which it was obtained in the form of filmy plates. 4.7 Gm. (= 82.4 p. c.) of this compound were isolated.

Bromine determinations according to Carius yielded 72.8 p. c. and 71.6 p. c., respectively, in two determinations, whereas the formula $CBr_3CH_2OCH_2CH_2OH$ calls for 73.4 p. c.

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SOME CONSTITUENTS OF COMMERCIAL CHERRY GUM.*

BY C. L. BUTLER AND LEONARD H. CRETCHER.

The chemistry of the plant gums (1), as well as of other acid polysaccharides such as pectins, mucilages, hemicelluloses and algins, has not received much detailed attention from research workers until quite recently. This is particularly true of the acidic nuclei of these materials. This problem was attacked long ago by O'Sullivan (2), who believed that gums arabic, gedda and tragacanth contained as acidic nucleus a stable organic acid of the formula $C_{23}H_{38}O_{22}$. Robinson (3) later obtained an acid of similar composition from the gum of *Cochlospermum Gossypium.*

Recent researches in this field have not confirmed the C_{23} acids of O'Sullivan and Robinson as the nucleus of plant gums, since gum arabic (1), (4), mesquite gum (5) and flaxseed mucilage (6) were shown to contain aldobionic acids ($C_{12}H_{20}O_{12}$), which are composed of one uronic acid and one sugar group as stable nuclei. The soluble fraction of gum tragacanth (7) appears to contain a C_{23} acid. This substance, however, differs from the monobasic C_{23} acid of O'Sullivan in that it is composed of one pentose and three uronic acid residues, all three carboxyl groups being free. Aldobionic acids have also been isolated from the hydrolysis products of the serologically specific carbohydrates from bacteria (8) and from hemicellulose of cottonseed hull bran (9).

In the course of our studies on the chemistry of the plant gums, we obtained a number of samples of cherry gum. A report on the composition of a sample collected from wild cherry trees in Indiana will be published elsewhere. In this paper will be found a description of some experiments with material purchased on the open market.

The acidity of cherry gum has been stated by Ehrlich (10) to be due to glucuronic acid. However, no experimental data are given in his report. A few references to investigations showing the presence of *l*-arabinose and *d*-galactose are to be found in the older literature (11). Van der Haar (12) reported the absence of methylpentoses and confirmed the presence of arabinose, galactose and the "glucuronic acid group" without demonstrating which uronic acid was present.

The sample used in the experiments to be described contained 12.8% moisture and 2.8% ash, the constituents of which are shown in Table I.

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TABLE I.—CONSTITUENTS OF COMMERCIAL CHERRY GUM ASH.

SiO_2	0.95%
Fe_2O_3 and Al_2O_3	3.61
CaO	86.17
MgO	9.22
Total	99.95%

It will be noticed that the ash differs from that of gum arabic in that the latter contains a considerable amount (about 20%) of alkali metals. Analyses for the sugar constituents ordinarily found in this type of substance were made on the ash-free gum by the usual methods (13). The results are shown in Table II.

TABLE II.—CONSTITUENTS OF COMMERCIAL CHERRY GUM ACID.

Uronic acid	30.1%
Pentose (furfural phloroglucid method)	13.3
Arabinose (diphenylhydrazone method)	11.8
Methyl pentose	4.9
Galactose	40.5
Methoxyl	3.0

Since many pectic substances have been shown to contain methoxyl groups, the gum was analyzed for this constituent by the Zeisel method. It was found to contain 3.0%. For purposes of comparison, other samples of cherry gum were gathered directly from the trees and analyzed for methoxyl content. As shown in the Experimental Part of this paper, all gave negative results. Peach and plum gums, however, both gave positive tests.

It is claimed (14) that European cherry gum is frequently a mixture of fruit gums, the term cherry gum being applied to any mixture of cherry, plum, peach and apricot gums. In view of this, and as a result of our experience with many samples of cherry gum, we are inclined to the idea that no authentic cherry gum of American origin contains methoxyl. The fact that the sample of gum collected from wild cherry trees in Indiana gave quite different results when submitted to hydrolysis, is further confirmation of the idea that the sample herein described is not botanically authentic. Little or no reliance can be placed on the botanical authenticity of plant gums bought on the open market. Obviously this is a very important factor in chemical studies of this kind.

