amide purified by recrystallization from acetone; m. p. 93–94°, $[\alpha]^{25}D$ +52° (C = 1% in methanol).

Anal. Calcd. for $C_6H_{13}O_3N$: C, 48.96; H, 8.91; N, 9.52. Found: C, 49.08, 49.16; H, 8.57, 8.59; N, 9.73, 9.65.

Further repeated recrystallizations from acetone or from methanol–ether did not affect either the melting point or the specific rotation.

Racemic Sodium Pantothenate.—**A.**—A mixture of 1.70 g. of racemic sodium α,γ-dihydroxy-β,β-dimethylbutyrate and 0.89 g. of β-alanine[8] was heated to 175°, at which point fusion took place. The fused mass was maintained at 150° for an hour and allowed to cool in a desiccator. The glassy product was assayed by the bacterial growth method; the activity corresponded to a 91% yield of racemic sodium pantothenate.

B.—A mixture of 0.970 g. of the dry sodium salt[3] of β-alanine and 1.28 g. of α,γ-dihydroxy-β,β-dimethylbutyramide was heated with frequent stirring at 100°. The mixture melted and foamed with liberation of ammonia. After three hours, the mixture was cooled and a sample assayed by the bacterial growth method. The result showed a 70% yield of racemic sodium pantothenate.

Sodium *d*-Pantothenate.—**A.**—A solution of 55.5 g. of the sodium salt of alanine and 65 g. of (−)-α-hydroxy-β,β-dimethyl-γ-butyrolactone in 350 cc. of isopropyl alcohol was refluxed for three hours, diluted with an additional 350 cc. of isopropyl alcohol and cooled. The crystalline sodium *d*-pantothenate, which separated slowly, was collected and recrystallized from isopropyl alcohol; $[\alpha]^{25}D$ 27.04° (C = 5%, in water, l = 2 dm.); yield 110 g. or 91%.

(8) Clarke and Behr, "Organic Syntheses," Vol. 16, John Wiley & Sons, Inc., New York, N. Y., p. 1.

It separates in clustered aggregates of parallel fibers. In crude samples, the fibers may be cemented together by an isotropic impurity into flat bundles. The pure salt loses its crystalline character rather sharply at 122–124° and becomes an isotropic glass which decreases in viscosity as the temperature is raised.

Anal. Calcd. for $C_9H_{16}O_5NNa$: N, 5.81; Na, 9.54. Found: N, 5.82, 5.73; Na, 9.32, 9.37.

Absolute ethyl alcohol may be substituted throughout the procedure outlined above but the greater solubility of sodium *d*-pantothenate in ethyl alcohol necessitates reducing the volume to one half, which is disadvantageous in the manipulation of the bulky product.

B.—A mixture of 3.4 g. of sodium (+)-α,γ-dihydroxy-β,β-dimethylbutyrate and 1.78 g. of β-alanine was fused at 180° for fifteen minutes, then cooled quickly. An estimate based upon specific rotation and bacterial growth assay indicated a yield of 61% of sodium *d*-pantothenate. Prolonged heating caused considerable racemization.

Acknowledgments.—The authors wish to express their indebtedness to Dr. L. A. Sweet, Dr. A. D. Emmett and Mr. R. D. Hummel for their interest and coöperation throughout this investigation, and to Mr. A. W. Spang for carrying out the microanalyses.

Summary

Sodium *d*-pantothenate has been obtained in a pure, crystalline form which offers advantages as a standard for this vitamin.

