rates during the later stages of the reaction may be the cause of the pressure drop observed. In our further work it is expected to study the composition of the reaction products obtained in runs of short duration where the total pressure has reached the maximum pressure of the longer runs. It is hoped that information from these and even shorter runs may help in the derivation of a possible reaction scheme for these condensations.

The authors wish to thank Mr. J. L. Wilson, who has assisted in this work as American Petroleum Institute Research assistant.

Summary

The condensation of methane, ethane, propane, butane and ethylene has been studied in electrical discharge. It has been found that these reactions are quite similar to the condensations caused by alpha rays. The following factors give evidence of this similarity of reaction: (1) the pressure changes as a function of the time; (2) the free hydrogen produced during the reaction; (3) the relative amount of hydrogen and methane in the hydrogen–methane fraction of the resultant gases; (4) the percentage of liquid conversion; (5) the average composition of liquid condensate; (6) the percentage of the hydrocarbons reacted. All of these factors are quite similar for both types of condensation and it is argued that both types of reaction must be caused by the same mechanism. A reaction scheme is discussed on the basis of the ion cluster theory. The usual ideas are amplified in one respect in that it is assumed that the larger molecules are ionized not only by electron impact but also by electron exchange.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARIZONA]

THE COMPOSITION AND STRUCTURE OF MESQUITE GUM[1]

BY ERNEST ANDERSON AND LOUISE OTIS

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Previous investigations[2] have shown that mesquite gum yields *l*-arabinose and *d*-galactose on hydrolysis and that it contains a hexose uronic acid. When the work described in this article was begun, the gum was assumed to be the salt of a complex organic acid composed of the above substances. This investigation has established the presence of methanol and *d*-glucuronic acid as constituents of the gum and has shown conclusively that it

[1] The material in this article is extracted from a thesis submitted by Louise Otis in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Northwestern University.

[2] C. Morfit, *Am. J. Sci.*, **19**, 264 (1855); R. H. Forbes, "The Mesquite Tree: Its Products and Uses," Arizona Agricultural Experiment Station, Bulletin No. 13 (1895); E. Anderson, L. Sands and N. Sturgis, *Am. J. Pharm.*, **97**, 589 (1925); E. Anderson and L. Sands, *Ind. Eng. Chem.*, **17**, 1257 (1925); THIS JOURNAL, **48**, 3172 (1926).

is the salt of an organic acid composed of four molecules of *l*-arabinose, three molecules of *d*-galactose, one molecule of methanol and one molecule of *d*-glucuronic acid, combined with the loss of eight molecules of water.

During the course of the research the free monobasic acid of which mesquite gum is a salt, was prepared and analyzed. This complex molecule was then hydrolyzed in 3% sulfuric acid, first at 80° and finally in the autoclave at fourteen pounds' pressure. This process gave successively less complex monobasic acids, which were isolated in the form of calcium salts and analyzed. From a study of the composition and reactions of the various products isolated it is possible to deduce some facts in regard to the method of linkage of the original molecule.

Identification of an Ether Linked Methoxy Group in Mesquite Gum.—It was shown by von Fellenberg[3] that a glucosidic methoxy group can be removed from naturally occurring compounds by heating at 80 to 90° with a 2% solution of sodium hydroxide. An ether linked methoxy group, on the other hand, cannot be removed by the above method but is removed by mixing the compound with 72% sulfuric acid and boiling for ten minutes. The presence of any free methanol formed in this way can be accurately detected by use of Denigès' method.[4] When the above test was applied to mesquite gum it was negative for the glucosidic methoxy but positive for the ether methoxy group. However, all the salts formed by partial hydrolysis of mesquite gum gave positive tests for both the glucosidic and ether methoxy groups. As a check on the accuracy of the method for distinguishing between the two types of methoxy groups when applied to methylated sugars, a sample of tetramethylglucose[5] was tested. This sample showed the presence of both glucosidic and ether methoxy groups. It thus appears that while von Fellenberg's method is suitable for distinguishing between the two types of union in the natural products for which it was devised, it cannot be used to distinguish between the two types of union in the methylated sugars.

