petroleum ether; m. p. 138.5–139° (corr.). Solutions of the compound in alcohol have a decidedly pungent taste accompanied by a slightly bitter taste.

Anal. Calcd. for $C_{16}H_{18}O_2N_2S$: C, 63.53; H, 6.00; S, 10.6. Found: C, 64.04; H, 6.06; S, 10.4.

Preparation of *o*-Tolylvanillylthiourea (α-*o*-Tolyl-β-*p*-hydroxy-*m*-methoxybenzylthiourea), $CH_3C_6H_4NHCSNHCH_2C_6H_3(OCH_3)(OH)$.—Equimolecular quantities of *o*-tolylisothiocyanate and vanillylamine are mixed and then warmed. The compound, obtained in 80% yield, on treatment with charcoal and recrystallization from alcohol gave colorless crystals; m. p. 138–138.5° (corr.); it is soluble in acetone, fairly soluble in ethyl alcohol, methyl alcohol, chloroform or benzene, very slightly soluble in ether or carbon tetrachloride and insoluble in water or petroleum ether. Solutions of the compound in alcohol have a decidedly pungent taste accompanied by a slightly bitter taste.

Anal. Calcd. for $C_{16}H_{18}O_2N_2S$: C, 63.53; H, 6.00; S, 10.6. Found: C, 63.51; H, 5.95; S, 10.7.

Summary

Six different substituted ureas and thioureas have been described; these ureas, being the carbamic or thiocarbamic amides of vanillylamine, are the analogs of the pungent principle of cayenne pepper—a carboxylic amide of the same amine. Three of the thiocarbamides were found to have the property of pungency but to a lesser degree than capsaicin. None of the compounds has a sweet taste, the effect of the phenyl and tolyl groups, which are known to repress the sweetness of compounds, predominating over the favorable effect of the methoxy group; the slightly bitter taste which is characteristic of many thioureas was also observed in several of these compounds.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE ALGINIC ACID FROM MACROCYSTIS PYRIFERA[1,2]

BY WILLIAM L. NELSON AND LEONARD H. CRETCHER

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The earlier researches on the chemistry of the carbohydrates in algae were mostly concerned with the isolation and identification of the sugars formed on the hydrolysis of the plant as a whole. The first attempt at separation of a particular carbohydrate component was made by Stanford[3] and was based on the fact that most marine algae contain a highly polymerized acid fraction which may be extracted by means of dilute alkali

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[1] Presented before the Organic Chemistry Division of the American Chemical Society at the Swampscott Meeting, September, 1928.

[2] *Cf.* Cretcher and Nelson, *Science*, **67**, 537 (1928), for a preliminary discussion of this subject.

[3] Stanford, *Chem. News*, **47**, 254, 267 (1883).

and precipitated by the addition of mineral acid after the removal of the alkali-insoluble residue by filtration.

This substance has been called alginic acid or algin, and in the form of its salts it has a variety of important industrial uses.

Algin was thought by Stanford to contain nitrogen, but later investigations by Krefting,[4] Hoagland and Lieb,[5] as well as our own, have demonstrated that when pure it is nitrogen free. Stanford was apparently interested only in the commercial development of seaweed products, and it was not until 1913 that the algae were again investigated from the standpoint of the original carbohydrate complexes contained in them. Kylin[6] at this time isolated acidic materials from the plants which he later[7] submitted to acid hydrolysis. He reported that the hydrolysis of alginic acid produced apparently only pentoses.

At about the same time, Hoagland and Lieb[5] contributed the results of a careful investigation of the carbohydrates in algae. In the course of their work they prepared alginic acid from the *Macrocystis pyrifera.* After a thorough purification the material was obtained free of more than traces of ash and nitrogen. The neutralization equivalent was found to be 325. Analytical data indicated a compound of formula $C_{21}H_{27}O_{20}$ containing two replaceable hydrogen atoms. It was submitted to acid hydrolysis, the water-insoluble fraction removed by filtration and the filtrate treated with phenylhydrazine. An osazone was isolated having melting point, optical rotation and solubilities in close correspondence to those of the osazone of *d*-xylose.