DETROIT, MICH. RECEIVED JULY 5, 1941

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

The Constitution of Arabo-galactan. I. The Components and Position of Linkage*

BY E. V. WHITE

The water-soluble gum of the western larch has been isolated in 12–18% yield[1] by water extraction of larch sawdust. Schorger and Smith[1] named the substance "e galactan" since they were unable to identify any monosaccharide other than galactose in the products of acid hydrolysis although they observed that furfural was obtained upon distillation by the Tollens method. Later investigators[2–5] have shown that the furfural originates from a pentose constituent and have identified *d*-galactose and *l*-arabinose as the products of hydrolysis. The two monosaccharides were found in six to one molecular ratio, and larch gum, re-named "arabo-galactan," was assumed tentatively to be a homogeneous polysaccharide with the empirical formula $[(C_5H_8O_4)(C_6H_{10}O_5)_6]_n$. In later investigations the individuality of the arabo-galactan complex has been questioned and Huseman,[6] from viscosity studies, reported the degree of polymerization of the gum as being between 180 and 280 units. Similarly, Peterson and co-workers[7] fractionated arabo-galactan derivatives and concluded since their preparations were non-homogeneous that in all probability the original arabo-galactan

* Presented before the Division of Cellulose Chemistry at the Detroit Meeting of the American Chemical Society, Sept. 8–13, 1940.

(1) Schorger and Smith, *Ind. Eng. Chem.*, **8**, 494 (1916).
(2) Wise and Peterson, *ibid.*, **22**, 362 (1930).
(3) Wise, Hamer and Peterson, *ibid.*, **25**, 184 (1933).
(4) Peterson, Maugham and Wise, *Cellulose Chem.*, **15**, 109 (1934).
(5) Wise and Unkauf, *ibid.*, **14**, 20 (1933).
(6) Huseman, *J. prakt. Chem.*, **155**, 13 (1940).
(7) Peterson, Barry, Unkauf and Wise, THIS JOURNAL, **62**, 2361 (1940).

was a mixture. This conclusion has been supported recently by Hirst, Jones and Campbell[8] as a result of hydrolysis studies performed upon the methyl ether derivative.

The function of the gum in the metabolism of the larch tree is not known. Apparently it represents a true polyose, although, as Norman[9] points out, it cannot be regarded as a hemicellulose because of its ready solubility in water. From the standpoint of constitution, arabo-galactan is interesting, not only because of its unique role as a polysaccharide but also because of the galactose–arabinose association. This combination is relatively common in the annual plants and the structural similarity of the two monosaccharides has been noted often in connection with possible mechanisms for plant synthesis.[9]

Discussion of Results

In this investigation, arabo-galactan was separated from larch sawdust by the well-known method of water extraction followed by fractional precipitation of the aqueous extract with alcohol. The various fractions were identical in properties and yielded the typical inflected curve of amorphous compounds showing graded solubility in mixed solvents. Re-fractionation of any fraction gave a similar solubility relationship. The product was a white powder, soluble in water, acid and dilute alkali but insoluble in organic solvents. It reduced Fehling solution very slightly, hydrolyzed in mineral acid to the component monosaccharides and yielded furfural by the Tollens method in amount corresponding to 13.9% arabinose. By the usual method of calculation, therefore, one molecular proportion of arabinose is associated with six units of galactose in arabo-galactan.

The reproducibility of the product was demonstrated by conversion to the fully acetylated derivative[10] followed, after purification, by saponification to the original compound. The saponified product gave the same yield of furfural as the original substance, indicating that a fractionation was not effected in the purification of the acetate and also that neither acetylation nor saponification resulted in degradation of the material.

In order to determine the manner in which the various galactose units of arabo-galactan are linked to each other and to the arabinose fraction, the methyl derivative of the polysaccharide was subjected to examination. Methylated arabo-galactan was prepared by treating larch gum with dimethyl sulfate and alkali. The product, upon methanolysis with methyl-alcoholic hydrogen chloride, underwent simultaneous hydrolysis and glycoside formation and yielded quantitatively a mixture of the glycosides of the component sugars. The resulting sirup was separated sharply into petroleum ether-soluble and -insoluble fractions. The latter crystallized yielding the α- and β-methyl glycosides of 2,4-dimethyl-*d*-galactose. The yield of the petroleum ether insoluble fraction corresponded approximately to three molecular proportions of 2,4-dimethyl galactose on the basis of methylated arabo-galactan wherein six units of galactose are associated with one unit of arabinose. A substantial proportion of the galactose units are engaged therefore in oxygen linkage at the three and six positions in the original polysaccharide.