The linkage of the methoxy group in mesquite gum seems more stable than a glucosidic linkage could be. This is shown by the following facts. Mesquite gum was hydrolyzed at 100° for twenty-six hours in 3% sulfuric acid solution. The salts obtained from this hydrolysis were further hydrolyzed in 3% sulfuric acid in the autoclave at fourteen pounds' pressure for seven hours. The liquid in which this last hydrolysis was carried out showed only a trace of methanol and the salts obtained after neutralization gave a very strong test for methanol, showing that very little methanol had been removed during the hydrolysis. It was also found that oxidizing the

[3] T. von Fellenberg, *Biochem. Z.*, **85**, 44 (1918).

[4] M. G. Denigès, *Compt. rend.*, **150**, 529 (1910).

[5] We are indebted to Dr. F. W. Upson of the University of Nebraska for the sample. It melted at 85° and boiled at 153–156° under 0.2-mm. pressure.

salts with nitric acid of specific gravity 1.15 did not remove the methoxy group to any appreciable extent. It thus appears that the methoxy group is present in mesquite gum as an ether.

The Position of the Methoxy Group in the Organic Acid Occurring in Mesquite Gum.—The approximate position of the methoxy group in the molecule was determined by studying the methoxy content of the various hydrolytic products of mesquite gum. If the gum is hydrolyzed at 80° for six hours, all of the arabinose is removed. Crystalline *l*-arabinose can be obtained quantitatively, and as the salt formed at the same time contains galactose, a uronic acid and a methoxy group, the methoxy is not attached to the arabinose. If this salt is hydrolyzed further, pure crystalline galactose can be obtained as well as a salt containing only a trace of galactose, a uronic acid and the methoxy group. Therefore, the methoxy is not attached to the galactose but is attached to the uronic acid. Nothing definite can be said as to which carbon atom in the uronic acid this methoxy group is joined, except that it cannot be to carbon atom one or six, since it is present as an ether, not as a glucosidic group.

The Identification of *d*-Glucuronic Acid.—The presence of *d*-galacturonic acid or *d*-glucuronic acid in the free condition in a mixture can be established by oxidizing the uronic acid with bromine and obtaining mucic acid or saccharic acid, both of which can be identified. In mesquite gum, however, no simple uronic acid is present but a stable methoxyuronic acid. The gum must be hydrolyzed and the methoxy group removed if the uronic acid is to be identified by conversion to mucic or saccharic acid. Numerous unsuccessful attempts were made to identify mucic or saccharic acid among the products by hydrolyzing mesquite gum and oxidizing the resulting mixture with bromine. Finally some calcium salts obtained by hydrolyzing the gum first in the boiling water-bath and then in the autoclave were freed from sugars by dissolving in water and precipitating with alcohol. These salts were converted to the free acid by treatment with sulfuric acid and the acid was purified by dissolving in alcohol. Approximately 30 g. of this acid was placed in an evaporating dish with 200 cc. of nitric acid, specific gravity 1.15, and the solution concentrated on the water-bath to a gum. This gum was dissolved in water and again concentrated. The acids were neutralized with calcium carbonate, the mixture heated and the calcium oxalate filtered off from the hot solution. The calcium in the filtrate was precipitated by addition of potassium carbonate, filtered and the solution made acid with glacial acetic acid, filtered and concentrated on the water-bath to a small volume. After standing in the refrigerator for some days, the crystals were filtered off and recrystallized from water and acetic acid. They appeared to be identical with potassium acid saccharate crystals made from glucose and with the crystals pictured in van der Haar.[6] The percentage of potassium was determined by conversion to potassium sulfate.

Anal. Calcd. for $KHC_6H_8O_8$: K, 15.75. Found: K, 15.89, 15.81.