This cherry gum, like the better known gum tragacanth, is not completely dissolved by water. When digested for thirty-six hours with five times its weight of water, about 12% remained undissolved. Preliminary experiments were made on the water-soluble fraction of the gum, but later work indicated that identical hydrolysis products were obtained using the whole gum as starting material.

It has been reported (15) that partial hydrolysis of gum arabic with 1–1 cold hydrochloric acid yields a gum acid which precipitates with anti-pneumococcus sera. We desired to compare the properties of similarly treated cherry gum with those of gum arabic in this respect. We are indebted to Dr. Robert Koch, Institute of Pathology, The Western Pennsylvania Hospital, Pittsburgh, Pa., for testing samples of this partially hydrolyzed material and the water-soluble fraction of cherry gum against anti-pneumococcus sera, Types I, II and III. In dilutions

from 1:50,000 to 1:100 the solutions caused no cloudiness when added to the sera. Control tubes with pneumococcus cultures gave positive precipitation tests.

The reaction of (1–1) hydrochloric acid on this cherry gum led to the formation of an alcohol-insoluble intermediate gum acid and an alcohol-soluble sugar fraction. The quantities of alcohol-soluble and insoluble furfural phloroglucid (corrected for uronic acid) obtained from this gum acid, on analysis, were so small that the presence of pentose or methyl pentose in the material was quite doubtful. The substance had a neutralization equivalent of 672. It consisted of approximately 66% free acid and 34% lactone. The calculated neutralization equivalent for such an acid-lactone mixture composed of three units of hexose and one of hexuronic acid ($C_{24}H_{40}O_{22}$) is 674, assuming that three molecules of water were lost in its formation.

An aldobionic acid was isolated after hydrolysis in boiling half-normal sulfuric acid, both from the intermediate gum acid and from the water-soluble fraction of the original gum. The complete identification of the aldobionic acid fraction was not accomplished. That the sugar half of the molecule is *d*-galactose was shown by isolation of this sugar after hydrolysis. The absence of glucuronic acid was shown by repeated failures to obtain acid potassium saccharate from oxidation products using either nitric acid or bromine-hydrobromic acid mixture. The fact that nitric acid oxidations invariably gave quantities of mucic acid corresponding roughly to half the aldobionic acid molecule instead of to the whole of it indicated the absence of galacturonic acid. This was confirmed by hydrolyzing the aldobionic acid and oxidizing the acidic fraction of the hydrolysis product. Neither mucic nor saccharic acid could be isolated.

A small amount of mucic acid was obtained by submitting the aldobionic acid to simultaneous hydrolysis and oxidation with bromine-hydrobromic acid mixture. That this could have been an oxidation product of the galactose half of the molecule was shown by the isolation of mucic acid when galactose was submitted to the same experimental conditions. The bromine-hydrobromic acid test, commonly used by workers in this field, therefore seems to be of uncertain value as a test for uronic acids.

Analysis by the Zeisel method showed that the aldobionic acid contained 5.7% methoxyl. The theoretical methoxyl content for an aldobionic acid containing one CH_3O group is 8.4. The substance therefore was a mixture of methylated and unmethylated material. Further purification was attempted by crystallization from acetic acid, and by fractional precipitation of the calcium salt. These experiments were not successful as in no case could an acid be isolated which had a methoxyl content even approaching the proper value for methylated aldobionic acid, nor could the unmethylated acid be obtained in pure condition. Since no difficulty was experienced in isolating galactose from the acid, it is quite probable that the methoxyl group is attached to the uronic acid half of the molecule (5). This would account for the failure to identify the uronic acid by the usual methods.

As stated above, the only sugars reported to date in cherry gum are *d*-galactose and *l*-arabinose. In this work, the presence of these sugars has been confirmed.[1] The small amount of methyl pentose present was not identified.

[1] The constituents of a sample of cherry gum collected directly from wild cherry trees in Indiana were found to be: *d*-mannose, *d*-galactose, *l*-arabinose, *d*-xylose, and *d*-glucuronic acid.

EXPERIMENTAL PART.

