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Note

Degradation and polymerization of methyl α- and β-D-glucopyranoside by piperidine

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Piperidine is known to be a reactive nucleophile in carbohydrate displacement-reactions[1,2] and has been found to cause ring-opening in carbohydrate carbonates[3] It has been observed to react with monosaccharides[4], acetylated monosaccharides[5], and *O*-acetylglycosyl halides[3] to afford the corresponding glycosylamines The glycosylamines initially formed are quite reactive, and undergo further reactions, such as the Amadori rearrangement[6] and dehydration reactions to form furan and pyran derivatives that readily undergo polymerization[7] This complex series of reactions, starting from monosaccharides, proceeding to amines, and ultimately leading to colored, ill-defined, polymeric material is called the nonenzymic, Browning reaction[7] The importance of this reaction lies in the fact that proteins and amino acids present in foodstuffs undergo a similar type of reaction with monosaccharides during roasting and other cooking, and this reaction, at least in part, provides the flavor and color to the foodstuff

We have previously found that a series of polysaccharides from the holocellulose portion of the bark of *Pinus taeda* (loblolly pine) can be removed, and degraded to chloroform-soluble, polymeric products, by extracting with hot piperidine[8]. In an effort to learn more about the reaction of piperidine with nonreducing carbohydrates, we have now studied the reaction of this base with methyl α- and β-D-glucopyranoside.

A mixture of the glucoside, malonic acid catalyst, and piperidine was boiled under reflux for seven days, these conditions are similar to those known to produce glycosyl derivatives of piperidine[6] Gas–liquid chromatographic analysis then indicated that all of the starting material had disappeared Elemental analysis of the chloroform-soluble fraction indicated that a large proportion of the piperidine had

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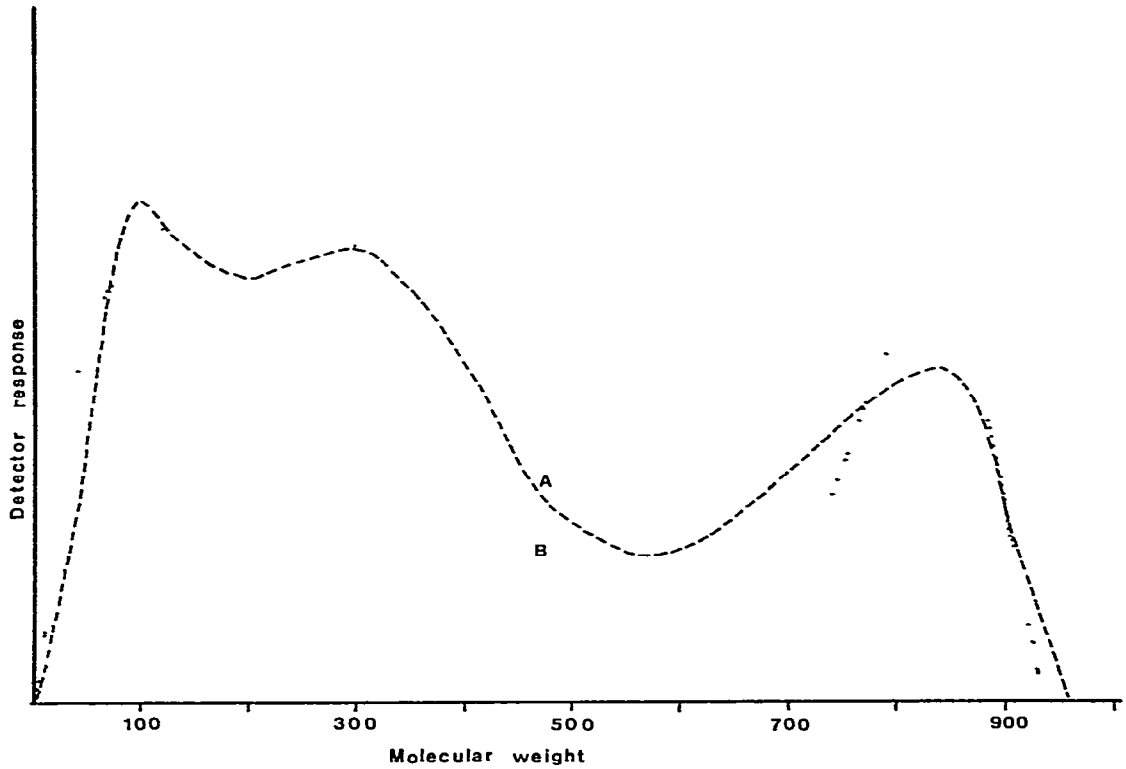

