6-Methoxy-1,2,3,4-tetrahydro-1-(ω-acetoxyacetyl)-naphthalene (III).—To 17 cc. of dry benzene containing 7.5 cc. of thionyl chloride and two drops of pyridine, 4.7 g. of 6-methoxy-1,2,3,4-tetrahydro-1-naphthoic acid was added. The mixture was allowed to stand for three hours and was warmed to 60° for two hours, until no further evolution of hydrogen chloride could be detected. The solvent and the excess thionyl chloride were removed *in vacuo*, and the crude acid chloride was distilled, b. p. 118–121.5° (2 mm.). The yield was 3.5 g. (68.4%).

A few drops of the acid chloride was washed from the side-arm of the distilling flask with a little dry benzene. Three drops of aniline was added and the solution was filtered from the aniline hydrochloride which precipitated. The benzene was evaporated and the residue was recrystallized from dilute alcohol, m. p. 127–129°. After several recrystallizations from aqueous ethanol, the **anilide** was obtained as a fine powder, m. p. 130.5–132°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.84; H, 6.81. Found: C, 76.60; H, 6.94.

The purified acid chloride was dissolved in 10 cc. of dry benzene and added dropwise during ten minutes to an ice-cold dry ether solution of diazomethane prepared from 14 g. of nitrosomethylurea. The mixture was allowed to stand for one-half hour in an ice-bath and for one-half hour at room temperature, after which the solvent was removed *in vacuo*. The amorphous residue was dissolved in 7.5 cc. of acetic acid and heated for one-half hour on the steam-cone and allowed to stand overnight. The mixture was dissolved in 50 cc. of ether and was extracted with water and with 5% sodium bicarbonate until all of the acidic material was removed. After drying, the ether was removed *in vacuo* and the residue was distilled using a mercury vapor pump. A clear amber-colored oil, b. p. 142–142.5° (0.1 mm.), $n^{20}D$ 1.5519, was obtained. The material darkened rapidly, even though it was sealed in a glass vial. The analysis was conducted four days after the distillation.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.55. Found: C, 69.62; H, 6.98.

A semicarbazone was prepared in the usual manner for water-insoluble compounds. Several recrystallizations from 50% ethanol gave fine colorless needles, m. p. 158–159°.

Anal. Calcd. for $C_{16}H_{21}O_4N_3$: C, 60.17; H, 6.63; N, 13.16. Found[14]: C, 60.73, 60.54; H, 6.61, 6.74; N, 13.14.

(14) This analysis was conducted by Mr. Howard Clark of the Illinois State Geological Survey.

4-Acetoxy-1-(ω-acetoxyacetyl)-naphthalene (X). (a) From **4-Hydroxy-1-(ω-chloroacetyl)-naphthalene (IX).**—A solution of 1.63 g. of 4-hydroxy-1-(ω-chloroacetyl)-naphthalene and 2.4 g. of freshly-fused potassium acetate in 15 cc. of acetic acid and 20 cc. of acetic anhydride was boiled under reflux for five hours. The warm mixture was diluted with 50 cc. of water and the solvents were partly removed in a stream of air. The solid which separated was removed by filtration and recrystallized from dilute acetic acid, m. p. 114.5–115.5°. It weighed 1.55 g. (73%). Further recrystallization from dilute acetic acid or dilute ethanol gave colorless plates, m. p. 116–117°.

(b) From **4-Acetoxy-1-(ω-bromoacetyl)naphthalene**[11]. —A solution of 0.46 g. of 4-acetoxy-1-(ω-bromoacetyl)-naphthalene and 0.5 g. of freshly-fused potassium acetate in 10 cc. of acetic acid and 10 cc. of acetic anhydride was diluted with 20 cc. of water and the mixture was allowed to stand overnight, after which it was concentrated by evaporation. There was obtained 0.35 g. (81%) of colorless plates, m. p. 116–117°. Recrystallization from dilute acetic acid did not raise the melting point.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 67.33; H, 5.04.

Summary

The preparation of 4- and 6-acetoxy-1-acetoxyacetylnaphthalene has been reported. Neither compound showed any significant activity in prolonging survival of adrenalectomized rats.

6-Methoxy-1-acetoxyacetyl-1,2,3,4-tetrahydronaphthalene was prepared but proved to be an unstable oil.

