

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF IDAHO]

The Viscosities of Arabogalactan Solutions

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Arabogalactan is a water-soluble polysaccharide present in the Eastern, Western and Siberian varieties of the larch. Trimble¹ in 1898 described a water-soluble material extracted from larch wood, but he reported no quantitative data concerning it. Schorger and Smith² investigated it further and called it ϵ -galactan, believing that the only monosaccharide residue present in the molecule was galactose. Wise and Peterson,³ Wise and Unkauf,⁴ Nikitin and Soloviev,⁵ Barry⁶ and Woodruff⁷ have shown that arabogalactan contains both arabinose and galactose and that the proportion of sugar residues in the molecule is about one to six, respectively.⁸

As much as 17% of arabogalactan has been reported present in the heartwood of the Western larch,² yet little is known of its properties, functions in the tree, or its possible utilization. It seemed desirable to determine some of its physical properties because of this scarcity of information and also because the knowledge obtained could be applied to other problems under way in these Laboratories.

Viscosity measurements were chosen because they offer a means of obtaining some idea of the shape of large molecules in solution, and they may be used to determine the approximate molecular weight of such molecules.

Materials.—The arabogalactan was extracted from shavings taken from the butt of a Western larch tree. A system of counter-current extractions was used in which 400 g. of shavings was placed in a crock with sufficient water to saturate the fibers; then 4 liters of water was added. After four days the extract was poured on a fresh batch of water-soaked shavings while 4 liters of water was added to the extracted shavings. This process was repeated until the initial 4 liters of water had extracted 1600 g. of shavings. The concentrated extract was filtered through a filter bed of filter-aid and charcoal until clear and

colorless, then poured into four volumes of 95% alcohol. After drying the precipitate, a white powder was obtained having an ash content of 0.06% and an anhydrogalactose content of 85% (87.7% of theoretical). The product was dissolved in water, and filtered through fritted glass membranes in order to remove filter paper fibers and particles of dust that could not be removed by filtrations through fine filter paper. It was reprecipitated with alcohol and dried at 105°, before using.

The ether, acetone, dioxane, acetic acid and chloroform were analytical reagent grade. The alcohol was 95% U. S. P., and the chloroform was U. S. P. grade. Isobutyl alcohol, ethylenediamine (69.8%), Butyl Carbitol, Cello-solve and monoethanolamine were commercial solvents supplied by the Carbide and Carbon Chemicals Corp. The amyl acetate was a commercial product supplied by Sharples Solvent Corp. Merck activated charcoal was used for all decolorizations. Pfanzstiel Chemical Co. c. p. *d*-lactose and *d*-galactose were used also.

Methods.—An Ostwald viscometer was used throughout this work. The measurements were made in a thermostat kept within 0.1° of the temperature desired.

Densities were determined with a specific gravity bottle of about 50 ml. capacity, and the weights were corrected to readings in vacuum.

Calibrated volumetric flasks were used in making up solutions, and precautions were taken to have the solutions made up to volume at the temperature to be used for measurements.

The tests for solubility of arabogalactan in various solvents were purely qualitative. One-tenth of a gram of the solid was weighed and shaken with 40 to 60 ml. of the solvent. If the solid did not dissolve, the supernatant liquid was decanted and evaporated to dryness and the residue weighed. The solvent acted upon the solid for twenty-four hours at room temperature with intermittent shaking.

Results.—The viscosity measurements made with arabogalactan solutions at 20, 40, and 60° are plotted in Fig. 1. It will be seen that the viscosities of the solutions are directly proportional to the concentration until about 6% is reached. Viscosities of solutions from 6–10% in concentration showed greater and greater deviations from linearity.

Results at 25° with arabogalactan, galactose and lactose solutions are shown in Fig. 2. The viscosity measurements made by Pulvermacher⁹ with galactose and lactose are shown for comparison.

The density values for arabogalactan solutions at 25° have been converted to the reciprocals (specific volumes) and are plotted in Fig. 3.

(9) Pulvermacher. *Z. anorg. allgem. Chem.*, **113**, 141 (1920).

(1) Trimble. *Am. J. Pharm.*, **70**, 152 (1898).

(2) Schorger and Smith. *Ind. Eng. Chem.*, **8**, 494 (1916).

(3) Wise and Peterson, *ibid.*, **22**, 362 (1930).

(4) Wise and Unkauf. *Cellulosechem.*, **14**, 20 (1933).

(5) Nikitin and Soloviev. *J. Applied Chem. (U. S. S. R.)*, **8**, 1016 (1935); through *Chem. Abst.*, **30**, 5563 (1936).

(6) Barry, Thesis, N. Y. State College of Forestry, 1936.