Separation of Cherry Gum into Soluble and Insoluble Fractions.—Forty Gm. of coarsely ground gum containing 12.8% water and 2.8% ash were placed in a flask with 200 cc. of boiling water and thoroughly mixed. The mixture was kept on a water-bath for one-half hour and then was allowed to stand for 36 hours at room temperature. It was centrifuged and the clear heavy liquid was decanted off. The insoluble part was agitated with 100 cc. of cold water and the mixture again centrifuged. The wash liquor was added to the supernatant liquor first obtained. The insoluble residue was dried over night at 80°. It weighed 4.5 Gm.

To the combined supernatant liquors containing the soluble fraction of the gum, was added two volumes of 95% alcohol. The mixture was allowed to settle over night, and the milky liquor above the precipitated gum was then decanted. The curdy precipitate was washed with 95% alcohol, and dried at 80°. It weighed 24 Gm. An additional 5.5 Gm. of soluble gum was obtained from the mother liquor of the first precipitate by concentrating *in vacuo* to a syrup and reprecipitating with alcohol, making the total weight of soluble gum 29.5 Gm. $[\alpha]_D$ + 5.4. The substance did not reduce Fehling's solution.

Hydrolysis with Cold 18% Hydrochloric Acid.—Two hundred Gm. of finely powdered whole gum was added slowly, with stirring, to 500 cc. of 18% HCl. After standing for 24 hours at room temperature, practically all the material was in solution. The solution was strained through cloth into a 3-liter flask, which was then filled with 95% alcohol to precipitate the partially hydrolysed gum acid. After settling, the supernatant liquor was decanted, the sticky precipitate was macerated with 95% alcohol and washed with three successive portions of the same solvent. The substance dissolved in water to a cloudy solution, which was clarified by adding a little decolorizing carbon and shaking and then adding acetone until a small amount of the gum acid separated. The mixture was centrifuged and the clear liquor decanted. The thick gummy residue was mixed with water and treated with acetone as before, and again centrifuged. The process was repeated until only a small amount of gummy material containing all the carbon was left. The clear liquors were combined and precipitated with acetone. The product was dried *in vacuo* at 50°. The yield was 65 Gm. $[\alpha]_D$ + 32°.

A product having the same rotation was prepared by this method from the water-soluble part of the gum.

This material did not precipitate with pneumonia anti-sera.

Analyses.—Substance, 0.3106 Gm. required 3.06 cc. *N*/10 NaOH at room temperature (phenolphthalein) and 4.62 cc. in hot solution. Calculated for $C_{24}H_{40}O_{22}$: equivalent weight (67% free acid, 33% lactone), 674. Found: equivalent weight, 672. Only traces of pentose and methylpentose were present.

Hydrolysis of the Intermediate Gum Fraction with Half-Normal Sulphuric Acid.—Fifty Gm. of the partially hydrolyzed cherry gum acid was dissolved in one liter of 0.5 *N* sulphuric acid and boiled under a reflux condenser for 4.5 hours. The rotation after hydrolysis was $\alpha = +7.25$ in a 2-dcm. tube. The sulphuric acid was removed with barium hydroxide and the solution of sugar and sugar acid was concentrated to 250 cc. It was then heated in the water-bath with 10 Gm. of calcium carbonate for four hours. After cooling, the mixture was filtered

from the excess calcium carbonate and the calcium salt of the sugar acid was precipitated by the addition of one liter of alcohol. The salt was purified by dissolving in water, reprecipitating and washing with alcohol. Two fractions of salt were obtained; the first and less pure was colored and weighed 5 Gm. The main fraction weighed 16 Gm. after drying *in vacuo* at 75° for several hours. $[\alpha]_D$ + 68.8°.

Analyses.—Substance, 0.2000 Gm. 10.4 cc. *N*/10 iodine. Calculated for calcium aldobionate $(C_{12}H_{19}O_{12})_2Ca$: *N*/10 iodine, 10.7 cc.

Substance, 0.3925 Gm.: 0.0680 Gm. $CaSO_4$. Calculated for $(C_{12}H_{19}O_{12})_2Ca$: Ca, 5.3. Found: Ca, 5.2.