The petroleum ether-soluble fraction of the glycosidic sirup, containing the remaining methyl galactose units and the methylated arabinose fraction failed to crystallize and was distilled. The resulting sirup, on the basis of methoxyl content, contained methyl-trimethyl-galactoside, methyl-tetramethyl-galactoside and methyl-trimethyl-arabinoside in molecular ratio 1:2:1. A satisfactory separation of these components could not be obtained by fractional distillation and an arbitrary division was made, therefore, between the first half (A) and the second half (B) of the distillate.

The first portion (A) upon partial hydrolysis gave a reducing and a non-reducing fraction. The former after oxidation and treatment with methyl-alcoholic ammonia yielded the characteristic crystalline amide of 2,3,5-trimethyl-*l*-arabonic acid and established the terminal linkage of an arabofuranose unit in arabo-galactan. The isolation of this compound in appreciable yield indicates a direct connection to a galactose residue since in the event of a 6:1 galactan-araban complex for larch gum the relatively small proportion of terminal pentose could not be detected by the methods employed. Complete hydrolysis of the non-reducing fraction followed by treatment with aniline gave the anilide of 2,3,4,6-tetramethyl-*d*-galactose. In a separate experiment, wherein the

(8) Hirst, Jones and Campbell, *Nature*, **147**, 25 (1941).

(9) Norman, "The Biochemistry of Cellulose, the Polyuronides and Lignin," Oxford, Clarendon Press, 1937, pp. 74, 190–192.

(10) The yield of furfural obtained upon Tollens distillation of the acetyl derivative was not converted to arabinose since no conversion factor is available for the transformation.

distilled petroleum ether-soluble fraction of the glycosidic sirup was completely hydrolyzed and treated with aniline, the above anilide was obtained in yield corresponding to approximately two molecular proportions of galactose based upon the original larch gum.

The second half (B) of the distillate was completely hydrolyzed and treated with aniline. The anilide of 2,3,4,6-tetramethyl-*d*-galactose crystallized from the solution and upon concentration of the mother liquor a second compound separated which proved to be the anilide of 2,3,4-trimethyl-*d*-galactose. The isolation of this substance was confirmed in a separate experiment wherein the entire glycosidic sirup was fractionally distilled to yield an impure fraction of methyl-trimethyl-galactoside. Upon complete hydrolysis of this portion followed by oxidation and treatment with methyl-alcoholic ammonia, the amide of 2,3,4-trimethyl-*d*-galactonic acid was obtained.

Alcoholysis of arabo-galactan methyl ether yields, therefore, the glycosides of 2,4-dimethyl-*d*-galactose, 2,3,4-trimethyl-*d*-galactose, 2,3,4,6-tetramethyl-*d*-galactose and 2,3,5-trimethyl-*l*-arabinose. It is immediately apparent that both 1–3 and 1–6 oxygen linkages are present in the parent compound and that a substantial proportion of the galactose units are engaged at both the 3 and 6 positions. A branched chain structure is indicated and this is terminated by residues of galactopyranose and arabofuranose. The position of terminal residue union, which may be at the third or sixth carbon atoms of the di-linked galactose residues, is not known and is being investigated.

Experimental

Isolation and Purification of Arabo-galactan.—Larch sawdust, 1000 g. (20–80 mesh, prepared from the butt log of a mature tree), was steeped in 8 liters of distilled water for twenty-four hours at room temperature. The aqueous extract was filtered, clarified by filtration through standard Super-Cel and evaporated under reduced pressure at 60° to a sirup containing approximately 15% total solid. Ethyl alcohol (95%) was added slowly in a fine stream to the rapidly stirred sirup until a 40% alcoholic solution was obtained when a light precipitate of inorganic material, previously held in suspension, was removed. The further addition of alcohol to the clarified extract precipitated arabo-galactan as a sirup and this was substantially complete in 60% alcoholic solution. Alternatively, the 40% alcoholic liquor was placed in the ice-box whereupon arabo-galactan settled out as a viscous sirup. In either case, the supernatant alcoholic solution contained a small quantity of residual arabo-galactan together with certain water–alcohol-soluble glycosidic and tannic constituents of the larch wood.