By the above method approximately 1 g. of pure recrystallized potassium acid saccharate was obtained. Since this work was repeated on a later occasion, it is certain that *d*-glucuronic acid is present. A strong positive

[6] A. W. van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren," Gebrüder Borntraeger, Berlin, **1920**, p. 120.

test for methanol was obtained on the mother liquor from which the potassium acid saccharate separated out, showing that the methoxy group was interfering with the formation of the saccharic acid.

The Analytical Methods Used and the Value of the Various Determinations.—Since the methods used in the analysis of the gums are often inaccurate, a brief summary will be given of the determinations that were made and the value that should be attached to each before discussing the quantitative results of this work.

The substances were analyzed for calcium oxide as ash, carbon dioxide evolved by the *d*-glucuronic acid, free aldehyde, *d*-galactose, *l*-arabinose, methanol, carbon and hydrogen.

All samples, except those used for the carbon and hydrogen determinations, were dried to constant weight *in vacuo* over phosphorus pentoxide using an Abderhalden vacuum drier and a bath of boiling toluene. The samples for the carbon and hydrogen determinations were dried to constant weight *in vacuo* over phosphorus pentoxide at 85°.

The percentages of calcium oxide reported as ash in this article are slightly high. This is a logical result of the method used in the preparation of the salts, which was to add calcium carbonate to a water solution of sulfuric acid and the organic acid, filter off the calcium sulfate and precipitate the calcium salt of the organic acid by addition of alcohol. It is difficult under these conditions to free the salt completely from calcium sulfate even by repeatedly dissolving in water and precipitating by alcohol. A trace of calcium sulfate in the salt increases considerably the percentage of ash without seriously affecting the other determinations.

The naphthoresorcinol test[7] was used as a qualitative test for a hexose uronic acid, while the carbon dioxide method of Lefèvre[8] as given by van der Haar was followed in the quantitative determination of the uronic acid. This is an accurate method and the results are reliable.[8c,d]

The method employed for determining the free aldehyde group was that of Cajori,[9] using an alkaline iodine solution as the oxidizing agent. The percentage of free aldehyde found by this method in the calcium salts of the monobasic acids was slightly less than the theoretical. This may in part be due to a slight oxidation of the aldehyde group of the salts during their formation.

The free acid of which mesquite gum is a salt, as well as the dibasic acids formed by oxidizing the aldehyde group of the monobasic acids with barium hypoiodite, all absorbed some iodine although they should have no free aldehyde group. This is easily explained. The free acid was prepared by

[7] C. A. Browne, "Handbook of Sugar Analysis," John Wiley and Sons, Inc., New York, **1912**, p. 393; J. A. Mandel and C. Neuberg, *Biochem. Z.*, **13**, 148 (1908); B. Tollens, *Ber.*, **41**, 1788 (1908); B. Tollens and F. Rorive, *ibid.*, **41**, 1783 (1908).

[8] (a) A. W. van der Haar, Ref. 6, p. 71; (b) C. G. Schwalbe and G. A. Feldtmann, *Ber.*, **58**, 1534 (1925); (c) W. H. Dore, THIS JOURNAL, **48**, 232 (1926); (d) A. D. Dickson, H. Otterson and K. P. Link, *ibid.*, **52**, 775 (1930); (e) J. R. Bowman and R. B. McKinnis, *ibid.*, **52**, 1209 (1930).

[9] F. A. Cajori, *J. Biol. Chem.*, **54**, 617 (1922).

treating mesquite gum in water solution with cold hydrochloric acid, precipitating the product with alcohol. If in this process an occasional molecule was partly hydrolyzed, the product would absorb iodine and thus show a small percentage of free aldehyde. Also if during the oxidation of the monobasic acids with barium hypoiodite insufficient time were allowed for the completion of the process, the resulting acids would show a small amount of aldehyde.