The alcoholic mother liquor containing the sugar was concentrated to a thick sirup *in vacuo*. The sirup was dissolved in alcohol and placed in the ice-box to crystallize. Fifteen Gm. of white sugar crystals were obtained. $[\alpha]_D$ = +80.5. $[\alpha]_D$ galactose = +80.5.

The Aldobionic Acid.—A solution of 14 Gm. of calcium aldobionate in 50% alcohol was treated with an alcoholic solution of the calculated amount of oxalic acid to remove the calcium. After filtering, the calcium-free liquid was concentrated to a sirup *in vacuo*. Alcohol was added until no further precipitate was formed and the alcoholic and the alcohol-insoluble material was filtered off. The filtrate was again concentrated and treated with alcohol. A further small quantity of alcohol-insoluble material was precipitated. The filtrate from this precipitate was completely soluble in alcohol. The solvent was evaporated under reduced pressure and the acid was dried to constant weight at 70° *in vacuo*. The yield was 8.8 Gm. $[\alpha]_D$ + 89.8°.

Analyses.—Substance 0.4760 Gm.: AgI, 0.2025 Gm. Calculated for methylated aldobionic acid, $C_{13}H_{22}O_{12}$: CH_3O, 8.4. Found: CH_3O, 5.7.

Substance, 0.1928 Gm.: *N*/10 NaOH, 5.1 cc. at room temperature (phenolphthalein); in hot solution, 5.5 cc. Calculated for $C_{13}H_{22}O_{12}$: equivalent weight, 368. Found: equivalent weight, 350.5.

Substance, 0.1928 g.: 10.4 cc. *N*/10 iodine. Calculated for CHO: *N*/10 iodine, 10.4.

Substance, 0.5471 Gm.: CO_2, 0.0662 Gm. (Lefevre method). Calculated for $C_{13}H_{22}O_{12}$: uronic acid, 52.4. Found: uronic acid, 53.2.

Substance, 0.2106 Gm.: CO_2, 0.3167 Gm.; H_2O, 0.1037 Gm. Calculated for $C_{12}H_{22}O_{12}$: C, 42.1; H, 6.0. Found: C, 41.0; H, 5.5.

These figures point strongly to a mixture of methylated and unmethylated aldobionic acid.

An acid having the same properties as those described above was isolated after hydrolysis of whole commercial cherry gum in *N*/2 sulphuric acid.

Hydrolysis of the Aldobionic Acid with 1 N Sulphuric Acid.—Four Gm. of aldobionic acid was dissolved in 25 cc. of 1 *N* sulphuric acid and the solution was boiled gently for 16 hours under a reflux condenser. The sugar fraction was separated by methods described above. It was crystallized from glacial acetic acid and from alcohol. The purified sugar melted at 165°. $[\alpha]_D$ + 80.8. $[\alpha]_D$ galactose + 80.5; melting point 168° (12). On oxidation with nitric acid (sp. gr. 1.15) mucic acid was formed. After thorough washing with water and alcohol, the sample melted at 218.5°. The hexose of the aldobionic acid is therefore galactose. The acidic fraction (isolated as calcium salt) was oxidized with bromine

water after removal of the base with oxalic acid. Neither mucic acid nor acid potassium saccharate could be isolated from the oxidation product.

Hydrolysis of the Aldobionic Acid with Hydrobromic Acid in the Presence of Bromine.—The reaction was carried out as previously described (1, 8). Three Gm. of aldobionic acid was used. The bromine and the greater part of the hydrobromic acid were removed by evaporating repeatedly *in vacuo*. The solution was finally concentrated to 5 cc. and allowed to stand in the ice-box for several days, during which time fine crystals formed in the liquid. These were filtered off and washed. They melted at 210–212°. The crystals were dissolved in *N*/10 NaOH. The solution was acidified with hydrochloric acid and again placed in the ice-box to crystallize. The recrystallized material melted at 220–221° corr. and did not depress the melting point of a sample of pure mucic acid melting at 220° C. The yield was very low.

No acid potassium saccharate could be isolated from the mother liquor.