Solution of the sirup in water followed by a second and third similar treatment removed the last traces of the above impurities and yielded a purified extract of arabo-galactan. The product was isolated by slowly precipitating the extract into excess, rapidly stirred ethyl alcohol followed by filtration of the precipitate which settled out. In an alternative procedure, the extract was precipitated into glacial acetic acid and the product removed by filtration. After washing with fresh precipitant, ether and light petroleum the product was dried yielding a white amorphous powder, readily soluble in water, acid and dilute alkali, but insoluble in organic solvents; yield 112 g.

Anal. Calcd. for $[(C_6H_{10}O_5)_6(C_5H_8O_4)]$: arabinose, 13.6. Found: furfural phloroglucide, 12.1; arabinose equivalent, 13.9.

Acetylation of Arabo-galactan.—Ten grams of arabo-galactan was acetylated by boiling in 50 cc. of acetic anhydride containing 1 g. of fused sodium acetate. The product was isolated in the usual manner and purified by solution in hot ethyl alcohol (95%) followed by decolorization with norite. Upon cooling arabo-galactan acetate separated as a sirup which was dissolved in acetone, precipitated into water, washed and dried; yield 16.2 g.

In an alternative procedure, 5 g. of arabo-galactan concentrated in water solution was precipitated into excess of rapidly stirred glacial acetic acid. The precipitate was washed with fresh acetic acid, settled in the centrifuge and treated with 25 cc. of pyridine. The peptized mixture was transferred to 100-cc. r. b. flask, treated with 10 cc. of acetic anhydride and warmed at 50° until solution was complete. After standing overnight at room temperature the product was isolated in the usual manner, dissolved in fresh pyridine (20 cc.) and acetylated at room temperature for twenty-four hours using 10 cc. of acetic anhydride. The acetate was isolated in the usual manner and purified as in the first method; yield 7.8 g.

Anal. Calcd. for $[(C_6H_{10}O_5)_6(C_5H_8O_4)(C_2H_2O)_{20}]$: $COCH_3$, 44.2. Found: $COCH_3$, 44.2 (either procedure); furfural phloroglucide, 7.9.

Saponification of Arabo-galactan Acetate.—Three grams of arabo-galactan acetate was dissolved in 75 cc. of acetone and titrated slowly with 70 cc. of 0.5 *N* sodium hydroxide. The solution remained clear during addition of the alkali but upon standing a flocculent precipitate settled out. The mixture was titrated with water to maintain a homogeneous solution and after one hour excess ethyl alcohol was added to precipitate the product. The supernatant liquor was decanted and the precipitate dissolved in fresh water. Excess alkalinity was neutralized with mineral acid and alcohol again added in excess. The precipitated product was then isolated as described in the isolation of arabo-galactan; yield 2.1 g.

Anal. Calcd. for $[(C_6H_{10}O_5)_6(C_5H_8O_4)]$: arabinose, 13.6. Found: furfural phloroglucide, 12.2; arabinose equivalent, 14.0.

Methylation of Arabo-galactan.—One hundred grams arabo-galactan, dissolved in 100 cc. water was methylated at 25° under nitrogen using 285 cc. methyl sulfate and 855 cc. of 30% sodium hydroxide. The reagents were added

dropwise and simultaneously with vigorous stirring over a period of five hours. After complete neutralization of the methyl sulfate, the product was freed from salt by dialysis and the liquor concentrated under reduced pressure at 60°. Four methylations were carried out in this manner and the product was extracted finally by shaking the dialyzed concentrated liquor with chloroform. After washing and drying the chloroform extract, an aliquot portion was dropped slowly into excess rapidly stirred light petroleum. The precipitate, upon washing and drying, was a white powder, soluble in water and all solvents except petroleum ether; slightly soluble in ethyl ether. The methylated product could not be separated into fractions and re-methylation did not increase the methoxyl content; yield 93 g.

Anal. Calcd. for $[(C_6H_{10}O_5)_6(C_5H_8O_4)(CH_2)_{20}]$: OCH_3, 44.8. Found: OCH_3, 44.3.

