[CONTRIBUTION FROM THE WOOD CONVERSION LABORATORY OF THE UNIVERSITY OF IDAHO]

The Constitution of Mesquite Gum. I. The Methanolysis Products of Methylated Mesquite Gum*

BY E. V. WHITE

The gum-like exudation of the mesquite tree, *Prosopis juliflora*, usually referred to as Mesquite Gum, has been described in several early publications.[1a,b,c]

The substance is primarily carbohydrate in character and yields furfural and carbon dioxide when distilled in the usual manner with hydrochloric acid. The proximate analysis given by the early authors shows some variation. Later studies by Anderson and co-workers[2a,b,c,d] are considerably more complete and are directed toward a knowledge of the constitution of the polysaccharide. Anderson and Sands[2c] found that hydrolysis of the gum gave 50.7% *l*-arabinose, 18.7% *d*-galactose and 13% of an aldehyde lactone belonging to the glucuronic acid group. The uronic acid was evaluated later by Anderson and Otis[2d] as a methoxy-glucuronic acid and the approximate position of the methoxyl group indicated. The analytical data obtained by a study of the products resulting from partial to complete hydrolysis of the gum led these authors to propose a tentative structural formula for the substance. In this representation, four arabinose anhydride units, united by straight chain linkage, are joined to a chain of three galactose residues which in turn is linked with 3-methoxy-glucuronic acid. The authors point out that the method of linkage shown is assumed. Unfortunately they believed galactose analysis by the mucic acid method[3] gave low results in the case of mesquite gum and based their formula on a 4:3:1 ratio for the components although the actual data given approximates more closely a 4:2:1 ratio for arabinose, galactose and methoxy-glucuronic acid, respectively.

In order to determine the positions at which the various components of mesquite gum are joined with each other and to finally elucidate the structure of the repeating unit, the methyl ether derivative was subjected to examination. The crude gum was not purified prior to reaction, other than for mechanical separation of deleterious constituents, lest partial hydrolysis of the acid sensitive components occur. A concentrated water solution of the substance was filtered and treated with methyl sulfate and alkali by a well known procedure. After several treatments, the sodium salt of mesquite gum methyl ether was obtained and converted to the free acid derivative. The ether was then subjected to methanolysis using hydrochloric acid as catalyst and resulted in partial esterification of the acid groupings together with simultaneous hydrolysis of the anhydride linkages and methyl glycoside formation. The sirup thus obtained was separated into several fractions and the individual components thereof identified through crystalline derivatives.

In this manner it was found that the uronic acid component of the gum occurs as a terminal residue since 2,3,4-trimethyl-methyl-glucuronoside and its ester were isolated from the methanolysis sirup. The compound was identified both as the crystalline amide and as the saccharolactone methyl ester which was prepared by hydrolysis of the uronoside followed by oxidation of the reducing group and formation of the ester from the corresponding acid derivative.

A portion of the arabinose fraction of the gum also occupies a terminal position and occurs in the furanose configuration since 2,3,5-trimethyl-methyl-arabinoside is a component of the methanolysis sirup. This compound was identified, after separation, by hydrolysis of the pentoside followed by oxidation to the free acid. Treatment of the latter with ammonia furnished the well known amide of 2,3,5-trimethyl-arabonic acid in crystalline form. The remaining portion of the arabinose fraction, also in furanose form, was found to be linked in the polysaccharide by oxygen bridge at the first and second carbon atoms. This particular method of linkage has not been reported previously in the case of arabinose and still further demonstrates the variety of ways whereby monosaccharide units are united in the complex polysaccharides. Methanolysis of mesquite gum methyl ether thus furnished 3,5-dimethyl-methyl-arabinoside. The presence of a free hydroxyl group at the second carbon atom of this molecule was established by formation of a well-defined osazone from the free sugar without loss of methoxyl. The furanose ring structure became apparent when methylation of the pentoside to the fully methylated derivative, followed by hydrolysis, oxidation of the free sugar to the acid and treatment with ammonia gave 2,3,5-trimethyl-arabonic acid amide.