(7) Woodruff, M.S. Thesis, University of Idaho, 1937, under the direction of Dr. E. C. Jahn, now at Syracuse University.

(8) Barry⁶ disagrees with this ratio and the significance attached to it. On the basis of specific viscosity measurements of the propionyl and benzoyl derivatives of arabogalactan from various sources and because he was able to fractionate these derivatives, he concluded that arabogalactan is a mixture of araban and galactan.

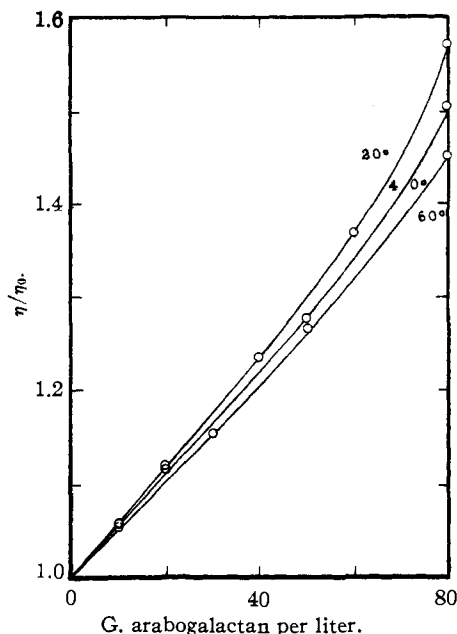


Fig. 1.—Effect of temperature on the relative viscosities of arabogalactan solutions.

By extrapolation to 100% arabogalactan a specific volume is obtained of 0.65 ml. per g.

The tests for solubility indicate that arabogalactan is so difficultly soluble in any of the solvents tried that viscosity measurements were limited to water systems. Arabogalactan was soluble to about a 0.2% solution in carbon tetrachloride,

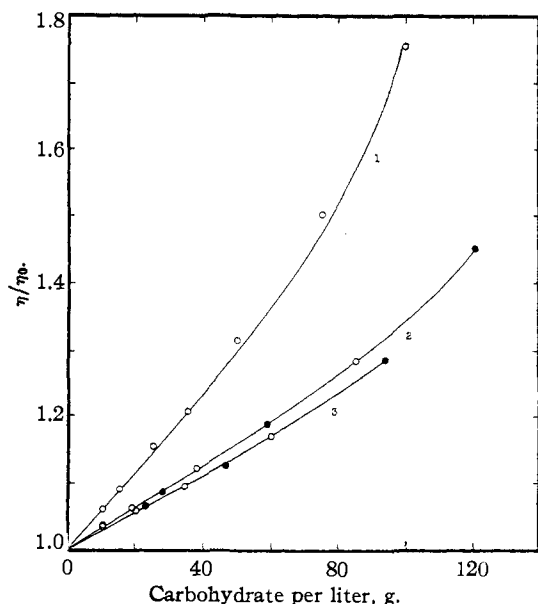


Fig. 2.—Comparison of the relative viscosities of arabogalactan (1), lactose (2), and galactose (3) at 25°; ● Pulvermacher's results.

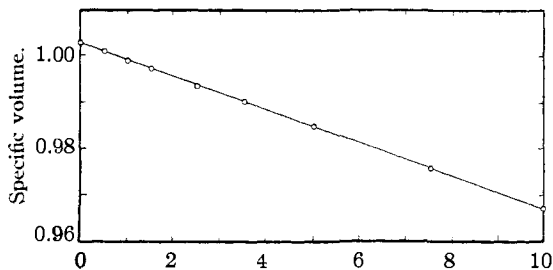


Fig. 3.—Specific volumes of arabogalactan solutions.

ethylenediamine (69.8%) Cellosolve and monoethanolamine. About a 0.1% solution could be formed in Butyl Carbitol. Arabogalactan was insoluble in the other solvents tried.

Discussion

There are several equations available which correlate viscosities and the percentage of the volume of a solution occupied by the dispersed substance. Einstein's¹⁰ equation $\eta/\eta_0 = 1 + 2.5 \phi$ where η is the viscosity of the solution, η_0 is the viscosity of the pure medium, and ϕ is the fraction of the volume occupied by the dispersed substance, is probably the most widely known. Hatschek's¹¹ equation $\eta/\eta_0 = 1 + 4.5 \phi$ has received attention also. A purely empirical equation obtained by Kunitz¹²

$$\eta/\eta_0 = \frac{1 + 0.5 \phi}{(1 - \phi)^4}$$

probably expresses the facts better than either of the theoretical equations.¹³

The viscosity data have been used in calculating values of ϕ by all three equations. The specific volume also has been calculated by dividing ϕ by the percentage concentration of the arabogalactan solution. The values calculated are shown in Table I.