The percentages of *d*-galactose were determined by the mucic acid method, following as closely as possible the directions of van der Haar.[10] The results were in all cases low. It is now generally recognized that this determination should not be classed as a quantitative process.[11] When the method is applied to gums and pectins the results are often very inaccurate. In one case von Fellenberg reports[11] 54.8% galactose where the calculated is 75.6%. It seems that the accuracy of the determination depends largely on the nature of the linkage in the molecule. In the case of gum arabic the last molecule of galactose is easily removed[12] and in this case the galactose can be accurately determined.[13] On the other hand, the last molecule of *d*-galactose is very difficult to remove from mesquite gum and in this case the method yields lower percentages than the theoretical.

The percentage of arabinose was determined by mixing the sample with 12% hydrochloric acid, distilling off the furfural and precipitating it as the phloroglucide.[14] The directions given in the "Official Methods of Analysis" were followed. The results obtained on the free organic acid were about 2% lower than the theoretical. All of the other substances analyzed gave from 3 to 7% arabinose by this method, though no arabinose was actually present. This method is known to be only approximately quantitative. The yield of furfural from arabinose is not quantitative and the amount varies with different operators.[15] Furthermore, the furfural is contaminated with products that vitiate the results. Hexoses give hydroxymethylfurfural, which precipitates along with the furfural.[16] In addition hexose uronic acids yield furfural under the conditions of the determination and the yield is less than the theoretical.[8d] In the case of *d*-glucuronic acid an accurate factor has been worked out for correcting the

[10] A. W. van der Haar, Ref. 6, p. 125.

[11] F. Ehrlich, *Chem.-Ztg.*, **41**, 197 (1917); T. von Fellenberg, *Biochem. Z.*, **85**, 118 (1918).

[12] F. Weinmann, *Ber.*, **62**, 1637 (1929).

[13] C. L. Butler and L. H. Cretcher, THIS JOURNAL, **51**, 1519 (1929).

[14] "Official Methods of Analysis of the Association of Official Agricultural Chemists," Washington, D. C., **1924**, 2d ed., p. 120; A. W. van der Haar, Ref. 6, p. 61.

[15] N. C. Pervier and R. A. Gortner, *Ind. Eng. Chem.*, **15**, 1167, 1255 (1923).

[16] R. A. Gortner, "Outlines of Biochemistry," John Wiley and Sons, **1929**, p. 525; A. G. Norman, *Biochem. J.*, **23**, 524 (1929).

weight of the furfural phloroglucide for the furfural evolved by the hexose uronic acid.[17] No such factor is known for methoxyglucuronic acid. It is obvious that the accuracy of this determination is not great.

The presence of the methoxy group was determined qualitatively by means of the Denigès test for methanol.[3,4] The amount of methoxy was determined quantitatively by the Zeisel method.[18] The percentage found in all the monobasic acids checked the theoretical very closely. In the case of the dibasic acids formed by oxidizing the monobasic acids with an alkaline solution of barium hypoiodite, the percentages of methoxy were slightly low. This is easily accounted for by the fact that an alkaline solution seems to remove traces of methoxy from the methylated sugars.

The percentages of carbon and hydrogen were determined by Dr. E. Yusa at the University of Vienna and checked satisfactorily.

Attempts were made to determine the molecular weight of the free acid from mesquite gum by the cryoscopic method. However, no constant freezing point could be obtained. Since the substance is a free acid, its minimum molecular weight was determined by titrating with sodium hydroxide solution.