Alginic acid, on the basis of these observations, might be considered a compound composed of an unknown acidic nucleus in combination with pentose sugars.

That the acidic nucleus in algin from *Laminaria* is glucuronic acid was recently suggested by Atsuki and Tomoda.[8] The idea that this algin does contain a uronic acid was rendered probable by the fact that their preparation lost 20% of its weight as carbon dioxide when boiled with hydrochloric acid (d. 1.06). No evidence, however, was presented by these authors in proof of the configuration of the acid.

Schmidt and Vocke[9] have hydrolyzed alginic acid from *Fucus serratus* and claim to have isolated, from the hydrolysate, *d*-glucuronic acid in the form of its cinchonine salt. Proof of the identity of this salt is limited to the determination of its melting point and is inconclusive.

The present authors are of the opinion that Schmidt and Vocke's method

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[4] Krefting, English Patents, **11,** 583 (1896); **12,** 416 (1898).

[5] Hoagland and Lieb, *J Biol. Chem.*, **23,** 287 (1915).

[6] Kylin, *Z. physiol. Chem.*, **83,** 171 (1913).

[7] Kylin, *ibid.*, **94,** 337 (1915).

[8] Atsuki and Tomoda, *J. Soc. Chem. Ind.* (*Japan*), **29,** 509 (1926).

[9] Schmidt and Vocke, *Ber.*, **59,** 1585 (1926).

of hydrolysis does not completely liberate the monomolecular uronic acids from their polymers and the cinchonine salt which they prepared and which melted at 204° was not of a simple C_6 aldehyde sugar acid. We have submitted the algin from *Fucus serratus* to more drastic hydrolysis and have obtained from the product a cinchonine salt melting at 152°. This is the melting point of the cinchonine salt of the C_6 aldehyde acid which we have isolated from *Macrocystis pyrifera.* The two acids are probably identical and are surely not glucuronic. It is to be admitted, however, that more than one uronic acid may be present in *Fucus serratus.*

We have isolated the alginic acid from *Fucus serratus, Laminaria agardhii* and *Macrocystis pyrifera.*[10]

In the case of the first mentioned algin, no analytical work has been done on the original material. The algins from the *Laminaria agardhii* and *Macrocystis* have, however, been studied analytically. These acids, free of more than traces of ash and nitrogen, were dried over phosphorus pentoxide to constant weight. They gave strong naphtho-resorcin tests and were therefore thought to contain uronic acids. Titration with standard alkali gave neutralization equivalents varying, with different samples, from 176 to 184. Carbon and hydrogen determinations indicated the formula $(C_6H_8O_6)_n$, while boiling with hydrochloric acid caused the liberation of carbon dioxide to the extent of 24–25%. The pure acids do not reduce Fehling's solution. These facts indicate that algin is a polyuronic acid in which all carboxyl groups are free and all aldehyde groups conjugated.

But little study beyond the determination of the analytical data has been made of the algin from *Laminaria agardhii.* That from *Macrocystis pyrifera* has been hydrolyzed to the free C_6 aldehyde acid, which was not obtained in crystalline condition. It did not have the properties of either *d*-galacturonic or *d*-glucuronic acid. These are the only aldehyde sugar acids which have been found in nature to date. That it was neither a mixture of these acids nor either of them in impure form was indicated by the fact that neither mucic nor saccharic acid could be isolated after oxidation with bromine or nitric acid and that the pure cinchonine salt of the aldehyde acid did not have properties in correspondence with those of the galacturonic or glucuronic salts of this alkaloid.