In regard to the galactose fraction of the gum, it was found that all units occur in pyranose configuration and are trebly linked at the first, third, and sixth carbon atoms. This became evident when the crystalline alpha and beta isomers of

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(1) (a) Proctor, *Am. J. Pharm.*, **27**, 224 and 542 (1855); (b) Morfit, *Am. J. Sci.*, **19**, 264 (1855); (c) Forbes, *Arizona Expt. Station Bull.*, **13** (1895).

(2) (a) Anderson, Sands and Sturgis, *Am. J. Pharm.*, **97**, 589 (1925); (b) Anderson and Sands, *Ind. Eng. Chem.*, **17**, 1257 (1925); (c) Anderson and Sands, THIS JOURNAL, **48**, 3172 (1926); (d) Anderson and Otis, *ibid.*, **52**, 4461 (1930).

(3) A. W. van der Haar, "Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsauren," Gebrüder Borntraeger, Berlin, 1920, p. 120.

2,4-dimethyl-methyl-galactoside were separated from the methanolysis sirup and further identified as the corresponding anilide formed by treatment of the free sugar with aniline.

Mesquite gum, therefore, in common with many of the polyuronides, is to be represented by a branched rather than a straight chain structure. The extent of such branching, since it is concerned only with the galactose fraction, can be determined from the molar ratio of the various components. The latter was evaluated by quantitative fractional vacuum distillation of the methanolysis sirup and analysis of the individual fractions for methoxyl content. Calculation based on these results, given in Table II, provides a molar ratio of 1:3:2:1 for trimethyl-methyl-arabinoside, dimethyl-methyl-arabinoside, dimethyl-methyl-galactoside and trimethyl-methyl-glucuronoside. The over-all ratio as applied to the original gum thus becomes 4:2:1 for arabinose, galactose and methoxy-glucuronic acid, respectively, and agrees well with that calculated from the results of Anderson and Otis[2d] based upon entirely different procedures.

The manner in which the various monosaccharide units are united to form the repeating unit of the molecule is not yet known although relatively few possible combinations fulfill the requirements established by the molar ratio given above. Similarly, the exact position occupied by the naturally occurring aliphatic methoxyl group of the glucuronic acid residue has not been determined.

Experimental

Methylation of Mesquite Gum.—One hundred grams of crude mesquite gum was dissolved in 150 cc. of water and filtered to remove bark, seeds, sand, etc. The residue was washed with 50 cc. of water and the combined filtrates methylated at 25° under nitrogen using 300 cc. of methyl sulfate and 600 cc. of 30% sodium hydroxide solution. The reagents were added dropwise and simultaneously with vigorous stirring over a period of three hours. Acetone was added in 20-cc. portions as required to reduce foam and viscosity. After complete neutralization of the methyl sulfate, the reaction mixture was allowed to settle into two phases and the lower layer consisting of the inorganic reaction products was siphoned from the insoluble, partially methylated, sodium salt of mesquite gum. After four similar treatments, methylation of the available aliphatic hydroxyl groups was complete and the sodium salt was dialyzed against water, filtered and evaporated to a sirup under reduced pressure. The free acid was precipitated by adding the sirup in a fine stream to an excess of cold, rapidly stirred, 0.2 *N* sulfuric acid. The precipitate was collected in a basket-head centrifuge, washed free from sulfate ion with water and dissolved while moist in chloroform. Excess water was then removed and after drying over anhydrous magnesium sulfate, the solution was evaporated to a thick sirup. Anhydrous ether was added slowly with stirring and a small quantity of incompletely etherified material was precipitated and removed from the diluted ether solution. Distillation of the ether, finally under reduced pressure, gave a white friable resin; yield 97 g. (found: MeO, 39.3).

Methanolysis of the Free Acid of Mesquite Gum Methyl Ether.—Ninety grams of the free acid of methylated mesquite gum was dissolved in anhydrous pure methanol and diluted with anhydrous methanol–hydrochloric acid solution to give 4% hydrochloric acid in a methanol solution containing 20% of the gum. After reaction in sealed tubes of the Carius type in a rocking furnace maintained at 110° for six hours, excess acidity was neutralized by addition of silver carbonate. The filtered solution was evaporated to a sirup, taken up in anhydrous ether and a small quantity of inorganic and tarry material removed by filtration. Distillation of excess solvent gave a sirupy residue; yield 93 g.