Preparation and Analysis of the Free Acid of Mesquite Gum.—The method used by Ehrlich in preparing pectic acid[19] was found to work satisfactorily in preparing and purifying the free acid of mesquite gum: 300 g. of mesquite gum was dissolved in 600 cc. of water, filtered, 60 cc. of concentrated hydrochloric acid added and the gum precipitated by addition of 15 liters of 85% ethanol. This precipitate was dissolved in 300 cc. of water and 40 cc. of concentrated hydrochloric acid diluted with 40 cc. of water added. The precipitate was again dissolved and thrown down by addition of 5.5 liters of 88% ethanol. This process was repeated five times. The gum was then dissolved in 250 cc. of water and 1350 cc. of 95% ethanol added to precipitate a small amount of gum and thus eliminate any metallic salts that might be present. The solution was centrifuged and the clear solution poured into a large volume of 95% ethanol. The precipitated material was allowed to settle, triturated with a pestle, filtered, washed with absolute alcohol and ether. The free organic acid finally obtained was a white amorphous powder which was practically free from ash, completely free from chlorides and readily soluble in water. A 0.008 *N* solution showed a P_H of 3.4. Table I gives the results of the analysis of this acid. The figures obtained check very closely the values calculated for a compound consisting of one molecule of methoxyglucuronic acid joined to three molecules of *d*-galactose and four molecules of *l*-arabinose with the loss of seven molecules of water.

Partial Hydrolysis of Mesquite Gum to Digalactoso and Trigalactoso Methoxy-*d*-glucuronic Acids.—When mesquite gum was hydrolyzed at 80° with 3% sulfuric acid, all the *l*-arabinose and part of the *d*-galactose were removed. The resulting solution was

[17] F. Ehrlich and F. Schubert, *Biochem. Z.*, **169**, 65 (1926).

[18] H. Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," J. Springer, Berlin, **1916**, p. 739; E. S. Kipping and W. H. Perkin, "Organic Chemistry," W. and R. Chambers, London, **1909**, p. 498; O. Kamm, "Qualitative Organic Analysis," John Wiley and Sons, **1923**, p. 172; J. T. Hewitt and T. S. Moore, *J. Chem. Soc.*, **81**, 318 (1901); W. H. Perkin, *ibid.*, **83**, 1367 (1903).

[19] F. Ehrlich, *Z. angew. Chem.*, **40**, 1305 (1927).

neutralized with calcium carbonate, the calcium sulfate filtered off and the calcium salts precipitated by pouring into alcohol. These crude salts were separated by the method of Levene[20] into five fractions, all of which were analyzed. The most soluble and least soluble portions corresponded to definite compounds. The details of this experiment are given below.

Four kilos of mesquite gum was hydrolyzed in 500-g. lots as follows.

Five hundred grams of mesquite gum was dissolved in 3 liters of distilled water, strained through a fine piece of cheese cloth, 60 cc. of concentrated sulfuric acid added (making approximately a 3% sulfuric acid solution) and the flask immersed in a water-bath at 80° and heated for eleven hours. The solution was neutralized with calcium carbonate, filtered and concentrated on a large evaporating dish over boiling water in the presence of an excess of calcium carbonate. When the volume was about 500 cc., it was filtered with suction and the filtrate poured into a large volume of 95% ethanol and left to stand overnight to settle. The alcohol was poured off, the thick sirupy material stirred with fresh 95% ethanol, and then extracted twice for one hour each time with boiling ethanol. The thick, gummy residue was dissolved in enough water so that a fine flocculent precipitate was obtained on pouring it slowly into a large volume of 95% ethanol to precipitate the salts. The gummy residue was extracted twice for two hours with hot 95% ethanol and dissolved in water, heated in the boiling water-bath with norit, filtered and precipitated by pouring into a large volume of 95% ethanol; 744 g. of air-dried, dark brown salts was obtained from the 4 kg. of gum. These dark brown salts were purified as follows: 100 g. of salts was dissolved in 750 cc. of water and then 150 cc. of 6 *N* sulfuric acid and 150 g. of norit (previously boiled with 6 *N* sulfuric acid and washed with water) were added. The mixture was heated rapidly and boiled for one minute, cooled under the tap and filtered. The filtrate was neutralized with calcium carbonate, filtered and the filtrate concentrated by vacuum distillation in a water-bath at 80°, filtered again and the salts precipitated by pouring into a large volume of 95% ethanol. This treatment gave a white salt. The total yield from the 744 g. of crude salts was 423 g.

