencia orange.

Isolation of Bitter Substances from Valencia Oranges.—Approximately 11 kg. of green Valencia oranges were peeled to remove the flavedo, which was discarded. The fruit was then halved and burred to remove the juice, which was immediately screened to take out the pulp. Seeds were removed from the pulp by coarse screening, after which the pulp was mixed with the white albedo and ground in a food chopper. The seeds were similarly ground to an oily paste. Seeds, juice and pulp were then separately extracted with benzene, the extracts evaporated to small volume, and precipitated with petroleum ether. A good yield of an apparently amorphous white bitter substance was obtained from the pulp, a moderate yield from the seeds, but none from the juice, which yielded only a non-bitter brownish wax.

The bitter precipitates from the pulp, and from the seeds, were purified separately by the methods which were used for the purification of the Navel isolimonin. Both fractions crystallized from hot alcohol in thin hexagonal leaflets, m. p. 290° with decomposition. It was evident both from appearance and from the melting points that these two fractions were identical, and that they were also identical with the crystalline substance which had been obtained by the acid treatment of the Navel isolimonin. A mixed melting point of 291–292° for these three fractions establishes their identity beyond question. The solubility was similar to that of isolimonin, except for somewhat greater solubility in benzene. Water-alcohol solutions were intensely bitter.

Like isolimonin this substance formed water-soluble sodium salts with alcoholic sodium hydroxide, and was precipitated in its original form when the solution was acidified. Analysis of the three fractions separately showed equivalent weights by saponification of 229, 230, and 231. Determined molecular weights were 445, 449, and 468, respectively. Two lactone groups are indicated.

Limonin, as described by Koller and Czerny, crystallizes in thin shining rhombohedral leaflets, melting at 280° with decomposition. Titration gives an equivalent weight of 235, and two lactone groups are indicated. Feist and Schulte report that citrolimonin crystallizes in thin shining leaflets, m. p. 304°. From the combustion analysis the formula was calculated as $C_{26}H_{30}O_8$ (molecular weight 470), and by titration two lactone groups were indicated. It seems highly probable, as admitted by Koller and Czerny, that these investigators are dealing with the same substance.

The existence of the substance isolated by us as the major bitter constituent of the orange seed, is good evidence that it is actually limonin. This is confirmed by the crystalline form, by the melting point, which falls midway

TABLE I

COMPARATIVE ANALYTICAL DATA ON THE BITTER SUBSTANCES FROM VALENCIA AND NAVEL ORANGES

Properties	Isolimonin			Hexahydrolimoninic acid		Limonin				Citrolimonin
	Navel Crystallized from alcohol	Navel Crystallized from acetone and water	Reported by Koller and Czerny	From isolimonin by hydrolysis	Reported by Koller and Czerny	From isolimonin by hydrolysis	From Valencia pulp	From Valencia seeds	Reported by Koller and Czerny	Reported by Feist and Schulte
Crystalline form[a]	Rhombic plates	Square plates	Warty crystals	Light colored globular aggregates	Not described	Thin shining hexagonal leaflets	Thin shining hexagonal leaflets	Thin shining hexagonal leaflets	Thin shining leaflets	Shining plates from Mc chloride
M. p. (corr.), °C.[c]	262–264 dec.	240–242 dec.	264 dec.	175–177	178 dec.	292 dec.	290 dec.	290 dec.	280 dec.	304
Specific rotation (22°) in acetone	−112°	−102°	....	−70°	....	−114°	−106°	−108°	−142.85°[b]	−135°[b]
Carbon, % (av.)	66.62	......	66.08	...	62.80	....	....	....	66.44	....
Hydrogen, % (av.)	6.24	......	6.85	...	8.03	....	....	....	6.58	....
Empirical formula (calculated)	$C_{26}H_{30}O_8$	......	$C_{23}H_{28}O_7$	...	$C_{23}H_{31}O_8$	....	....	....	$C_{23}H_{26}O_7$	$C_{26}H_{30}O_8$
Mol. wt. (calcd. from formula)	470	......	416	...	438	....	....	....	414	470
Equiv. wt. (from titration)	227	186	....	240	240	231	229	230	235	....
Mol. wt. (two equivalents)	454	372	....	480	480	462	458	460	470	....
Mol. wt. (Rast)	477 467	412	....	416 407	....	449	445	468	396 447	....
Taste	Very bitter	Very bitter	....	Very bitter	....	Very bitter	Very bitter	Very bitter	....	....

[a] Crystallized from 95% alcohol unless otherwise specified. [b] Determined in methylene chloride. [c] It is assumed that m. p. data taken from the literature are corrected values.

between the temperatures reported by the above workers, and by its solubility and chemical properties.

Formation of Non-bitter Salts.—By the saponification procedure which was used for the determination of equivalent weight, all the bitter substances formed easily water-soluble non-bitter sodium salts. Acidification with dilute hydrochloric acid reprecipitated the original substance. Further experimentation showed that Navel isolimonin was capable of forming similar salts with calcium, barium or magnesium hydroxide, calcium and barium chloride, and with triethanolamine. Because of scarcity of material, limonin and hexahydrolimoninic acid were tested only with sodium hydroxide.