6-Methoxy-1,2,3,4-tetrahydro-1-naphthoic acid was resistant to catalytic hydrogenation with nickel or platinum catalysis and to reduction by sodium amalgam and methanol in liquid ammonia–ether. The corresponding 6-hydroxy acid suffered loss of the hydroxyl group to yield decahydro-1-naphthoic acid on catalytic hydrogenation with nickel or platinum.

NOTRE DAME, INDIANA RECEIVED APRIL 9, 1947

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

The Constitution of Mesquite Gum. III. Hexamethyl-3-glucuronosido-methyl-galactoside Methyl Ester[1]

BY E. V. WHITE

The structural arrangement of the sugar anhydride units in the simple polysaccharides is determined generally without difficulty since only one monosaccharide type is present and this is united with neighboring units by a repetitive type of glycosidic linkage. On the other hand, the polymolecularity of the complex polysaccharides may present a very difficult problem in structural analysis. These macromolecules often contain uronic acid residues in addition to both pentose and hexose sugars of different ring structure and configuration. The individual units are united with each other by various methods of glycosidic linkage and three dimensional systems are a common occurrence. In general, the problem of structural representation in such instances is greatly simplified by isolation of disaccharide fragments through partial hydrolysis since these can be studied separately and their characteristics determined. The identification of such units always provides positive information as to a substantial portion of the repeating unit and correspondingly reduces the possibility for error in its representation.

The current investigation of mesquite gum from *Prosopis juliflora*[2a,b,c] has shown[3] that arabi-

(1) Presented at the regional meeting of the American Chemical Society, Washington–Idaho Border Section, Moscow–Pullman, May 2–3, 1947.

(2) (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).

(3) White, THIS JOURNAL, **68**, 272 (1946).

nose, galactose and methoxyglucuronic acid occur in the molar ratio of 4:2:1, respectively. The arabofuranose units are joined by glycosidic linkage through their first and second carbon atoms forming a chain terminated by arabofuranose. This is attached apparently to the remainder of the polysaccharide repeating unit at the three position of a galactose anhydride residue.[4] The question now arises as to the point of attachment of the terminal methoxyglucuronic acid unit. The present study was designed to provide this information and was successful because of the resistance of a methylated disaccharide uronic acid ester to alcoholysis of the glycosidic linkage. This was noted previously by Anderson and Otis[5] in connection with their studies on the hydrolysis of mesquite gum.

The free acid of fully methylated mesquite gum was prepared by a previously described method.[3] Treatment of the product with methyl alcoholic hydrogen chloride resulted in esterification and simultaneous fission of the more labile glycosidic linkages forming the corresponding methyl glycosides and uronosides. The latter were separated from the resulting sirup by conversion to the barium salts and extraction of the glycosidic component with ether. Re-esterification of the free acids followed by vacuum fractional distillation gave a heptamethyl disaccharide uronic acid ester which furnished a crystalline amide and formed 2,4-dimethyl-methyl-galactoside and trimethyl-methyl-glucuronoside·methyl ester upon methanolysis. The nature of the uronosidic linkage was established by Purdie methylation of the ester forming the octamethyl derivative which furnished the above uronic acid ester and 2,4,6-trimethyl-methyl-galactoside upon treatment with methanolic hydrogen chloride. It is apparent therefore that the uronic acid component of mesquite gum is attached to the three position of a galactose anhydride residue and the question is immediately raised as to which of the two galactose units known to be present in the repeating unit structure is engaged in this particular linkage. A consideration of the problem recalls those experiments showing that the araban side chain is also attached to the three position of a galactose residue.[4] It would appear therefore that both galactose units bear a side chain located at the third carbon atom. In one case this comprises the terminal methoxyglucuronic acid residue and in the second instance is a chain of four arabofuranose units united glycosidically through the first and second carbon atoms. In order to test the conclusions from these experiments further the fully methylated derivative of partially hydrolyzed mesquite gum[4] was examined. In this instance the new hydroxyl group formed by removal of the labile araban side chain is replaced by methoxyl and methanolysis of the derivative again furnished the heptamethyl disaccharide uronic acid ester described above. The araban side chain therefore cannot be attached to the galactose residue bearing the terminal uronic acid unit. If the above conclusions are valid, as would be indicated from the present evidence, the main chain or backbone structure of mesquite gum must consist of galactose anhydride units united glycosidically with each other through their first and sixth carbon atoms. It must be emphasized however that the above disaccharide uronic acid ester cannot be separated quantitatively by the partial hydrolysis technique and the uncertainties involved in the structural representation of the complex polysaccharides are well recognized. Further experimental investigations are therefore in progress in order to define more completely the structural characteristics of mesquite gum.

