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Note

Pyrolytic production of 1,6-anhydro-β-D-mannopyranose

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Pyrolytic depolymerization of natural polysaccharides is a useful method for preparation of anhydro sugars, because it employs inexpensive starting-materials and constitutes a rapid, one-step synthesis. High-temperature reactions of carbohydrates are, however, not specific, and the desired intramolecular-transglycosylation reactions which produce the anhydro sugars compete with dehydration, elimination, condensation, and charring reactions that lead to a wide variety of products[1–3]. It appears that pyrolysis often provides low yields of anhydro sugars due to catalysis of the latter reactions by impurities in the starting material[4].

Ivory-nut meal, from the nut of a South American palm tree (*Phytelephas macrocarpa*), is more than 50% (by weight) mannan, and is essentially a linear polymer of β-D-(1→4)-linked D-mannopyranosyl residues[5]. At one time, this material was used in the manufacture of shirt buttons, and is now mainly employed as an ingredient in abrasive polishes[5]. Pyrolysis of ivory-nut meal was shown by Hudson and co-workers[6] to yield 1,6-anhydro-β-D-mannopyranose (**1**), which was isolated as its 2,3-*O*-isopropylidene derivative (**2**) in 8.3% yield. By using trimethylsilylation–g.l.c. analysis, Gardiner[7] demonstrated that a 15.6% yield of **1** was present in an ivory-nut meal pyrolyzate. Generally, however, yields isolated are 5% or less[8], and are sufficiently irreproducible that Schuerch and co-workers[9,10] developed, and favored, a purely synthetic approach involving six steps proceeding from methyl α-D-mannopyranoside to the tribenzyl ether of **1**.

This situation is very similar to that encountered in the pyrolysis of generally available lignocellulosic materials, which provide very little levoglucosan (**3**; 1,6-anhydro-β-D-glucopyranose). It was recently found in this laboratory[11] that this problem could be solved by pretreatment of the substrate with acid, so that a good yield of levoglucosan could be obtained, even from sawdust. With the latter, the yield could be improved by a factor of ~10. In this article, we describe the results obtained by similar treatment of ivory-nut meal.

After complete hydrolysis of a sample of ivory-nut meal, trimethylsilylation–g.l.c. analysis of the resulting monosaccharides indicated 52% of anhydromannose(s)

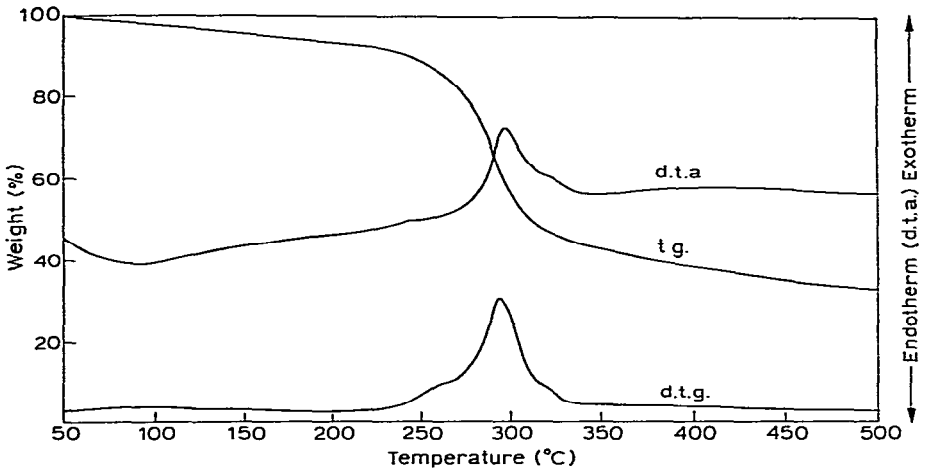

Fig. 1. Thermal analysis of untreated ivory-nut meal under nitrogen. [Thermogravimetry (t.g.), derivative thermogravimetry (d.t.g.), and differential thermal analysis (d.t.a.).]