It was shown by Salkowski and Neuberg[11] that glucuronic acid may be converted, by bacteria, into *d*-xylose. It is also well known that uronic acids lose carbon dioxide on treatment with hot aqueous mineral acids and that furfural is a product. It may be assumed that a pentose sugar is intermediate in this process and that the reaction is as follows:

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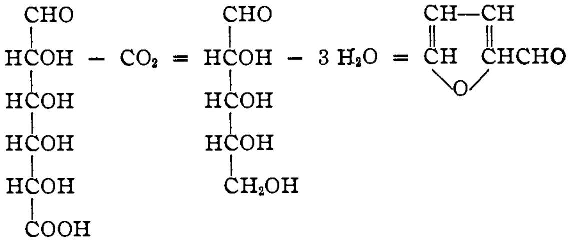
[10] Further investigation of *Fucus serratus* is now under way in this Laboratory and will be reported soon.

[11] Salkowski and Neuberg, *Z. physiol. Chem.*, **36**, 261 (1902); **37**, 464 (1903).



This would explain the formation of the pentoses which were reported by Kylin[7] and by Hoagland and Lieb.[5]

If the osazone isolated by the last mentioned investigators was actually that of *d*-xylose, it is identical with the osazone of the epimer of *d*-xylose, namely, *d*-lyxose. The identification of the uronic acid was thus simplified somewhat, inasmuch as it must be of such configuration as to form either *d*-xylose or *d*-lyxose on loss of carbon dioxide. A consideration of the conventional stereochemical formulas of the hexoses will reveal that of the sixteen possible hexuronic acids, only four can meet this condition. *d*-Glucuronic and *l*-iduronic would form *d*-xylose; *d*-mannuronic and *l*-guluronic would form *d*-lyxose. Glucuronic was excluded by experiment. Iduronic and guluronic being derivatives of sugars not as yet found in nature were thought improbable. Inasmuch as *d*-mannose is widely distributed in nature, and as we found mannitol in the *Macrocystis* to the extent of 4–5%, we assumed, as a working hypothesis, that the algin contained *d*-mannuronic acid. Evidence in support of this hypothesis is given in the Experimental Part.

Experimental Part

Isolation of Mannitol from Macrocystis Pyrifera.—One hundred and fifty grams of air-dried fronds were extracted by boiling in 1000 cc. of alcohol. After filtering, the fronds were extracted again with 500 cc. of alcohol. After filtering and washing with alcohol, the filtrate was evaporated to a small volume. During the evaporation, colorless needles separated from solution. The solution was filtered and the solid washed with alcohol. After once recrystallizing, the compound melted at 166°. The melting point of mannitol as determined by Landolt[12] is 166°. It was converted into a tribenzal compound according to the method of Fischer. The compound melted at 218–222° (corr.), the temperature of melting of tribenzalmannitol as determined by Fischer and Fay.[13]

Preparation of Alginic Acid from Macrocystis.—The air-dried fronds containing 18% moisture and 25.5% ash were washed several times with water and allowed to stand completely immersed in 0.5% hydrochloric acid for twenty-four hours. The acid was decanted and the process twice repeated. After again washing thoroughly with water, the leaves were covered with 2% sodium carbonate solution and allowed to stand overnight. Almost immediately on addition of the alkali the fronds swell, lose their shape and the solution becomes very viscous. Frequent stirring facilitates the

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[12] Landolt, *Z. physik. Chem.*, **4**, 366 (1889).

[13] Fischer and Fay, *Ber.*, **28**, 1975 (1895).

extraction of the alginic acid. The solution was diluted to the point where it could be filtered through a medium finely woven scrim without suction. The residue was extracted again with 2% sodium carbonate and filtered.

The combined filtrate was warmed to 60° and filtered, under suction, through a thin layer of decolorizing carbon on a coarse filter paper. After the solution had cooled to room temperature, the alginic acid was precipitated by the addition of hydrochloric acid under vigorous stirring. The precipitated acid was filtered on scrim and allowed to drain as dry as possible. It was then washed with water, transferred to a large crock, allowed to stand overnight under a large volume of 0.5% hydrochloric acid and filtered. This process of extraction with dilute acid is for the purpose of removing both ash and acid soluble nitrogen compounds. It was repeated thrice. The hydrochloric acid was then removed by several similar treatments with distilled water.