Methanolysis of Arabo-galactan Methyl Ether.—Twenty grams of methylated arabo-galactan was dissolved in 100 cc. of anhydrous pure methanol containing 2% dry hydrogen chloride. After reaction in a sealed tube maintained at 115° for six hours, excess acidity was neutralized by addition of silver carbonate. The filtered solution was decolorized with norite, evaporated to a sirup and taken up in anhydrous ether. A small quantity of tar was removed by filtration and the solution, evaporated to a sirup, was freed from the last trace of ether under vacuum at 60°; yield, 22.1 g.

Anal. Calcd. for $[(C_6H_{10}O_5)_6(C_5H_8O_4)(CH_2)_{20}(HOCH_3)_7]$: OCH_3, 51.8. Found: OCH_3, 50.6.

Separation and Identification of Methyl 2,4-Dimethyl-*d*-galactoside.—One hundred grams of the glycosidic sirup obtained by methanolysis of methylated arabo-galactan partially crystallized from methanol solution and after four days yielded 10 g. of crude crystals. Recrystallization from methanol gave β-methyl 2,4-dimethyl-*d*-galactoside, m. p. 165°,[11] $[\alpha]^{18}$ not measurable (*c* 5, in water).

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

The residual sirup was extracted with hot petroleum ether, leaving an insoluble residue which partially crystallized from acetone solution. After seven days 6 g. of crude crystals was obtained which upon recrystallization from acetone gave α-methyl 2,4-dimethyl-*d*-galactoside, m. p. 105°,[11] $[\alpha]^{18}$ +145° (*c* 2, in water).

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

Hydrolysis of both α- and β-methyl 2,4-dimethyl-*d*-galactoside (2 g.) with *N* sulfuric acid (20 cc.) for twelve hours at 85° gave 2,4-dimethyl-galactose. Upon treatment with aniline (1 cc.) in boiling ethanol for three hours the crystalline anilide of 2,4-dimethyl-galactose was obtained, m. p. 215°.[11]

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

The remaining petroleum ether insoluble sirup analyzed correctly for methyl-dimethyl-galactoside and upon hydrolysis and treatment with aniline gave the same anilide as above α-,β-isomers.

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

In a separate experiment 100 g. of glycosidic sirup gave 46.5 g. of sirup insoluble in hot petroleum equivalent to 3.36 molecular proportions of methyl-dimethyl-galactoside. Upon distillation the sirup crystallized completely as α- and β-methyl 2,4-dimethyl-*d*-galactoside.

Examination of Petroleum Ether-Soluble Fraction of the Glycosidic Sirup.—One hundred grams of the glycosidic sirup obtained by methanolysis of arabo-galactan methyl ether was extracted with hot petroleum ether yielding 53.5 g. of soluble product. The latter failed to crystallize and after distillation under high vacuum (110–130° bath, 0.2 mm.) gave 52.1 g. of colorless oil containing 59.1% OCH_3. This portion contained the arabinose fraction of the glycosidic sirup together with all the galactoside residues except the dimethyl derivatives and, by reason of petroleum ether solubility, these must be at least trimethyl substituted. On the basis of methoxyl content, calculation indicated a mixture of methyl-trimethyl-galactoside, methyl-tetramethyl-galactoside and methyl-trimethyl-arabinoside in molecular ratio 1:2:1. A satisfactory separation of these components could not be obtained by fractional distillation and an arbitrary division was made between the first half (A) and the second half (B) of the slowly re-distilled oil.

Identification of 2,3,5-Trimethyl-*l*-arabinose.—The first fraction (A) of the above distillate was suspected of containing the arabinose portion because of the lower boiling points of the pentose sugars. The glycosides of these monosaccharides furthermore are hydrolyzed more readily by mineral acid than the corresponding hexose derivatives. Accordingly, 20 g. of fraction (A) was hydrolyzed with 150 cc. of 0.1 *N* sulfuric acid for nine hours at 80°. Excess acidity was neutralized with barium carbonate and the solution decolorized with norite, filtered and evaporated under reduced pressure to a sirup. After drying by successive distillations with anhydrous methanol the sirup was extracted with petroleum ether, thereby yielding an insoluble reducing fraction (C), 7.5 g. and a soluble non-reducing portion (D), 9.0 g.