TABLE I

PYROLYTIC PRODUCTION[a] OF 1,6-ANHYDRO-β-D-MANNOPYRANOSE (1), 1,6-ANHYDRO-β-D-MANNOFURANOSE (5), AND 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (3) FROM IVORY-NUT MEAL

Pretreatment	*No. of water washes*	*Yield[b] (%)*						*Compound* 1 *in tar (%)*
		Char	*Tar*	1	3	5	*Ash*	
Untreated	0	32	20	5	0.5	0.4	1.29	25
M HCl, 15 h, 20°	1	30	41	16	1.8	1.2		39
	2	26	43	21	2.0	1.5		49
	3	26	43	21	2.0	1.3		49
0.5M HCl, 8 h, 20°	3	27	47	22	2.1	1.4		46
M HCl, 20 min, 60°	3	29	40	17	1.8	1.2		42
M HCl, 10 min, boiling	3	22	49	27	3.0	1.9	0.12	55
Conc. HCl, 3 min, boiling	3	27	49	15	7.0	1.0		31

[a]Pyrolysis of 1-g samples at 1.5 torr in an oven preheated to 370°. [b]Based on dry weight of nut-meal.

and 13% of anhydroglucose. Under the hydrolysis conditions, the sugars would be expected to be slightly degraded[12]; these figures are, thus, lower limits. An insoluble residue (6%; Klason lignin) remained after hydrolysis. The rest (~29% of the weight of nut-meal) still remains undetermined.

Thermal analysis of untreated ivory-nut meal (see Fig. 1) revealed a weight loss, starting at ~230° and peaking at 294°, which remained exothermic at all stages; a residue (33%) remained at 500°. This type of pyrolytic behavior is generally observed when the dehydration and charring reactions predominate over the transglycosylation reactions and the volatilization of the depolymerization products[2]. This conclusion was verified by vacuum pyrolysis of the untreated nut-meal on a 1-g scale at 370°,

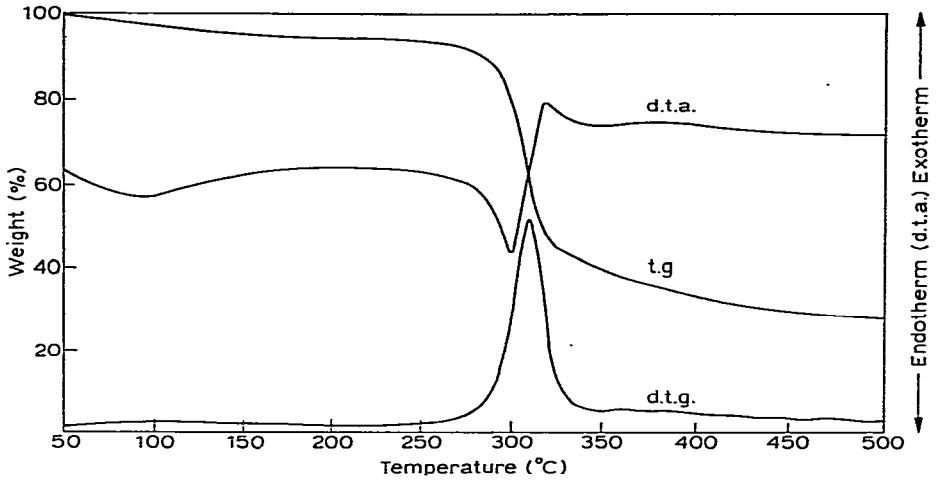

Fig. 2. Thermal analysis, under nitrogen, of ivory-nut meal after washing in boiling M HCl for 10 min.

and analysis of the pyrolyzate by trimethylsilylation–g.l.c. (see Table I). The results indicated that **1** was produced in only 5% yield, and constituted 25% of the tarry pyrolyzate. The untreated nut-meal contained considerable inorganic impurities, as shown by its ash content (1.29%), which could account for the thermal properties observed.

The ivory-nut meal was subjected to a variety of pretreatments with hydrochloric acid (see Table I) in attempts to improve the yield of **1**. Boiling with M hydrochloric acid for 10 min, followed by thorough washing with distilled water (which lowered the ash content from 1.29 to 0.12%), was the most successful treatment. Thermal analysis of this material (see Fig. 2) revealed a pattern entirely different from that depicted in Fig. 1. The weight loss, starting at ~270° and peaking at 310°, was associated with an initial endotherm peaking at 298° and a subsequent exotherm peaking at 318°. The elevated pyrolysis temperature, the appearance of the sharp endotherm, and the lessened residue (27%) at 500°, reflect a shift from the dehydration and charring reactions to the transglycosylation reactions and volatilization of the products. Vacuum pyrolysis provided a 27% yield of **1**, which constituted 55% of the tarry pyrolyzate. Thus, the acid pretreatment resulted in a greater than 5-fold increase in the yield of **1**, and more than doubled the concentration of this product in the tar.