The alginic acid so prepared is a very highly hydrated gel from which water cannot be removed by centrifugation or filtration.

In order to effect dehydration, the gel was treated with 95% alcohol and allowed to stand overnight. This treatment also extracts a considerable amount of alcohol-soluble brown pigment. The alcohol and most of the water were then removed from the alginic acid by means of a hydraulic press and the alcohol extraction repeated. After pressing the second time, a hard cake was obtained. This was broken into small pieces and allowed to dry in the air and finally, *in vacuo*, over phosphorus pentoxide. The yield of purified algin obtained was about 15% of the weight of the fronds taken.

Properties of Alginic Acid.—The most striking physical property of alginic acid is its remarkable power of adsorption of water and salts. Hoagland and Lieb[5] state that "it is capable of adsorbing 200 to 300 times its weight of water" and "salts to the extent of 60%." While we have made no attempt to discover the upper limit of water absorption, we can state that when free of salts and mineral acid the water adsorbed may be considerably higher than 200%. Only by repeated dialysis with dilute acid can the ash be reduced to 0.1%, which gives the purest sample we have been able to prepare. The ash remaining after careful purification is composed largely of iron.

Alginic acid is very slightly soluble in water. It liberates carbon dioxide from carbonates and may be titrated with alkali to a definite end-point (phenolphthalein). It does not reduce Fehling's solution but rapidly forms reducing substances if dried at 100° or if boiled with water or dilute acid. Considerable amounts of carbon dioxide are liberated under the same conditions. Because of this sensitivity of alginic acid, its optical rotation and acid value vary with the time and temperature of drying. This important fact has apparently escaped the observation of previous investigators. The optical rotation of sodium alginate prepared from the alginic acid of the *Macrocystis pyrifera* is $[\alpha]_D^{20} = -133°$.

Analysis of Alginic Acid

Titration with Alkali.—0.3035 g. of sample required 16.93 cc. of 0.1 *N* NaOH, corresponding to a neutralization equivalent of 179.

Uronic Acid Carbon Dioxide.—On boiling a sample of alginic acid for five hours with 12% hydrochloric acid, it lost 21.5% of its weight as carbon dioxide. This corresponds to 86% of uronic anhydride. The neutralization equivalent, however, indicated almost 100%. A sample was therefore boiled with 18% hydrochloric acid. After five hours 0.5519 g. lost 0.1462 g. of carbon dioxide. Calcd. for $C_6H_8O_6$: CO_2, 25. Found: CO_2, 24.65.

Carbon and Hydrogen.—Calcd. for $C_6H_8O_6$: C, 40.91; H, 4.55. Found: C, 41.21; H, 4.75.

Hydrolysis of Alginic Acid.—Hydrolysis was first attempted by boiling with distilled water. After boiling for a short time, water-soluble reducing substances were formed. It was thought that the progress of the hydrolysis could be followed by determination of the ratio of aldehyde to carboxyl by titration. A polyuronic acid would theoretically be completely degraded to C_6 aldehyde acid when this ratio became 1:1. After ninety hours' heating, this ratio was obtained. The aldehyde was determined by the iodine titration method of Willstätter and Schudel[14] and the carboxyl by standard alkali. On attempting to isolate the free uronic acid, it was found that the product of the hydrolysis was a substance containing too little aldehyde for the uronic acid and that the apparent formation of a uronic acid was the result of a slow increase of aldehyde from hydrolysis and a gradual loss of carbon dioxide from the carboxyl groups.

During this process the hydrolysis and loss of carbon dioxide is quite rapid at first but becomes very slow after some hours. Even after prolonged hydrolysis, a water-insoluble residue of polyuronic acid remains. Apparently the loss of carbon dioxide is coincident with or follows the hydrolysis, as the water-insoluble residue was shown by analysis to be 100% polyuronic anhydride.