(4) White, THIS JOURNAL, **69**, 622 (1947).

(5) Anderson and Otis, *ibid.*, **52**, 4461 (1930).

Experimental

Methanolysis of the Free Acid of Mesquite Gum Methyl Ether.—The methyl ether derivative of mesquite gum was prepared according to a previously described method[3] and isolated as the free acid. One hundred grams of the product was dissolved in 750 cc. of anhydrous methanol containing 4% hydrogen chloride and the solution heated under reflux on a water-bath for five hours. After cooling, excess acid was neutralized by addition of silver carbonate and the precipitate of silver chloride removed by filtering. The solution was evaporated to a sirup, taken up in ether, filtered and evaporated to dryness. A large part of the methylated pentoside components was removed by extraction of the sirup with light petroleum ether. This fraction was distilled, finally under high vacuum and the residue with boiling point greater than 100° combined with the original petroleum ether insoluble portion; yield, 52 g. In an alternative procedure to isolate the disaccharide uronic acid ester directly, the ether soluble extract was exhaustively extracted with hot high-boiling petroleum ether and the resulting sirup, after removal of solvent, fractionally distilled under high vacuum. The final distillate, b. p. 185° (0.2 mm.), distilled as a pale yellow sirup; yield, 10.5 g.

Anal. Calcd. for $C_{19}H_{34}O_{12}$: OCH_3, 48.6. Found: OCH_3, 48.5.

Separation of the Uronosidic Components of the Methanolysis Sirup.—The residual methanolysis sirup, after separation of the methylated pentosides, was dissolved in water and the solution made 0.3 *N* with excess barium hydroxide. After warming at 60° for three hours to saponify the methyl esters, excess alkalinity was neutralized with carbon dioxide gas. The precipitated barium carbonate was removed by filtration and the solution evaporated under reduced pressure to a sirup. Successive distillations with dry chloroform removed the last traces of water and the resulting sirup was carefully triturated with anhydrous ether. After a number of carefully adjusted fractional precipitations using an ether–acetone solvent combination the glycosidic components were separated from the ether insoluble barium salts. The free acids were regenerated therefrom using 2 *N* sulfuric acid in slight excess followed by removal of acidity with lead carbonate and of lead ion with hydrogen sulfide gas. The sirup obtained after removal of water was dissolved in methyl alcohol and esterified with diazomethane in ether solution. After removal of solvent and extraction of the product with ether a sirup was obtained which distilled fractionally under high vacuum, b. p. 185° (0.2 mm.); yield, 7.2 g.

Anal. Calcd. for $C_{19}H_{34}O_{12}$: OCH_3, 48.6. Found: OCH_3, 48.2.

Treatment of the sirup, 2.0 g., with methyl alcoholic

ammonia in the usual manner furnished a crystalline amide, m. p. 194°, recrystallized from acetone.

Anal. Calcd. for $C_{18}H_{33}O_{11}N$: OCH_3, 42.3. Found: OCH_3, 41.9.

Identification and Structure of the Methyl Ester of Hexamethyl-3-glucuronosido-methyl-galactoside.—The above methyl ester separated from the methanolysis sirup either by direct distillation or by the more difficult barium salt method gave evidence of being a methylated disaccharide uronic acid ester. In a separate experiment a portion of the sirup was heated under reflux for twenty-four hours with 2 *N* methanol–hydrogen chloride solution. The products of the reaction were found to be trimethyl-methyl-glucuronoside methyl ester and 2,4-dimethyl-methyl-galactoside together with unchanged starting material. In order to determine the position of the uronosidic linkage it thus became necessary to prepare the fully methylated derivative. Accordingly 10 g. of the sirup was dissolved in 25 cc. of methyl iodide and heated under reflux for twelve hours. Ten grams of silver oxide was added in 5-g. portions during this period. The reaction products were separated in the usual manner and the sirup, remethylated under similar conditions, was finally distilled under high vacuum, b. p. 175° (0.2 mm.), yield, 9.8 g.