Washing pretreatments at lower temperatures (20 and 60°) were slightly less effective, although acceptable pyrolytic yields of **1** (17–22%) were obtained. These treatments caused less degradation of the ivory-nut mannan than boiling with M hydrochloric acid (that gave ~80% recovery of washed nut-meal); rinsing with water, however, accounts for ~50% of the losses, and, as the nut-meal was abundantly available, the boiling treatment was preferred. A more vigorous treatment, with boiling, concentrated hydrochloric acid, resulted in extensive degradation of the D-mannan; interestingly, the resulting substrate gave a relatively high yield of levo-

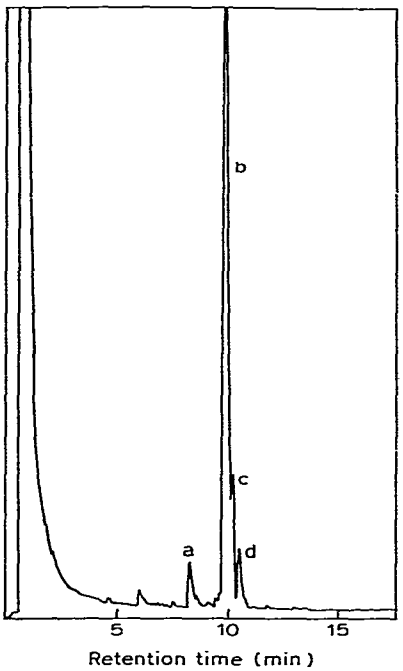

Fig. 3. G.l.c. of trimethylsilylated tar. [a, 1,5-Anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**4**); b, 1,6-anhydro-β-D-mannopyranose (**1**); c, 1,6-anhydro-β-D-glucopyranose (**3**); and d, 1,6-anhydro-β-D-mannofuranose (**5**).]

glucosan (**3**), indicating that the D-glucosyl residues in the nut-meal are less readily hydrolyzed than the D-mannosyl residues.

The g.l.c. analyses of the pyrolyzates revealed, in addition to **1**, small proportions of **3**, 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**4**), and a component presumed to be 1,6-anhydro-β-D-mannofuranose (**5**) (see Fig. 3). The last two compounds have been isolated from cellulose[4] and D-mannose[13] pyrolyzates, respectively. Compound **3** is evidently formed from the D-glucose content of the nut-meal, whereas **4** can be produced from both the D-mannosyl and D-glucosyl residues.

The necessity of washing out all traces of acid from the nut-meal was demonstrated by pyrolyzing substrates rinsed once, twice, and three times. The once-washed material gave more char, and less tar and[14] **1**, than the twice- and thrice-washed samples. It should be pointed out that, although inorganic impurities are known to have a detrimental effect on the yield of anhydro sugars, the possibility that the acid treatment produces other effects (besides the removal of the inorganic materials) cannot be overlooked. No general trend could be observed between the thermal-analysis data and the pyrolytic yield of **1**; all of the acid-washed and thoroughly rinsed samples gave thermal analyses very similar to that shown in Fig. 2.

Laboratory-scale preparation of **1** was, therefore, conducted using ivory-nut meal that had been washed with boiling, M hydrochloric acid. Ivory-nut meal proved to be an ideal pyrolysis substrate, because it is dense and does not melt or froth

during pyrolysis. Removal of chloroform-extractable impurities (6%) and some acetone-precipitated, polymeric material (2%) left a tar (32%) that contained **1** (20% yield, based on dry weight of ivory-nut meal) in 64% concentration. Treatment of an acetone solution of the tar with anhydrous copper(II) sulfate gave the 2,3-isopropylidene acetals **2** (of **1**) and **6** (of **5**), which could then be extracted into chloroform, while leaving the unsubstituted **3** and **4** in the aqueous phase. Recrystallization of the crude extract from 2-propanol led to the isolation of **2** in 17% yield from ivory-nut meal (~32% based on an ~52% content of D-mannan).

1,6-Anhydro-β-D-mannopyranose (**1**) was readily prepared by hydrolysis of **2** in 0.05M sulfuric acid solution at room temperature as previously reported[6]. The 17% yield of **2** is a two-fold increase over any pyrolytic preparation previously reported; the improvement resulted primarily from the application of acid pretreatment of the substrate, but faster removal of the pyrolysis products from the heated zone in the tube furnace that was employed could also have been a contributing factor. These improvements re-establish the value of pyrolysis as a reliable method for the preparation of **1**.

It is interesting that, as described in previous publications from this laboratory[15–19], on heating, 1,6-anhydroaldohexoses show a plastic phase-transition accompanied by a major change in entropy before melting at a higher temperature with only a minor change in entropy. The solid-state transition and melting of 1,6-anhydro-β-D-mannopyranose was observed at 91 and 208°, accompanied by ΔS values of 50.2 and 7.5 J·mol·deg.$^{-1}$, respectively[16]. Thermal analysis of the product obtained in this experiment, however, showed only the minor change in entropy at 208°, indicating that it must have crystallized directly in the plastic phase.