A sample of alginic acid was shown, by experiment, to lose 10% of the theoretical amount of carbon dioxide on boiling with distilled water for eighteen hours.

An air-dried sample of alginic acid containing 17% of moisture lost 0.82% (dry basis) of its carbon dioxide when dried at 100° for four and one-half hours.

Hydrolysis with Dilute Sulfuric Acid.—Hydrolysis with dilute sulfuric acid of various concentrations was attempted but soon abandoned because of the simultaneous loss of carbon dioxide.

It seems worthy of mention that we obtained, after hydrolysis with water for forty-two hours and then with 3% sulfuric acid for an additional five hours, a residue which was still a polyuronic acid. This residue was separated from the solution by centrifugation, was washed with water and alcohol, dried over phosphorus pentoxide and analyzed for aldehyde and uronic acid carbon dioxide. Its neutralization equivalent was 180. The carbon dioxide determination corresponded to 99.6% uronic anhydride, while the titration of aldehyde indicated a polyuronic acid, $C_{72}H_{98}O_{73}$, containing one free aldehyde and twelve carboxyl groups. The stability of this residue as to loss of carbon dioxide and its comparatively high resistance to hydrolysis indicate that the uronic acids in algin are not all similarly conjugated.

Hydrolysis with Nitric Acid.—It was thought that by treatment with nitric acid it might be possible, simultaneously, to hydrolyze and oxidize the aldehyde acid formed to a dibasic acid. At 55° with nitric acid of sp. gr. 1.2 the main product was oxalic acid. A water-insoluble residue was again obtained.

Hydrolysis with 80% Sulfuric Acid.—The hydrolysis of alginic acid was best accomplished in the following manner: 30 g. of the dry pulverized acid was thoroughly mixed with 90 g. of cold 80% sulfuric acid. The flask was stoppered and allowed to stand for five days at room temperature. The contents was then slowly poured into 900 cc. of water. The water-insoluble residue was removed by filtration and

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[14] Willstätter and Schudel, *Ber.*, **51**, 780 (1918).

washed with water and alcohol. This residue was a polyuronic acid and weighed 6 g. This substance is now being studied but will not be discussed further in this communication.

The filtrate was heated to the boiling point and treated with the calculated amount of barium carbonate to remove the sulfuric acid. The barium sulfate was filtered off and washed with hot water. The combined filtrate and washings was treated with barium carbonate, with stirring, and heated over a water-bath for two hours after the solution had become neutral to Congo Red. Long heating is necessary to convert the lactone of the aldehyde acid to the barium salt. The excess barium carbonate was removed by filtration and the filtrate evaporated under reduced pressure to 100 cc. The solution was allowed to stand in the ice box overnight. The small amount of dark brown precipitate formed was filtered off and discarded. The solution was treated with decolorizing carbon (Nuchar), filtered and evaporated, *in vacuo*, to 25 cc.; 100 cc. of 95% alcohol was added. The barium salt was precipitated as a heavy gum. After standing in the ice box for several hours, the supernatant liquor was removed by decantation. The gum was dried at 35–40° until it could be powdered. The yield of dry salt was 25 g. Analysis of this salt proved it to be mostly the barium salt of a C_6 aldehyde sugar acid, with small amounts of lactone and the barium salts of polyuronic acids which had escaped hydrolysis. No method was discovered for complete purification of this salt. On removal of the barium with sulfuric acid and evaporation of the solution, a sirup was obtained which we did not succeed in crystallizing.

Addition of excess barium hydroxide to a solution of the aldehyde acid causes the precipitation of a practically insoluble basic salt.

The Cinchonine Salt.—Inasmuch as the cinchonine salts of glucuronic and galacturonic acids have been described, a solution of the uronic acid was treated with cinchonine in the manner usual for the preparation of alkaloidal salts. The excess cinchonine was extracted with chloroform and the solution evaporated to a small volume. The cinchonine salt is quite soluble in water and separates, even from highly supersaturated solutions, very slowly. It was recrystallized from water to constant melting point and then once from alcohol. The alcohol crystallization did not alter the melting point, which was 152° corr. Melting is accompanied by effervescence.