To determine at what *p*H values the transition from the non-bitter salt to the bitter lactone took place, several series of samples were prepared containing 10% sugar, 1% citric acid, and 0.008% of the Navel isolimonin, which had been previously treated with sodium hydroxide to convert it to its tasteless form. Various amounts of sodium hydroxide were added to neutralize a portion of the acidity in each sample, producing a series of varying *p*H. These samples were heated for one hour on the steam-bath, cooled, tasted, and *p*H values determined. Bitterness developed in all samples having a *p*H value below 6.00. A similar series prepared from the bitter lactone instead of the salt showed that an excess of alkali was necessary to convert the lactone to the tasteless salt. Repetition of these tests using calcium salts instead of sodium gave similar results.

Discussion

The comparative analytical data obtained on the various bitter substances which have been prepared in this study are shown in Table I, together with the corresponding values reported by Koller and Czerny, and by Feist and Schulte for the similar bitter substances isolated by them.

A consideration of these values leaves little doubt that the Navel bitter constituent, which we have called isolimonin, is a true isomer of the citrolimonin described by the last-named workers. This is shown by apparent identity in equivalent weight, molecular weight and empirical formula. Koller and Czerny have not yet published sufficient data regarding the isolimonin obtained by them to make it entirely certain that these two substances are the same, but agreement in melting point makes it highly probable.

Navel isolimonin is precipitated in somewhat different form by dilution of an acetone solution with water. The crystals obtained in this way have a lower melting point and apparent molecular weight than those from hot alcohol, and are probably a hydrated form of the lactone. No tests have been made to determine whether this is actually the hydroxy acid or whether the differences in melting point and apparent molecular weight are merely due to the presence of water of crystallization.

From the analytical data it seems certain that the citrolimonin of Feist and Schulte is identical with the crystalline substance which we have prepared from Valencia orange seeds, from Valencia orange pulp, and by treatment of the Navel isolimonin with dilute hydrochloric acid. Since Koller and Czerny recently have acknowledged the likelihood that the limonin isolated by them is identical with citrolimonin, advancing as evidence the fact that by titration they obtained a molecular weight of 470, which corresponds with the formula $C_{26}H_{30}O_8$ as suggested by Feist and Schulte, it seems reasonable to assume that these substances are identical. The discrepancy in melting point can be attributed to difference in method, and perhaps to the degree of purity of the material used. Koller and Czerny performed all of their melting point determinations in evacuated tubes, Feist and Schulte used the micromelting point apparatus of Kofler, while the writer used the regular open tube method. The variation in nomenclature by these investigators is unfortunate, tending to promote confusion. For this reason, it seems logical to eliminate the name "citrolimonin," referring to this compound as limonin, as originally proposed by Bernay.

From a comparison of the physical characteristics, the melting points, and equivalent weights, there can be little doubt that the apparently amorphous substance which was obtained by the acid treatment of isolimonin is identical with the hexahydrolimonic acid which Koller and Czerny prepared by the hydrogenation of limonin. Data obtained by them indicated that this substance was formed by the addition of six hydrogen atoms and one molecule of water to the limonin molecule to give an empirical formula of $C_{23}H_{34}O_8$ for the hexahydrolimoninic acid. Accepting their revised views regarding the formula for limonin ($C_{26}H_{30}O_8$) this addition would bring the empirical formula for hexahydrolimoninic acid to $C_{26}H_{38}O_9$. This is difficult to understand, since this substance also resulted from the treatment of isolimonin with hydrochloric acid.

The relationship between these three bitter substances is not clear. Although limonin has been known and subjected to investigation for almost a century, no structural formula for the substance has as yet been advanced. Recent workers agree that the substance contains two lactone groups, and Koller and Czerny point out a probable analogy of structure with columbin, and hence with the strophanthic and crotonic substances, but this has not been definitely established.

For isolimonin Koller and Czerny have suggested a formula $C_{23}H_{28}O_7$ containing two active hydroxyl groups, and differing from limonin only in degree of hydrogenation. The substance which we have designated as Navel isolimonin, with an identical melting point, corresponds more nearly with the formula for limonin, $C_{26}H_{30}O_8$, indicating that these substances differ only through some rearrangement in the molecule. Hexahydrolimoninic acid apparently results from the splitting of one of the lactone rings and the formation of a carboxyl group. The scope of our present project does not include further investigation of the structure and relationship of these bitter substances.

It has been shown that the bitter substances of the pulp and peel of the orange are either identical with or closely related to the previously isolated bitter constituents of the seeds. In the edible portion of the fruit these substances apparently occur in easily water-soluble, non-bitter form. Hydrolysis to the bitter lactone takes place slowly in the acid juice, or in water with heating.

The nature of the non-bitter parent substance has not been investigated. Hall[10] hypothesized that hesperidin occurred in the fruit as an easily hydrolyzed complex, containing in addition glucose, and a third substance. It seems possible that this substance may be isolimonin.