EXPERIMENTAL

General methods. — Thermal analysis was conducted at 15°/min under a flow of nitrogen of 75 mL.min^{-1}, on 5-mg samples in loosely covered aluminum pans, using the apparatus reported previously[20]. Moisture contents were determined by oven-drying samples for 45 min at 120–125°. Pyrolyses were conducted in a tube-furnace apparatus as described[21]. Ash contents were determined by Galbraith Laboratories, Tennessee, with a final ashing temperature of 700°.

Hydrolysis of ivory-nut meal. — Hydrolysis was conducted as described for wood samples[12], employing 77% sulfuric acid to dissolve most of the sample, and then diluting to 3% with water and heating under reflux for 8 h. Samples were mixed with inositol (internal standard), made neutral with a basic resin, and analyzed by trimethylsilylation–g.l.c. as described for D-glucose[11].

Acid-washed substrates. — Ivory-nut meal was ground in a Wiley mill to pass through a 1-mm screen, and material of mesh <40 was sifted out. The remaining, coarse grains were then stirred with aqueous hydrochloric acid at the temperatures and for the times shown in Table I, and the meal was filtered from the aqueous acid by using a Büchner funnel without paper or suction. The grains of meal were largely

retained in the funnel, and were rinsed with several liters of distilled water ("once washed"). The second and third rinsings consisted in stirring the meal with distilled water for ~1 h, and then filtering, and washing in the Büchner funnel with more water. The meal was air-dried, and typically contained 4–10% of moisture.

1,6-Anhydro-2,3-O-isopropylidene-β-D-mannopyranose (**2**). — Ivory-nut meal (285 g, 7.0% content of moisture) was pyrolyzed in three batches at 5–10 torr in a tube furnace preheated to ~400°. The crude pyrolyzate, which was collected in a water-cooled condenser, was dissolved in warm water (800 mL) and the solution extracted with chloroform (4 × 300 mL). The extracts were combined, and evaporated to a black syrup (15.1 g, 6%) which was not further investigated. The aqueous phase was heated briefly with activated charcoal, filtered, and the filtrate evaporated to dryness. The residue was brought into solution by addition of an equal amount of acetone, and the solution was diluted to ~700 mL with acetone, at which stage a black syrup was precipitated. After being kept for several hours, the solution was decanted, and evaporated to an orange syrup (72.0 g, 27%). The black syrup precipitated was further processed by dissolving in methanol (100 mL) and pouring in a thin stream into acetone (400 mL); the resulting solution was filtered from a small, black precipitate (4.4 g), and the filtrate was evaporated to an orange syrup (13.4 g, 5%).

The syrups were combined, thoroughly dried at 60°/0.3 torr, dissolved in dry acetone (700 mL), and stirred with anhydrous copper(II) sulfate (400 g). The progress of the reaction was monitored by trimethylsilylation–g.l.c. analysis, which indicated that the concentration of **1** in the tar had been 64%, and that, after three days, the reaction was essentially complete. The copper sulfate was then removed by filtration, and washed with acetone (4 × 600 mL). The filtrates were combined, and evaporated to a crystalline mass which was partitioned between chloroform (500 mL) and water (250 mL); the aqueous phase was further extracted with chloroform (4 × 500 mL). The extracts were evaporated to a crystalline mass (67.7 g), shown by trimethylsilylation–g.l.c. analysis to be a 27:1 mixture of **2** and a component assumed to be 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannofuranose (**6**), retention times 7.3 and 8.0 min, respectively. Recrystallization from 2-propanol gave pure **2** as white needles in two crops (56.9 g, 17%). Recrystallized from the same solvent, it had m.p. 157–160°, $[\alpha]_D$ −58° (*c* 2.3, water) {lit.[6] m.p. 161–162°, $[\alpha]_D^{20}$ −58.8° (*c* 2.08, water)}.

1,6-Anhydro-β-D-mannopyranose (**1**). — The 2,3-*O*-isopropylidene derivative **2** (2.0 g) was dissolved in 0.05M sulfuric acid (35 mL), and the solution was allowed to stand for 12 h at room temperature. The solution was made neutral with a basic resin, and filtered, and the filtrate was evaporated to a syrup which was dried *in vacuo*. Compound **1** (0.80 g, 50%) crystallized from a solution of this syrup in ethyl acetate at −20°. Recrystallized from ethanol, it had m.p. 208–210° (uncorr.), $[\alpha]_D$ −127.4° (*c* 1.0, water) {lit.[6] m.p. 210–211°, $[\alpha]_D^{20}$ −127.6° (*c* 1.5, water)}.

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