Fraction (C), OCH_3–50.1, was distilled (95°, bath, 0.2 mm.). Four grams of the distillate was oxidized by the alkaline iodine method after Goebel[12] using 100% excess iodine. The product was recovered in the usual manner as the free acid, lactonized at 90° (15 mm.), extracted with ether and distilled (95°, 0.2 mm.); yield 3.3 g.

Anal. Calcd. for $C_8H_{14}O_5$: OCH_3, 49.0. Found: OCH_3, 49.1.

Treatment of the lactone (1.0 g.) with methyl-alcoholic ammonia at 0° for twelve hours yielded the crystalline amide upon removal of the solvent. Recrystallization from acetone gave the characteristic amide of 2,3,5-trimethyl-*l*-arabonic acid; yield 1.0 g., m. p. 136°,[13] $[\alpha]^{18}$ +20° (*c* 2.0, in 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 2,3,4,6-Tetramethyl-*d*-galactose.—The non-reducing fraction (D), 8 g., from the partial hydrolysis of portion (A) was distilled (82°, 0.2 mm.) yielding a colorless oil; yield 7 g.

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

(13) Hymphreys, Pryde and Waters, *J. Chem. Soc.*, 1298 (1931).

Anal. Calcd. for $C_{11}H_{21}O_6$: OCH_3, 62.0. Found: OCH_3, 61.9.

The product (6 g.) was completely hydrolyzed using *N* sulfuric acid (100 cc.) at 85° for fifteen hours. Excess acidity was neutralized with barium carbonate and the solution decolorized with norite, filtered and evaporated under reduced pressure to a sirup. This was dried, extracted with ether and distilled (115–117°, 0.2 mm.), yield 5.0 g.

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

One gram of the sirup, treated with 0.5 cc. of aniline in boiling ethanol for three hours gave a crystalline anilide. Recrystallization from absolute ethanol yielded 2,3,4,6-tetramethyl-*d*-galactose anilide; yield 0.8 g., m. p. 192°,[14] $[\alpha]^{18}$ −80°, changing to +40° (*c* 2.0, in acetone) (equilibrium value).

Anal. Calcd. for $C_{16}H_{25}O_5N$: OCH_3, 39.8; N, 4.50. Found: OCH_3, 39.8; N, 4.49.

Four grams of the sirup, oxidized with alkaline iodine after Goebel[12] using 100% excess iodine, gave 2,3,4,6-tetramethyl-galactonic acid which was isolated in the usual manner as the lactone; yield 3.2 g.

Anal. Calcd. for $C_{10}H_{18}O_6$: OCH_3, 53.0. Found: OCH_3, 52.9.

One gram of the lactone, dissolved in methyl alcohol and treated with methyl-alcoholic ammonia at 0° for fifteen hours gave the amide upon evaporation of the solvent under reduced pressure. Recrystallization from acetone gave the amide of 2,3,4,6-tetramethyl-*d*-galactonic acid; yield 1.0 g., m. p. 122°.[13]

Anal. Calcd. for $C_{10}H_{21}O_6N$: OCH_3, 49.5; N, 5.9. Found: OCH_3, 49.3; N, 6.0.

One gram of the lactone, dissolved in anhydrous ether and treated with an ethereal solution of phenylhydrazine in the usual manner gave a sirup which crystallized. Recrystallization from acetone yielded the phenylhydrazide of 2,3,4,6-tetramethyl-galactonic acid; yield 1.2 g., m. p. 138°.[15]

Anal. Calcd. for $C_{16}H_{26}O_6N_2$: OCH_3, 36.3; N, 8.2. Found: OCH_3, 36.3; N, 8.3.