TABLE I
RELATIVE VISCOSITIES AND PARTIAL VOLUMES OBTAINED FROM VARIOUS VISCOSITY EQUATIONS

C, g./l.	η/η_0 at 25°	Kunitz		Einstein		Hatschek	
		ϕ , %	V , ml./g.	ϕ , %	V , ml./g.	ϕ , %	V , ml./g.
20	1.118	2.50	1.25	4.72	2.36	2.62	1.31
40	1.235	4.68	1.17	9.38	2.35	5.21	1.30
60	1.372	6.90	1.15	14.88	2.48	8.25	1.37
80	1.538	9.20	1.15	21.50	2.69	11.95	1.49
100	1.758	12.00	1.20	30.20	3.02	16.80	1.68

The constancy of the values for the specific volume (V) of arabogalactan to a concentration

(10) Einstein, *Ann. Physik*, **19**, 289 (1906); **34**, 59 (1911).

(11) Hatschek, *Kolloid Z.*, **7**, 30 (1910).

(12) Kunitz, *J. Gen. Physiol.*, **9**, 715 (1925-1926).

(13) Gortner, "Outlines of Biochemistry," John Wiley and Sons, N. Y., 1938, p. 54.

of 60 g. per liter, regardless of the equation used, indicates that the molecule must be spherical. For the entire range of concentrations, the Kunitz equation shows greater constancy for the values of V .

Other evidence indicating a preference for the Kunitz equation comes from the density measurements. The specific volume obtained from those measurements is 0.65 ml. per g., and Fig. 1 indicates that the degree of solvation is low; consequently the lowest figures obtained for the specific volume by means of the viscosity equations should be more nearly correct. The values for V from the Kunitz equation are the lowest reported.

Whether or not the difference between the specific volumes obtained by the viscosity and the density methods represents the amount of water solvated by arabogalactan will require confirmation through measurements of the rate of diffusion of arabogalactan.

Staudinger¹⁴ has devised equations expressing the relation of specific viscosity $\eta_{sp} = (\eta/\eta_0 - 1)$ and the molecular weight. One of these equations can be used for this work. It is $\eta_{sp} = K_m CM/B$ where K_m is a constant determined from viscosity measurements with substances of similar natures of known molecular weights; C is the concentration in g. per liter; B is the "base weight," the molecular weight of the simplest repeating unit in the molecule; M is the molecular weight of the complete molecule.

Galactose was used to determine the value of K_m which was found to be 2.7×10^{-3} . The simplest repeating unit in arabogalactan is $[\text{C}_5\text{H}_8\text{O}_4 \cdot (\text{C}_6\text{H}_{10}\text{O}_5)_6]$, which has a base weight of 1104. Substituting these values in the Staudinger formula yields an average molecular weight of 2300 for arabogalactan.

This value agrees very well with that of Nikitin

(14) Staudinger, *Ber.*, **67**, 92 (1934).

and Soloviev,⁵ who obtained 2208 by chemical methods after they had found that cryoscopic methods were not applicable. (Schorger and Smith² report a value of 3286 using cryoscopic methods.) The agreement between the values obtained by Nikitin and Soloviev and the author may or may not be significant. Viscosity measurements of this kind should be made in a medium which will not be solvated by the dissolved material. The search for a solvent having a lower dipole moment than water proved fruitless. However, the greatest source of error in these experiments is the application of the constant, K_m , determined with galactose having a molecular weight of 180. Staudinger and Daumiller¹⁵ working with cellulose triacetates, Fordyce and Hibbert¹⁶ with polyoxyethylene glycols and Kraemer and van Natta¹⁷ with hydroxydecanoic acid derivatives have all shown that the constant, K_m , increases rapidly as the molecular weight of compounds of a homologous series decreases from a value of 2000. K_m is more nearly a true constant with compounds having a molecular weight above 2000. Values for K_m reported in the literature for various types of compounds vary from 0.2 to 2.3×10^{-3} ; consequently one can conclude that the molecular weight of arabogalactan is at least 2208 and may be even higher.

Summary

1. The viscosities of arabogalactan solutions having concentrations of from 1–8% have been measured at 20, 25, 40, and 60°.
2. Arabogalactan was found to have a spherical shape when dissolved in water.
3. The molecular weight of arabogalactan is at least 2208, the simplest formula being $(\text{C}_5\text{H}_8\text{O}_4 \cdot (\text{C}_6\text{H}_{10}\text{O}_5)_6)_2$.

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(15) Staudinger and Daumiller, *Ann.*, **529**, 219 (1937).

(16) Fordyce and Hibbert, *THIS JOURNAL*, **61**, 1912 (1939).

(17) Kraemer and van Natta, *J. Phys. Chem.*, **36**, 3175 (1932).