Fig 1 Molecular-weight profile (liquid chromatogram) of polymeric products obtained from the piperidine degradation of (A) methyl α-D-glucopyranoside, and (B) methyl β-D-glucopyranoside The liquid chromatogram was obtained by use of a u v detector and standards of known molecular weight

been incorporated into the degraded glucoside High-pressure, gel-permeation, chromatographic studies revealed that the product had a broad distribution of molecular weight (see Fig 1), extending from 100 to >900 The peak at 900 corresponded to the void volume of the column, and included materials having molecular weights ⩾900 Glycosyl derivatives of piperidine are known to undergo the non-enzymic, Browning reaction, and to afford polymeric materials Therefore, it is reasonable to presume that the same intermediate may be formed between the methyl α- and β-D-glucopyranoside and piperidine by slow displacement of the methoxy aglycon

The displacement of an alkyloxy aglycon (to produce the corresponding glycosylamine) by an aromatic amine has been observed with the labile, glycofuranoside ring-system[9] To the best of our knowledge, this is the first report of the amine displacement of an alkoxy aglycon in a glycopyranoside

EXPERIMENTAL

General — Elemental analyses were performed by the Heterocycle Chemical

Corp , Harrisonville, Missouri Nuclear magnetic resonance spectra were recorded with a Jeolco minimar spectrometer, tetramethylsilane was used as the internal standard Infrared spectra were recorded with a Perkin–Elmer 137 G spectrophotometer Gas–liquid chromatography (g l c) of the compounds was performed, after per(trimethylsilyl)ation with Trisil (Pierce Chemical Company, No 48999), with a Perkin–Elmer Model 900 gas chromatograph equipped with a hydrogen-flame detector. A stainless-steel column (182 9 cm × 3 16 mm o d) packed with 5% of SE-30 on Chromosorb W, with a program of temperatures of 100–200° (8°/min) and a helium flow-rate of 35 ml/min was used for all g l c analyses Liquid chromatography (l c) was performed with a Waters Associates, Inc , Model 202–401 liquid chromatograph equipped with an ultraviolet detector A stainless-steel column (121 9 cm × 9 48 mm o d), packed with Poragel (60 A, Waters Associates, No 26900), and eluted with chloroform at the rate of 0 9 ml/min, was used for all determinations of molecular weight by l c α-D-Glucopyranose pentaacetate, α-cellobiose octaacetate, and poly(propylene glycol) (Water Associates, No 41994) were used as standards for calibration of molecular weights

Degradation of methyl α-D-*glucopyranoside by piperidine* — A solution of anhydrous methyl α-D-glucopyranoside (3 0 g, 15 4 mmol) and malonic acid (2 0 g, 19 2 mmol) in piperidine (40 ml) was boiled under reflux for 7 d The excess of piperidine was evaporated *in vacuo*, and the residue was dried for 24 h in a vacuum oven at 50° G l c analysis of the product then showed no evidence of the glucopyranoside starting-material[10] A solution of the residue in chloroform was washed twice with 5% aqueous sodium hydroxide and several times with water, dried (anhydrous magnesium sulfate), and evaporated *in vacuo* The resulting dark-brown syrup was dried overnight in a vacuum oven at 50°, to yield 1 42 g of a dark-brown liquid, ν_{max}^{film} 3330, 2860, and 1630 cm^{-1}, n m r data ($CDCl_3$) singlets at δ 1 64, 2 05, and 3 42

Anal. Found C, 63 57, H, 10 39, N, 10 57

Degradation of methyl β-D-*glucopyranoside by piperidine* — Anhydrous methyl β-D-glucopyranoside (3 0 g, 15 4 mmol) was degraded with piperidine by the procedure described for methyl α-D-glucopyranoside The yield of dark-brown liquid was 1 31 g, ν_{max}^{film} 3340, 2860, and 1630 cm^{-1}, n m r data ($CDCl_3$) singlets at δ 1 62, 2 04, and 3 43

Anal Found C, 63 91, H, 11 01, N, 10 36

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