Resolution of the Methanolysis Sirup into Uronosidic and Glycosidic Components.—Ninety-two grams of the methanolysis sirup was dissolved in water and barium hydroxide solution added to make 500 cc. of 0.3 *N* base. The reaction was warmed at 60° for two hours with stirring to hydrolyze the uronoside esters after which excess base was neutralized with carbon dioxide gas. The precipitated barium carbonate was removed by filtration using Norite and Super-Cel and the filtrate evaporated to a sirup under reduced pressure. Residual water was removed by successive distillation with dry chloroform and the sirupy residue taken up in anhydrous pure ether. This solution was added as a fine stream to an excess of rapidly stirred pure ether and the precipitated barium salts removed by filtration. The filtrate was evaporated to a sirup and extracted several times with petroleum ether to remove the pentoside fraction.

Preliminary experiments showed that the petroleum ether insoluble residue contained appreciable quantities of incompletely hydrolyzed material. Therefore, having removed the major portion of the acid sensitive uronosidic and pentoside components as the barium salt and petroleum ether-soluble fractions, respectively, the residue was retreated with methanol–hydrochloric acid solution followed by hydrolysis and extraction as described above. The resulting fractions were combined with those from the first treatment and yielded 25.2 barium salts, 41.6 g. soluble in petroleum ether and 28.5 g. soluble in ether but insoluble in petroleum ether.

Examination of the Barium Salts Separated by Alkaline Hydrolysis of the Methanolysis Sirup.—Twenty-five grams of the barium salts separated by alkaline hydrolysis of the methanolysis sirup were dissolved in water and barium sulfate precipitated by careful addition of a slight excess of 2 *N* sulfuric acid. After filtration, the excess of sulfuric acid was neutralized with lead carbonate and, following removal of lead sulfate, residual lead ion was precipitated with hydrogen sulfide gas. The solution, thus freed from inorganic material, was evaporated under reduced pressure to a sirup and residual water removed by successive distillation with chloroform. The residue was extracted with ether, filtered and evaporated to a sirup; yield 17.7 g. The product was then treated with 200 cc. of 4% anhydrous methanol–hydrogen chloride solution in a sealed tube at 110° for six hours to complete glycosidic hydrolysis and effect a partial esterification of the uronosidic component. After neutralizing excess hydrochloric acid with silver carbonate and filtering, the methyl alcohol was removed by distillation. The residue was taken up in ether, filtered, evaporated to a sirup and distilled fractionally under high vacuum. The results of this separation are given in Table I.

TABLE I

Fraction	B. p., °C. (0.2 mm.)	OMe	Yield, g.	Uronoside equivalent, g.
I	92	58.6	8.0	7.6
II	125	41.7	3.9	
III	165	49.4	6.0	6.0
Total, 2,3,4-trimethyl-methyl-glucuronoside				13.6

Fraction I was shown to be the methyl ester of 2,3,4-trimethyl-methyl-glucuronoside while Fraction II crystallized as 2,4-dimethyl-methyl-galactoside. Fraction III proved to be 2,3,4-trimethyl-methyl-glucuronoside since retreatment with methanol–hydrogen chloride solution as above again yielded the ester together with unchanged acid.

Identification of 2,3,4-Trimethyl-*d*-glucuronic Acid.—The methyl ester of 2,3,4-trimethyl-methyl-*d*-glucuronoside upon treatment with methyl alcoholic ammonia at room temperature furnished the corresponding amide which crystallized in good yield upon removal of solvent. Recrystallization from alcohol–ether gave the amide of 2,3,4-trimethyl-methyl-*d*-glucuronoside; m. p. 183.[4]

Anal. Calcd. for $C_{10}H_{19}O_6N$: OCH_3, 49.8; N, 5.6. Found: OCH_3, 49.9; N, 5.6.