This salt was separated by fractional precipitation as follows. It was dissolved in three times its weight of water (400 g. of salt dissolved in 1200 cc. of water). This solution was filtered through a double filter paper to remove the calcium sulfate. After standing overnight and being filtered again, 2400 cc. of 95% ethanol (two times the

TABLE I

ANALYTICAL DATA AND PHYSICAL CONSTANTS

	Methoxyglucuronic +3 galactoses +4 arabinoses $-7H_2O$. Free acid of mesquite gum		(Methoxyglucuronic +3 galactoses $-3H_2O$-H)$_2$Ca salt 1		(Methoxy-glucuronic +galactoses $-2H_2O$-H)$_2$Ca salt 2		(Methoxy-glucuronic +1 galactose $-H_2O$-H)$_2$Ca salt 3	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Molecular weight	1222	1222	.....	1426	.....	1102	...	778
Specific rotation	+70.8°	.....	+16.8°	.....	+38.5°	.....	...	....
Ash, %	0.07	0.0	4.31	3.93	5.34	5.08	7.46	7.20
Carbon dioxide, %	3.55	3.60	6.24	6.17	7.91	7.99	10.00	11.31
Free aldehyde, %	0.48	0.0	2.40	4.07	5.04	5.26	6.99	7.46
Galactose, %	26.77	44.2	59.74	75.73	48.79	65.33	23.90	46.27
Arabinose, %	47.02	49.1	5.03	0.0	7.17	0.0	2.91	0.0
Methoxy, %	2.86	2.54	3.90	4.35	5.78	5.63	...	....
Carbon, %	45.46	44.2	41.94	42.07	41.34	41.38	...	....
Hydrogen, %	6.39	6.06	6.09	5.75	6.12	5.63	...	....

[20] P. A. Levene and H. Sobotka, *J. Biol. Chem.*, 71, 471 (1927); W. F. Goebel, *ibid.*, **72**, 813 (1927).

volume of water) was added. It was left to stand overnight, thus allowing the gummy matter to separate out, and in the morning the clear supernatant liquid was decanted and concentrated in vacuum. From this solution the calcium salt was precipitated as described before and 67 g. of this most soluble salt was obtained. The gummy residue was dissolved in 535 cc. of water, 1070 cc. of 95% ethanol added and the liquid centrifuged to hasten the separation of the liquid and residue. In this way five different fractions were precipitated. The final residue gave the least soluble salt (96 g.). All the fractions were analyzed, but the most soluble and least soluble were the only fractions that were pure compounds. The analyses of these two compounds are given in Table I. The least soluble salt (Salt 1) is the calcium salt of methoxyglucuronic acid joined to three molecules of galactose with the loss of three molecules of water. The most soluble salt (Salt 2) is the calcium salt of the methoxyglucuronic acid joined to two molecules of galactose with the loss of two molecules of water.

Oxidation of Digalactoso and Trigalactoso Methoxyglucuronic Acids to Dibasic Acids.—The calcium salts of digalactoso and trigalactoso methoxy-*d*-glucuronic acids (Salts 1 and 2) were oxidized by barium hypoiodite solution[21] and the resulting dibasic acids isolated as the calcium salts in the form of a white amorphous powder. These salts gave the naphthoresorcinol test and on treatment with 12% hydrochloric acid gave carbon dioxide, thus proving the presence of a hexose uronic acid. This fact proves that the free aldehyde group in the digalactoso and trigalactoso methoxyglucuronic acids was on the galactose and not on the uronic acid. The dibasic salt 1A obtained by oxidation of the monobasic salt (1) is the calcium salt of one molecule of methoxyglucuronic acid joined to two molecules of galactose and one molecule of galactonic acid with the loss of three molecules of water. The dibasic salt 2A obtained by the oxidation of the monobasic salt (2) is the calcium salt of one molecule of methoxyglucuronic acid joined to one molecule of galactose and one molecule of galactonic acid with the loss of two molecules of water. The analyses of these salts are given in Table II.