Anal. Calcd. for $C_{25}H_{32}O_8N_2$: N, 5.72. Found: N, 5.95; 5.58. 0.2451 g. was dissolved in water and the cinchonine precipitated by addition of 5 cc. of 0.1*N* NaOH and filtered off. The filtrate was titrated for aldehyde. Calcd. for $C_{25}H_{32}O_8N_2$: 0.1 *N* iodine required, 10 cc. Found: 9.6 cc. *Optical rotation.* 0.3016 g. in 25 cc. of H_2O in a 2-decimeter tube gave an observed rotation of $+2.74°$; $[\alpha]_D^{25} = +113.6°$.

The physical constants of the cinchonine salts of *d*-glucuronic and *d*-galacturonic acids given in the literature are as follows: glucuronic, m. p. 204°,[15] 199–200°;[16] $[\alpha] = 138.6°$,[15] 135°,[16] 139.9°;[17] galacturonic, m. p. 158°;[17] $[\alpha] = 134°$.[17]

Oxidation of the Aldehyde Acid.—Inasmuch as many of the dicarboxylic sugar acids are known and some of them are quite well characterized, it was thought that our unknown uronic acid could best be identified by oxidation to a dibasic acid. The method of oxidation was as follows:[18] 8 g. of the barium salt of the aldehyde acid was

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[15] Neuberg, *Ber.*, **33**, 3317 (1899).

[16] Ehrlich and Rehorst, *ibid.*, **58**, 1989 (1925).

[17] Schwalbe, *ibid.*, **58**, 1536 (1925).

[18] This method of oxidizing an aldose by bromine water in the presence of a buffering salt such as barium benzoate was suggested to us by C. S. Hudson. An article fully describing the method and its application to various sugars will be published in the near future by C. S. Hudson and H. S. Isbell.

dissolved in 250 cc. of water, 12 g. of barium benzoate and 5 cc. of bromine were added and the solution was allowed to stand at room temperature for three days. The excess bromine was removed by blowing a rapid stream of air through the solution and the precipitated benzoic acid removed by filtration. The solution was next extracted with chloroform to remove the dissolved benzoic acid.

Barium carbonate was added, with heating and vigorous stirring. It was heated for one and a half hours after the solution became neutral to Congo Red. It was then treated with decolorizing carbon and filtered. The filtrate was evaporated to 70 cc. under reduced pressure. On cooling, a small amount of brown material precipitated and was removed by filtration. The filtrate was poured into two volumes of alcohol. The solid barium salt was filtered off and ground under 50% alcohol. It was then filtered and washed with alcohol of the same strength. Barium was removed from the salt by sulfuric acid. After filtration the solution was evaporated to a sirup, which was treated with absolute alcohol. This precipitated traces of salts and a small amount of sticky carbohydrate material. The alcoholic solution was filtered and evaporated to a sirup which could not be induced to crystallize, even after samples of it were seeded with a crystal of *d*-mannosaccharic dilactone or mucic acid. A sample was neutralized with 50% potassium hydroxide and then acidified with acetic acid but no potassium acid saccharate could be isolated from the reaction product.

The Diamide.—A sample of the sirup was treated with an excess of concentrated ammonia. On standing for some hours in the ice box a white crystalline compound was deposited. It was filtered off and washed with cold water, then with alcohol and finally with ether. It was recrystallized from hot water to constant melting point and rotation.

Anal. Calcd. for $C_6H_{12}O_6N_2$: N, 13.46. Found: N, 13.35.

The compound melted at 189° with decomposition. A mixed melting point with *d*-mannosaccharic diamide was 189°. The melting point of mannosaccharic diamide was found to be 189° by Fischer[19] and 188–189.5° by Hudson.[20] Our sample of this diamide prepared from mannose melted at 189°.