In another experiment the methyl ester (5 g.) was hydrolyzed on a boiling water-bath with 50 cc. of *N* sulfuric acid for twenty-four hours. This treatment apparently removes both the ester and uronosidic methyl groups and the product was isolated as the barium salt after neutralization of the hydrolyzate with barium carbonate followed by filtration and removal of water. The barium salt, thus obtained, was oxidized directly by the alkaline iodine method after Goebel[5] using 100% excess iodine and the saccharic acid, isolated as the lactone (4.2 g.) was esterified by treatment with 100 cc. of 3% methanol–hydrogen chloride at 110° for six hours. The lactone-ester, separated in the usual manner and distilled (b. p. 110°, 0.2 mm.), crystallized spontaneously upon standing. After washing with 1:1:1::alcohol:ether:petroleum ether, recrystallization from alcohol furnished the methyl ester of 2,3,4-trimethyl-*d*-saccharolactone; m. p. 107,[6] specific rotation +55° (25°, *c* 2, methanol, equil.).

Anal. Calcd. for $C_{10}H_{16}O_7$: OCH_3, 50.0. Found: OCH_3, 50.0.

Examination of the Glycosidic Components of the Methanolysis Sirup.—The glycosidic components of the methanolysis sirup were partially separated by fractional distillation under high vacuum wherein the distillation residue from the petroleum ether soluble fraction was added to the ether soluble extract prior to its distillation. The individual fractions were analyzed for methoxyl content and the relative proportions of the various components calculated therefrom. These are shown in Table II together with pertinent data from Table I.

TABLE II

ANALYSIS OF METHANOLYSIS PRODUCTS FROM MESQUITE GUM METHYL ETHER

Fraction	Temp., °C.	Yield, g.	OMe	Arabinoside Tri-Me	Arabinoside Di-Me	Galactoside Di-Me	Uronoside Tri-Me
I	55–60	15.3	55.3	11.6	3.7		
II	60–65	3.6	49.6	0.4	3.2		
III	65–70	3.7	48.0		3.4	0.3	
IV	70–75	14.7	47.3		11.8	2.9	
V	75–80	12.3	46.9		9.3	3.0	
VI	85–100	1.1	45.2		0.5	0.6	
VII	100–125	14.4	42.1			14.4	
Residue		5.2					
				12.0	31.9	21.2	
From Table I						3.9	13.6
Total grams				12.0	31.9	25.1	13.6
Molar ratio found				1.04	2.97	2.02	0.97
Molar ratio calcd.				1.00	3.00	2.00	1.00

The molar ratio of the components calculated from these data indicates that the methanolysis sirup from the free acid of methylated mesquite gum yields trimethyl-methyl arabinoside, dimethyl-methyl-arabinoside, dimethyl-methyl-galactoside and trimethyl-methyl-glucuronoside or its ester in the proportion 1:3:2:1, respectively.

Identification of 2,3,5-Trimethyl-*l*-arabinose.—Fraction I, Table II, gave evidence of consisting chiefly of a trimethyl pentoside apparently present in the furanose form because of its ready hydrolysis in dilute acid solutions. Accordingly, five grams of the material was hydrolyzed with 50 cc. of 0.1 *N* sulfuric acid on a boiling water-bath for eight hours. The free sugar was isolated as a sirup after neutralizing excess acid with barium carbonate, filtering inorganic matter and evaporating excess water. The sirup was extracted with ether, filtered and solvent removed under reduced pressure; yield 4.8 g.

Anal. Calcd. for $C_8H_{16}O_5$: OCH_3, 48.5. Found: OCH_3, 48.0.

The free sugar (4 g.) was oxidized with alkaline iodine using 100% excess iodine and the product recovered in the usual manner as the free acid, lactonized 90° (15 mm.), extracted with anhydrous ether and distilled (95°, 0.2 mm.); yield 3.5 g.

Anal. Calcd. for $C_8H_{14}O_5$: OCH_3, 49.0. Found: OCH_3, 49.0.

Treatment of the lactone with methyl-alcoholic ammonia at room temperature for twenty-four hours furnished a crystalline amide upon removal of solvent. Recrystallization from acetone gave the characteristic amide of 2,3,5-trimethyl-*l*-arabonic acid; m. p. 136°,[7] specific rotation +20° (18°, *c* 2, water).

Anal. Calcd. for $C_8H_{17}O_6N$: OCH_3, 44.9; N, 6.7. Found: OCH_3, 44.9; N, 6.8.