TABLE II

ANALYSES OF SALTS

	(Methoxyglucuronic + 2 galactose + 1 galactonic − 3 H_2O-2H)Ca salt (1A)		(Methoxyglucuronic + 1 galactose + 1 galactonic − 2 H_2O-2H)Ca salt (2A)	
	Found	Calcd.	Found	Calcd.
Molecular weight	....	748	.....	586
Specific rotation	+2.7°	....	+12.8°	....
Ash, %	6.53	7.49	9.74	9.55
Carbon dioxide, %	6.21	5.88	8.06	7.51
Free aldehyde, %	0.34	0.00	0.23	0.00
Galactose, %	57.28	72.19	46.30	61.43
Arabinose, %	5.35	0.00	5.11	0.00
Methoxy, %	3.40	4.14	4.75	5.29
Carbon, %	40.48	40.11	38.10	38.91
Hydrogen, %	5.89	5.35	5.27	5.12

Partial Hydrolysis of Mesquite Gum to Monogalactoso Methoxyglucuronic Acid.—When mesquite gum is hydrolyzed for a longer time than when preparing the digalactoso and trigalactoso methoxyglucuronic acids, the monogalactoso methoxyglucuronic acid can be obtained. The following procedure was used. One kilo of mesquite gum was hydrolyzed in 500-gram lots as follows: 500 g. of mesquite gum was dissolved in 3

[21] W. F. Goebel, *J. Biol. Chem.*, **72**, 809 (1927).

liters of water and 60 cc. of concentrated sulfuric acid dissolved in 200 cc. of water added. This solution was hydrolyzed in a water-bath at 85° for twenty hours. It was neutralized with calcium carbonate, treated with norit, filtered and the filtrate concentrated in vacuum, using paraffin to prevent foaming, until the liquid had a refractive index of 1.38. The salt was reprecipitated by pouring into a large volume of ethanol and worked up as described under the preparation of the other salts. It was dissolved in 250 cc. of hot water, filtered and precipitated again by pouring into a large volume of ethanol. One kilo of gum gave practically 300 g. of salt. This 300 g. of salt was dissolved in water, 57 cc. of concentrated sulfuric acid added and the solution diluted to 1800 cc. It was heated in a water-bath at 80 to 85° for fourteen hours, neutralized with calcium carbonate, heated with norit, filtered and the filtrate concentrated in vacuum. The salt was precipitated from this solution by pouring into a large volume of alcohol; the yield of salt was about 200 g. This salt was separated by fractional precipitation. It was dissolved in 300 cc. of water, 600 cc. of 95% ethanol added and the liquid concentrated, etc., giving the most soluble salt. The gummy residue was dissolved in 225 cc. of water and some salt precipitated by addition of 450 cc. of 95% ethanol. This process was repeated four times, when the gummy residue was worked up giving the least soluble portion of the salts.

All the fractions were analyzed and the least soluble portion was found to be a fairly pure sample of the calcium salt of methoxyglucuronic acid joined to one molecule of galactose with the loss of one molecule of water. The analysis for this salt (Salt 3) is given in Table I.