Oxidation of the Aldobionic Acid with Nitric Acid.—A sample of 1.5 Gm. aldobionic acid was oxidized in the usual way with 15 cc. of nitric acid, sp. gr. 1.15. The yield of mucic acid was 0.44 Gm., corresponding to 0.60 Gm. galactose, or 40.0%. It was impossible to demonstrate the presence of saccharic acid in the filtrate from the mucic acid.

Numerous larger scale oxidation experiments using up to 60 Gm. of aldobionic acid were carried out. The yield of mucic acid, in all cases, corresponded to less than half the aldobionic acid molecule. No saccharic acid was found in the filtrate from the mucic acid.

Oxidation of Galactose with Bromine-Hydrobromic Acid Mixture.—Four Gm. of galactose was treated as previously described with this reagent. The yield of mucic acid was 0.13 Gm.

Analysis of Cherry Gum Acid.—A sample was prepared from the water-soluble fraction of the gum by the method of Neubauer (16) and analyzed according to the usual methods (12).

Analyses.—Subs., 0.3434 Gm.: CO_2 (Lefevre method), 0.0235 Gm. Found: uronic acid, 30.1. Subs. 1.000 Gm.: *N*/10 NaOH (phenolphthalein) in hot solution, 15.65 cc. Found: equivalent weight, 639. Subs. 0.2960 Gm.: alcohol-insoluble furfural phloroglucide, 0.0600 Gm. correction for uronic acid, 0.0297 Gm. leaving 0.0303 Gm. insoluble phloroglucide due to pentose; alcohol soluble phloroglucide 0.0054 Gm. Found: pentose (calc'd. as arabinose), 13.3; methyl pentose (calc'd. as rhamnose hydrate), 4.9 (doubtful). Substance, 1.000 Gm.: arabinose diphenylhydrazone, 0.2485 Gm. Found, arabinose 11.8. Substance, 1.000 Gm.: mucic acid 0.288 Gm. Found: galactose, 40.5. Substance, 0.4870 Gm.: AgI, 0.1215 Gm. Found: CH_3O, 3.3.

The Methoxyl Content of Fruit Tree Gums.—0.3000 Gm. soluble cherry gum (Eimer and Amend) gave 0.0670 Gm. AgI. Found: CH_3O, 3.0%.

0.3000 Gm. cherry gum, wild (Indiana), gave no AgI. Found: CH_3O, 0.0%.

0.3000 Gm. cherry gum, domestic (Ohio), gave no AgI. Found: CH_3O, 0.0%.

0.5000 Gm. cherry gum, domestic, dark red sweet (Penna.), gave no AgI. Found: CH_3O, 0.0%.

0.5000 Gm. cherry gum, domestic, red sour (Penna.), gave no AgI. Found: CH_3O, 0.0%.

0.5000 Gm. peach gum, domestic, gave 0.0165 Gm. AgI. Found: CH_3O, 0.4%.

0.5000 Gm. plum gum, domestic, gave 0.0390 Gm. AgI. Found CH_3O, 1.0%.

SUMMARY.

Hydrolytic studies on a sample of cherry gum purchased on the open market were carried out. In common with all plant gums studied to date this gum was found to contain uronic acids. The aldobionic acid fraction was shown to contain galactose and unidentified methylated uronic acids.

Apparently authentic American cherry gum does not contain methoxyl.

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PITTSBURGH, PA.

PRELIMINARY INVESTIGATION OF CERTAIN PHYSICAL AND CHEMICAL PROPERTIES OF THE VOLATILE OILS FROM AUTHENTIC PLANT PRODUCTS.

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This investigation was undertaken to obtain information regarding the volatile oils of plant products official in the U. S. P. and N. F. as well as of other plant products which may be used as drugs. The work has been limited chiefly to plant products regularly imported that contain appreciable quantities of volatile oil. The volatile oils present in these plant products are usually the important constituents. It is believed the following information will be valuable in suggesting volatile oil standards.

Where the amount of moisture present is reported, the determination was made by the xylol method. The distillation of the volatile oils was carried to complete exhaustion by the use of the Clevenger apparatus,[1] which may now be obtained by Emil Greiner Co., New York, N. Y.

The physical constants were determined at 20° C. The chemical characteristics were determined by methods outlined in U. S. P. X. Unless otherwise stated the products examined represented imports.

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