Identification and Structural Proof of 3,5-Dimethyl-*l*-Arabinose.—Examination of Fraction IV, Table II, indicated a readily hydrolyzable constituent and analysis suggested a dimethyl pentoside. Ten grams of the material, hydrolyzed with 100 cc. of 0.1 *N* sulfuric acid on a boiling water-bath for nine hours followed by isolation of the product in the usual manner, provided a reducing sirup which was shown to be 3,5-dimethyl-*l*-arabinose; yield 9.7 g.

Anal. Calcd. for $C_7H_{14}O_5$: OCH_3, 34.8. Found: OCH_3, 34.5.

One gram of the free sugar treated with 2 g. of phenylhydrazine hydrochloride and 3 g. of sodium acetate in 15 cc. of water at 85° for twenty minutes furnished a crystalline substance upon cooling the solution. Filtration followed by recrystallization from alcohol–water yielded a well-defined crystalline osazone in good yield; m. p. 170°.

Anal. Calcd. for $C_9H_{24}O_3N_4$: OCH_3, 17.4; N, 15.7. Found: OCH_3, 16.7; N, 16.1.

Oxidation of the free sugar (3 g.) with alkaline iodine using 100% excess iodine produced the lactone of the corresponding arabonic acid when isolated in the usual manner; yield 2.8 g. Distillation of the sirup under high vacuum (b. p. 118°, 0.2 mm.) resulted in spontaneous crystallization and after recrystallization from ether furnished 3,5-dimethyl-1-arabonolactone; m. p. 78°, specific rotation −43° (25°, *c* 1.5, abs. chloroform).

Anal. Calcd. for $C_7H_{12}O_5$: OCH_3, 35.2. Found: OCH_3, 35.2.

Treatment of the lactone with methyl-alcoholic ammonia gave the corresponding amide upon removal of solvent and recrystallization from acetone furnished 3,5-dimethyl-1-arabonic acid amide, m. p. 145°.

Anal. Calcd. for $C_7H_{15}O_6N$: OCH_3, 32.1; N, 7.3. Found: OCH_3, 32.1; N, 7.2.

The position occupied by the oxygen ring in the original pentoside was investigated by methylation of the glycoside with dimethyl sulfate and alkali to provide the fully methylated derivative. The product was extracted from the reaction mixture with chloroform, evaporated to a sirup, taken up in petroleum ether and distilled; b. p. 58° (0.2 mm.). Five grams of this product was hydrolyzed with 100 cc. of 0.1 *N* sulfuric acid on a boiling water-bath for eight hours and the resulting free sugar isolated in the usual manner. Oxidation of the latter with alkaline iodine using 100% excess iodine furnished the free acid which was isolated in the usual manner as the lactone and distilled; b. p. 95° (0.2 mm.), yield 4.5 g.

Anal. Calcd. for $C_8H_{14}O_5$: OCH_3, 49.0. Found: OCH_3, 49.0.

(4) Smith, *J. Chem. Soc.*, 1732 (1939).

(5) Goebel, *J. Biol. Chem.*, **72**, 809 (1927).

(6) Smith, *J. Chem. Soc.*, 1733 (1939).

(7) Humphreys, Pryde and Waters, *ibid.*, 1298 (1031).

Treatment of the lactone with methyl-alcoholic ammonia at room temperature furnished the crystalline amide of 2,3,5-trimethyl-*l*-arabonic acid in good yield and established the furanose structure of the original pentoside; m. p. 136° (from acetone); specific rotation +20° (18°, *c* 2, water).

Anal. Calcd. for $C_8H_{17}O_5N$: OCH_3, 44.9; N, 6.7. Found: OCH_3, 44.9; N, 6.8.

Identification of 2,4-Dimethyl-*d*-galactose.—Fraction VII, Table II, crystallized spontaneously and was dissolved in methyl alcohol. Partial crystallization took place upon standing and recrystallization from methanol gave β-methyl-2,4-dimethyl-*d*-galactoside; m. p. 165°,[8] specific rotation not measurable (20°, *c* 5, water). The residual sirup freed from methyl alcohol, partially crystallized from acetone solution and after recrystallization from the same solvent furnished α-methyl-2,4-dimethyl-*d*-galactoside; m. p. 105°,[8] specific rotation +145° (20°, *c* 2, water).