0.1552 g. of the diamide, prepared from algin according to methods already described, in 50 cc. of water, gave $\alpha = -0.304°$ in a 4-dm. tube, as an average of eight readings; $[\alpha]^{20}_{D} = -24.46°$. The rotation of *d*-mannosaccharic diamide, as determined by Hudson,[20] is $[\alpha]^{20}_{D} = -24.4°$.

The Di-phenylhydrazide.—A sample of the sirup was heated on a water-bath with an excess of phenylhydrazine acetate. The di-phenylhydrazide formed was very insoluble in hot water or alcohol. It was extracted once with boiling water and thrice with hot alcohol. It melted with decomposition at 212°.

d-Mannosaccharic di-phenylhydrazide was prepared from pure crystalline *d*-mannosaccharic dilactone. It melted at 212°. This is also the melting point reported by Fischer.[19] A mixture of the two hydrazides melted at the same temperature.

Our thanks are due to Thornley and Company of San Diego, California, for their kindness in supplying us with the fronds of *Macrocystis pyrifera.*

Summary

1. Pure alginic acid has been prepared from the *Macrocystis pyrifera* and shown to be a polymer of the anhydride of an aldehyde sugar acid in which all aldehyde groups are conjugated and all carboxyl groups free.

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[19] Fischer, *Ber.*, **24,** 539 (1891).

[20] Hudson, This Journal, **41,** 1141 (1919).

2. The uronic acid has not been obtained in crystalline condition. It may be oxidized to a dibasic C_6 sugar acid. The diamide and diphenylhydrazide of this acid correspond in properties to the analogous compounds prepared from pure *d*-mannosaccharic dilactone.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

TIN TETRAPHENYL AS A PHENYLATING REAGENT

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Certain of the organo-metallic compounds have been used as phenylating reagents. Mercury[1] and magnesium diphenyl[2] have been used to introduce the phenyl groups into certain compounds. Aryl tin halides were first made by the reaction of mercury diphenyl and stannic chloride.[3] Later the reaction between tin tetraphenyl and halogens to form mono-, di and triaryl halides has been carefully studied.[4] More recently Goddard and his co-workers[5] have isolated products from tin tetraphenyl and thallic chloride, while no derivatives were obtainable with the chlorides of mercury and sulfur with tin tetraphenyl.

Since tin tetraphenyl is comparatively rich in phenyl groups, and since its toxicity is much lower than that of mercury diphenyl, it seemed desirable to study the possibilities of using it as a reagent for introducing the phenyl group into organic compounds. In this paper are presented the reactions of tin tetraphenyl with the following types of compounds: halogens, alkyl halides, acyl halides, sulfur, nitric acid and sulfuryl chloride.

Experimental Part

1. Action of Halogens.—Bromine and chlorine react violently with tin tetraphenyl. Even at 0° they react energetically to give excellent yields of the corresponding monohalides of benzene. The reaction using iodine is less active and low yields of phenyl iodide are obtained. Iodine monochloride reacts very readily and produces a good yield of phenyl iodide. No halogen disubstitution products of benzene were detected under the conditions of the experiment.

Bromobenzene.—Twelve and seven-tenths grams of bromine was slowly added with a dropping funnel to 8.5 g. of tin tetraphenyl in a round-bottomed flask connected with a reflux condenser, the flask being cooled in an ice-salt mixture. The bromine was rapidly taken up, forming a colorless liquid, until most of the bromine had been

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[1] Dreher and Otto, *Ann.*, **154**, 97 (1870).

[2] Waga, *ibid.*, **282**, 323 (1894).

[3] Aronheim, *ibid.*, **194**, 145 (1878).

[4] Polis, *Ber.*, **22**, 2918 (1899); Krause, *ibid.*, **51**, 912 (1918); Chambers and Scherer, THIS JOURNAL, **48**, 1055 (1926).

[5] Goddard and Goddard, *J. Chem. Soc.*, **121**, 256 (1922); Goddard, Ashley and Evans, *ibid.*, **121**, 978 (1922).