In the Valencia orange the bitter-forming constituent apparently exists in less soluble form than in the Navel, since the juice, even from immature fruit, is not prone to become bitter.

It is hoped that in the near future an investigation can be made regarding the nature of the non-bitter parent substance in both Navel and Valencia oranges, its probable function in the plant, and the end-products of its natural enzymic hydrolysis.

Acknowledgment.—The writer wishes to express his appreciation to his co-workers, Dr. E. F. Bryant and Mr. R. L. Logg, for their aid in the analysis and isolation of these bitter substances.

Summary

The bitter principle of the Navel orange has been isolated and identified as isolimonin, a

---

[10] J. A. Hall, THIS JOURNAL, **47**, 1191 (1925).

previously reported constituent of orange seeds. This substance occurs in the albedo, the center fibrovascular bundle, and in the section covering of the fruit, in non-bitter water-soluble form. When these tissues are ruptured it is extracted into the juice, where it is slowly converted to the intensely bitter lactone form. It is shown that this substance has a higher molecular weight than that previously reported, corresponding to the formula $C_{26}H_{30}O_8$. It is apparently an isomer of limonin, and of citrolimonin. The probable identity of these last named substances is discussed.

Limonin, which has heretofore only been reported in the seeds of citrus fruit has been isolated also from the pulp of the Valencia orange.

Both limonin and isolimonin form non-bitter water-soluble salts with alkali and alkaline earth metals, from which they are precipitated unchanged upon acidification.

Treatment of isolimonin with dilute hydrochloric acid in acetone solution gave fractions of limonin, and of hexahydrolimoninic acid. This latter substance has been obtained previously only by the catalytic hydrogenation of limonin. It appears that limonin results from a molecular rearrangement in the isolimonin, and that hexahydrolimoninic acid is produced by the splitting of a lactone ring, to form a carboxyl group.

ONTARIO, CALIF. RECEIVED OCTOBER 4, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY]

The Action of Chlorine Water on Some β-Amyloses

BY HARRY H. FLETCHER[1] AND T. CLINTON TAYLOR[2]

Introduction

Industrial technologists have known for over ten years that if chlorine water is mixed with a starch dispersion, the viscosity of the dispersion drops after ten to twenty minutes of treatment.[3] The appearance of this chlorine-treated starch, the optical rotation of its dispersion, and the blue color with iodine remain unchanged. Nevertheless, the viscosity drop indicates that the chlorine water probably has begun to break the starch particles into smaller ones,[4,5] although this breakdown is still in too early a stage to be detected by other means. With two exceptions, the chemical and physical nature of the action of chlorine water on starch has not been investigated. Craik[6] found that the optical rotation of a potato starch dispersion gradually increased during several days' contact with hypochlorous acid at room temperature. However, the optical rotation is not so sensitive to slight changes in the structure of the starch as is the viscosity. Recently Rassow and Lobenstein measured the viscosity decrease during the reaction between potato starch and an alkaline hypochlorite solution.[7] They noticed also that the dispersion became more acidic during the course of the reaction. This they attributed to oxidation of aldehyde groups to carboxylic acids with concurrent reduction of the hypochlorous acid to hydrochloric acid.

Rassow and Lobenstein determined the reducing power of their starch dispersions after alkaline treatment only. The work described herein extends it into acid regions. As will be shown later, the results obtained in solutions of *p*H less than 7 were, so far as we are aware, entirely new and unexpected.

Outline of Procedure

Rassow and Lobenstein used Fehling's solution to measure the reducing power of their dispersions. As this reagent is not very satisfactory for rapid analysis,[8] the recently standardized alkali-labile procedure was used in these new determinations.[9] When the hot alkaline digestion is omitted, the iodine consumption of the carbohydrate, determined and calculated in the usual manner, will be

---

[1] Present address: U. S. Rubber Products, Inc., Gen. Labs., Passaic, N. J.

[2] The experimental work described herein was completed just before the death of Prof. Taylor in April, 1936. As the present author is no longer engaged in research on starch or related materials, he relinquishes this field with the hope that others will be interested in continuing this investigation.

[3] (a) Watson and Kent-Jones, U. S. Patent 1,519,014 (1924); (b) Neumann and Kalning, *Landw. Jahrb.*, **61**, 305 (1925); (c) Neumann and Kalmius, *Rass. intern. Agr.*, 444 (1926); (d) Staudt, Can. Patent 274,290 (1927); (e) Frey, U. S. Patent 1,897,251 (1933).

[4] Staudinger and Schweitzer, *Ber.*, **63B**, 2323 (1930).

[5] Hatschek, "Viscosity of Liquids," D. Van Nostrand Co., Inc., New York, 1928, pp. 196–201.

[6] Craik, *J. Soc. Chem. Ind.*, **43**, 171 (1924).

[7] Rassow and Lobenstein, *Kolloid Beihefte*, **33**, 179 (1931).

[8] Amick, *J. Phys. Chem.*, **31**, 1441 (1927).

[9] Taylor, Fletcher and Adams, *Ind. Eng. Chem., Anal. Ed.*, **7**, 321 (1935).