Anal. Calcd. for $C_{20}H_{36}O_{12}$: OCH_3, 52.9. Found: OCH_3, 51.1.

Treatment of the sirup with methyl alcoholic ammonia in the usual manner furnished a crystalline amide, m. p. 156°, recrystallized from acetone–petroleum ether.

Anal. Calcd. for $C_{19}H_{35}O_{11}N$: OCH_3, 47.9. Found: OCH_3, 47.2.

The sirup again proved to be very resistant to alcoholysis. Nine and one-half grams of the substance was heated under reflux with 2 *N* methanol–hydrogen chloride for twenty-four hours and the reaction products separated in the usual manner. Distillation of the resulting sirup under high vacuum furnished three fractions. The final distillate, Fraction III, 2.4 g., (b. p. 175°, 0.2 mm.), proved to be unchanged starting material. Fraction I, 4.0 g. (b. p. 92°, 0.2 mm.), and Fraction II, 2.9 g. (b. p. 110°, 0.2 mm.), were combined, dissolved in water and warmed at 60° for three hours in 0.3 *N* barium hydroxide solution. The barium salt of trimethyl-methyl-glucuronoside, thus formed, was separated in the usual manner from the glycosidic component which was finally distilled under reduced pressure, b. p. 95–100° (0.2 mm.), furnishing trimethyl-methyl-galactoside; yield, 2.4 g.

Anal. Calcd. for $C_{10}H_{20}O_6$: OCH_3, 52.5. Found: OCH_3, 52.3.

Hydrolysis of the glycosidic methyl group with *N* sulfuric acid followed by isolation of the free sugar in the usual manner gave a sirup which was distilled under high vacuum, b. p. 110° (0.2 mm.); yield, 2.2 g.

Anal. Calcd. for $C_9H_{18}O_6$: OCH_3, 41.9. Found: OCH_3, 41.9.

One gram of the sirup upon treatment with 0.5 g. of aniline dissolved in 20 cc. of absolute methyl alcohol and heated under reflux for three hours furnished the crystalline anilide of 2,4,6-trimethyl-galactose after removal of the solvent, m. p. 178°,[6] needles recrystallized from alcohol–ether.

Anal. Calcd. for $C_{15}H_{24}O_5N$: OCH_3, 31.4. Found: OCH_3, 31.4.

Examination of Partially Hydrolyzed Mesquite Gum Methyl Ether.—Mesquite gum was treated with dilute sulfuric acid in a previously described manner[4] to remove the labile arabinose component and the resistant residue, methylated by the Haworth method, was isolated as the sodium salt. Fifty grams of the product was dissolved in 100 cc. of methanol and triturated with methanol–hydrochloric acid. The precipitate of sodium chloride was removed and the acid concentration of the filtrate adjusted to 4% in a solution containing 15% gum. After heating under reflux for five hours excess acid was neutralized with silver carbonate. Silver chloride was filtered off and the solution evaporated to a sirup, extracted with ether and re-evaporated. The residue was exhaustively extracted with hot, high-boiling petroleum ether and after removal of solvent the sirup was distilled fractionally under high vacuum. The final distillate, b. p. 180° (0.2 mm.) distilled as a pale yellow sirup; yield 8.0 g.

Anal. Calcd. for $C_{19}H_{34}O_{12}$: OCH_3, 48.6. Found: OCH_3, 48.4.

Treatment of the sirup with methyl alcoholic ammonia in the usual manner furnished the previously described crystalline amide of pentamethyl 1,3-glucuronosido-methyl-galactoside, m. p. 194°.

Anal. Calcd. for $C_{18}H_{33}O_{11}N$: OCH_3, 42.3. Found: OCH_3, 41.8.

Summary

1. A heptamethyl disaccharide uronic acid ester has been isolated from the products of partial hydrolysis of mesquite gum methyl ether.

2. Complete methylation of the ester furnishes the methyl ester of hexamethyl-3-glucuronosido-methyl-galactoside whose structure is proven.

3. The uronic acid component of mesquite gum is attached by glycosidic linkage to the third carbon atom of a galactose residue.

4. Some of the structural characteristics of mesquite gum are discussed.

MOSCOW, IDAHO RECEIVED MAY 1, 1947

(6) Hirst and Jones, *J. Chem. Soc.*, 1487 (1939).