In a separate experiment an aliquot portion of the distilled petroleum ether-soluble fraction of the glycosidic sirup was hydrolyzed completely using *N* sulfuric acid. The product was isolated in the usual manner and treated with aniline in boiling ethanol for three hours. After removal of the solvent the anilide of 2,3,4,6-tetramethyl-galactose crystallized and upon concentration of the mother liquor a further small yield was obtained. Thus, using 10 g. of starting material 6.1 g. of crude crystals was obtained corresponding on a molecular basis with 1.71 moles of methyl-tetramethyl-galactoside in the total glycosidic sirup.

Identification of 2,3,4-Trimethyl-*d*-galactose.—The second half (B) of the divided petroleum ether-soluble fraction of the glycosidic sirup obtained by methanolysis of methylated arabo-galactan consisted of a mixture of methyl-tetramethyl-galactoside and methyl-trimethyl-galactoside. Accordingly, 20 g. of the oil was completely hydrolyzed using 150 cc. of *N* sulfuric acid at 85° for fifteen hours. The product was isolated in the usual manner and distilled (115–130°, 0.2 mm.) yielding a sirup (15 g.). The latter, 10 g., upon treatment with aniline (5 cc.) in boiling ethanol for three hours followed by evaporation of solvent and extraction with light petroleum, gave a product which crystallized from ether–alcohol. This proved to be the anilide of 2,3,4,6-tetramethyl-galactose, m. p. 192°. Upon evaporation of the mother liquor a second anilide slowly crystallized from ether solution. After recrystallization from ether–alcohol the anilide of 2,3,4-trimethyl-*d*-galactose was obtained; yield 0.7 g., m. p. 162°,[16] $[\alpha]^{18}$ −60° changing to +40° (equilibrium value) (*c* 2.0, in methyl alcohol).

Anal. Calcd. for $C_{15}H_{24}O_5N$: OMe, 31.4; N, 4.7. Found: OMe, 31.4; N, 4.8.

The identification of 2,3,4-trimethyl-galactose was confirmed in a separate experiment wherein the entire glycosidic sirup obtained by methanolysis of methylated arabo-galactan was distilled and fractionated. An impure sirup, (7 g., 115–125°, 0.2 mm.), corresponding in analysis with trimethyl-methyl-galactoside was obtained and this was hydrolyzed competely using 75 cc. of *N* sulfuric acid at 85° for fifteen hours. The product was isolated in the usual manner and fractionally distilled (150° bath, 0.2 mm.) giving a colorless sirup; yield 3 g. The latter, 2.5 g., was oxidized by the alkaline iodine method after Goebel,[12] isolated as the lactone and distilled (150° bath, 0.2 mm.); yield 1.9 g.

The lactone, 0.5 g., when treated with methyl-alcoholic ammonia at 0° for twelve hours gave an amide which crystallized upon removal of the solvent. Recrystallization twice from acetone yielded the amide of 2,3,4-trimethyl-galactonic acid; yield 0.4 g., m. p. 165°,[17] $[\alpha]^{18}$ +30° (*c* 2.0, in water).

Anal. Calcd. for $C_9H_{19}O_6N$: OCH_3, 39.2; N, 5.9. Found: OCH_3, 39.2; N, 5.8.

Acknowledgment.—The author wishes to thank the State Hospital South, Idaho, for the loan of a polarimeter which was used during the latter part of the investigation.

Summary

1. The reproducibility of "arabo-galactan," a water soluble gum present in larch wood, *Larix occidentalis*, is demonstrated.

2. The methyl ether of arabo-galactan upon treatment with methyl-alcoholic hydrogen chloride yields the glycosides of 2,4-dimethyl-*d*-galactose, 2,3,4-trimethyl-*d*-galactose, 2,3,4,6-tetramethyl-*d*-galactose, and 2,3,5-trimethyl-*l*-arabinose.

3. The position of oxygen linkage of the various components of arabo-galactan is established.

MOSCOW, IDAHO RECEIVED APRIL 9, 1941

(14) Hirst and Jones, *J. Chem. Soc.*, 1482 (1939).
(15) Smith, *ibid.*, 1047 (1940).
(16) McCreath and Smith, *ibid.*, 390 (1939).
(17) Smith, *ibid.*, 1735 (1939).