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Note

New procedure for preparing trimethylsilyl derivatives of polysaccharides

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The trimethylsilyl derivatives of such polyhydroxy compounds as carbohydrates are generally prepared for purposes of their characterization or analysis by gas–liquid chromatography. However, in investigating the preparation of trimethylsilyl derivatives of polysaccharides of high molecular weight, our objective was quite different, as we wished to prepare new, lipid-soluble derivatives of polysaccharides for possible industrial applications.

Prior to the present work, the preparation of trimethylsilyl derivatives of several polysaccharides had been described[1–5]. All of these reports described a silylation reaction conducted under heterogeneous conditions by use of chlorotrimethylsilane[6] in the presence of pyridine. Our experience in this area indicated that these reagents yield, as a by-product, ammonium chloride, which is very difficult to remove from nonvolatile, trimethylsilyl derivatives of high molecular weight, and so the trimethylsilylated polysaccharides reported in the literature[1–5] must have been contaminated by this impurity. Our new procedure precludes the formation of this impurity; furthermore, it involves the use of anhydrous acetone to precipitate the trimethylsilyl derivative of the polysaccharide from the reaction mixture. Previous authors had used methanol, which could cause desilylation of the trimethylsilyl derivative *via trans*-silylation of methanol.

RESULTS AND DISCUSSION

The trimethylsilyl derivatives of alginic acid, cellulose, chitin, dextran I, dextran II, pectin, xylan, and the propylene glycol ester of alginic acid were prepared by using a new silylation procedure, as follows.

The polysaccharide was dissolved in formamide by heating for 1–2 h at 50°. The solution was cooled to room temperature, an excess of hexamethyldisilazane was added, the mixture was heated for 2 h at 70°, and the trimethylsilyl derivative of the polysaccharide was precipitated by pouring the reaction mixture into anhydrous acetone. The solid was filtered off, repeatedly washed with anhydrous acetone, and dried, yielding the product as a colorless, amorphous powder. The infrared (i.r.)

spectra of these derivatives, as Nujol mulls, had characteristic, strong peaks at 1250 and 845 cm^{-1}, due to C–Si stretching vibrations. The degrees of substitution, calculated from analyses for silicon, are given in Table I.

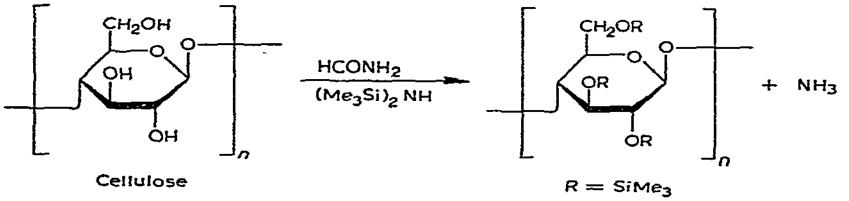

TABLE I

SILICON ANALYSIS AND DEGREE OF SUBSTITUTION (D.S.)

Polysaccharide	*Equiv. wt. of unsubstituted, monomeric residue*	*Si found (%)*	*D.s. (found)*	*D.s. (calc.)*
Cellulose	162	21.92	3.0	3
Dextran II	162	21.96	2.9	3
Dextran I	162	19.15	2.2	3
Propylene glycol ester of alginic acid	234	11.41	1.4	3
Pectin	190	15.73	1.8	2
Alginic acid	176	11.50	1.0	2
Chitin	203	6.19	0.6	2
Xylan	132	7.21	0.6	2

The data given in Table I indicate that complete silylation occurred for cellulose only. In all other cases, various degrees of (incomplete) trimethylsilylation were achieved. The solubility of these derivatives in such organic solvents as benzene, chloroform, and toluene was found to increase with the increase in degree of silylation, the per(trimethylsilyl)ated products being completely soluble in them. The trimethylsilyl groups in these derivatives are readily cleaved by treatment with water at room temperature. The new trimethylsilyl derivatives of polysaccharides reported here are expected to find a variety of industrial applications.

EXPERIMENTAL

Cellulose, chitin, dextran I (mol. wt. 5×10^6–40×10^6), dextran II (mol. wt. 17,700), pectin, and xylan, were purchased from Sigma Chemical Company, St. Louis, Missouri. Generous samples of alginic acid and the propylene glycol ester of alginic acid were given to us by Kelco Company, San Diego, California. A Beckman IR-8 spectrophotometer was used for recording the i.r. spectra. Silicon analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

General procedure for the preparation of trimethylsilyl derivatives of polysaccharides. — A suspension of the polysaccharide (5 g) in formamide (100 ml usually, but see later) was heated at 50° with vigorous stirring (mechanical stirrer); after ~1 h, a clear, viscous solution was usually obtained (but see later). This was allowed to cool to room temperature, and hexamethyldisilazane (100 ml) was slowly added. The mixture was heated for 2 h at 70°, with stirring, cooled to room temperature, and poured into anhydrous acetone (500 ml) with vigorous stirring. The resulting precipitate of the trimethylsilyl derivative was filtered off, washed several times with acetone, and dried for 3 h at 50°/0.1 torr, giving a colorless, amorphous powder. Its i.r. spectrum showed strong peaks at 1250 and 845 cm^{-1}, characteristic of C–Si stretching vibrations. Silicon analyses and the calculated degrees of substitution are given in Table I.

The general procedure described was used for the preparation of trimethylsilyl derivatives of alginic acid, cellulose, dextran II, and the propylene glycol ester of alginic acid. Dissolution of pectin and xylan required 200 ml (instead of 100 ml) of formamide per 5 g of solute. Dextran I and chitin (5 g of either) did not dissolve in 200 ml of formamide; however, these two polysaccharides swelled to a considerable extent when heated with formamide for 5–6 h at 80°.

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