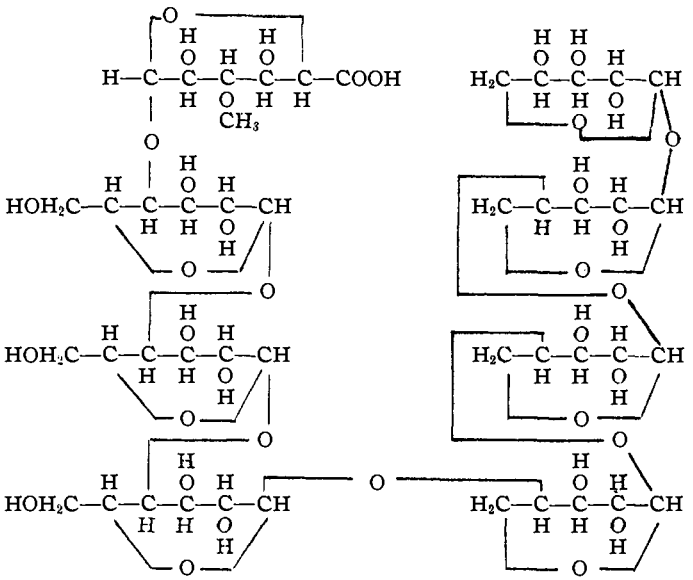
The Structure of Mesquite Gum.—From the work reported above certain facts can be deduced in regard to the structure of the complex organic acid occurring in mesquite gum.

The arabinose must be joined to the molecule by some kind of loose union, since it can be removed completely when the gum is hydrolyzed for six hours with 3% sulfuric acid at 80°. As the free gum does not reduce Fehling's solution, there must be either a dicarbonyl union involving at least one molecule of arabinose or a glucosidic union between the aldehyde of the end arabinose and some hydroxyl in the molecule. Since the compounds of the uronic acid with one, two or three molecules of galactose reduce Fehling's solution, there are only four possible positions for a dicarbonyl union—between the first and second, second and third, third and fourth molecules of arabinose or between the fourth molecule of arabinose and the first molecule of galactose. As immediately upon hydrolysis the molecule begins to reduce Fehling's solution, it seems logical to assume that the dicarbonyl union is between the first two molecules of arabinose, but as no compounds containing part of the arabinose attached to the molecule could be obtained, this position could not be proved. If, however, it is a glucosidic linkage, it could be between the aldehyde group of the first arabinose and any of the numerous hydroxyl groups in the molecule.

On the other hand, the galactoses are quite firmly attached in the molecule. As the different degradation products contain only one free aldehyde group and as one after another of the galactose molecules can be removed by hydrolysis, it seems as if these molecules must be joined together in a chain by means of glucosidic linkages with a free aldehyde group on the end galactose molecule. To which hydroxyl of the sugar the aldehyde is joined is mere conjecture. As in many polysaccharides the aldehyde is joined to the hydroxyl of the fourth carbon atom, this is likely to be the case here. Whatever this linkage is, it can be broken when the gum is hydrolyzed at 80° with 3% sulfuric acid.

As was pointed out when considering the dibasic acids, there is conclusive evidence that the linkage between the galactose and the uronic acid is through the aldehyde

group of the acid and an hydroxyl of the sugar. Methylation studies will be necessary to prove which atom of the galactose is involved in this union. The structure given in the diagram summarizes the results of this study of the acid occurring in mesquite gum.



Tentative structural formula of the complex organic acid occurring in mesquite gum.

Summary

Mesquite gum is the inorganic salt of an organic acid consisting of four molecules of arabinose, three molecules of galactose and one molecule of methoxyglucuronic acid united with the loss of seven molecules of water. This pure acid was prepared and its composition substantiated by preparation of three degradation products: (1) the calcium salt of methoxyglucuronic acid joined to three molecules of galactose with the loss of three molecules of water, (2) the calcium salt of methoxyglucuronic acid joined to two molecules of galactose with the loss of two molecules of water, (3) the calcium salt of methoxyglucuronic acid joined to one molecule of galactose with the loss of one molecule of water. The composition of Salts 1 and 2 was further verified by oxidizing them and obtaining: (1A) the calcium salt of methoxyglucuronic acid joined to two molecules of galactose and one molecule of galactonic acid with the loss of three molecules of water, (2A) the calcium salt of methoxyglucuronic acid joined to one molecule of galactose and one molecule of galactonic acid with the loss of two molecules of water.

Work is now in progress on the methylation of mesquite gum.

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