Hydrolysis of both isomers, and the residual sirup (2 g.) with 25 cc. of *N* sulfuric acid on a boiling water-bath for ten hours gave 2,4-dimethyl-galactose and this, upon treatment with aniline (1 cc.) in ethanol solution under reflux for three hours, gave the anilide upon removal of solvent. Recrystallization from methanol furnished the anilide of 2,4-dimethyl-*d*-galactose in good yield; m. p. 215°.[9]

Anal. Calcd. for $C_{14}H_{21}O_5N$: OCH_3, 21.9; N, 5.2. Found: OCH_3, 21.9; N, 5.2.

(8) Smith, *J. Chem. Soc.*, 1736 (1939).

(9) Smith, *ibid.*, 1737 (1939).

Summary

1. The methyl ether of mesquite gum has been prepared by treatment of the polysaccharide with dimethyl sulfate and alkali.

2. Methanolysis of mesquite gum methyl ether using methanol–hydrogen chloride yields a sirup which is shown to contain 2,3,5-trimethyl-methyl-arabinoside, 3,5-dimethyl-methyl-arabinoside, 2,4-dimethyl-methyl-galactoside and 2,3,4-trimethyl-methyl-glucuronoside.

3. The ratio of the above components was found to be as 1:3:2:1, respectively. The ratio of arabinose to galactose to methoxy-glucuronic acid in mesquite gum is therefore 4:2:1.

4. From these data it is concluded that one molecule of methoxy-glucuronic acid and one of arabinose occupy terminal positions in the repeating unit of mesquite gum. The remaining units of arabinose are joined by glycosidic linkage at the first and second carbon atoms while the galactose residues are trebly linked at the first, third and six positions.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF UNIVERSAL OIL PRODUCTS COMPANY]

The Mechanism of the Alkylation of Paraffins. II. Alkylation of Isobutane with Propene, 1-Butene and 2-Butene

BY LOUIS SCHMERLING

In connection with the study of the mechanism of the alkylation of isoparaffins with olefins, it became of interest to compare the products obtained by the alkylation of isobutane with 1-butene and with 2-butene. According to the recently proposed alkylation mechanism,[1] these butenes should yield different octanes as the major alkylation products. The literature contains no comparative data on the structure of the isobutane alkylates obtained with pure 1-butene and with pure 2-butene in the presence of aluminum chloride. In the present paper experiments which were carried out to obtain the desired information are described and the results are discussed in the light of the proposed mechanism of the reaction.

The use of anhydrous aluminum chloride as catalyst for the alkylation of isobutane with olefins often results in a complex mixture of products because of the ease with which secondary reactions (especially isomerization, cracking and hydrogen transfer) occur. Formation of by-products in the case of alkylation by propene and butenes may be greatly minimized by carrying out the reaction at −35°.[2] An alternative means of preventing their formation consists in so modifying the catalyst as to decrease its activity for the side reactions without substantially affecting its alkylating activity. A modification which was found to be particularly suitable and which was therefore used in the present investigation consists of the addition complex of equimolecular amounts of aluminum chloride and methanol, $AlCl_3 \cdot CH_3OH$.

Aluminum chloride monomethanolate is a crystalline compound which is stable at temperatures below 70°; at higher temperatures it decomposes, forming hydrogen chloride and methoxy-aluminum dichloride, further heating of which yields methyl chloride and oxyaluminum chloride.[3] It very readily catalyzes the alkylation of benzene, in which it is soluble, and of isobutane, in which it is not. On the other hand, the product of the reaction of aluminum chloride with two molecular proportions of methanol (*i. e.*, $AlCl_3 \cdot 2CH_3OH$) is not an alkylation catalyst.

Tables I and II summarize the results obtained by the alkylation of isobutane with 1-butene and with 2-butene in the presence of aluminum chloride monomethanolate, hydrogen chloride being used as promoter. Data for the alkylations in the presence of aluminum chloride are included for purpose of comparison.

(1) L. Schmerling, THIS JOURNAL, **66**, 1422 (1944); **67**, 1778 (1945).

(2) H. Pines, A. V. Grosse and V. N. Ipatieff, *ibid.*, **64**, 33 (1942).

(3) J. F. Norris and B. M. Sturgis, *ibid.*, **61**, 1413 (1939).