

ANALYSIS OF SUGARS DERIVED FROM THE HYDROLYSATES OF WOOD PULP, SHOULDER MATERIAL AND UNFRACTIONATED CELLULOSE TRIACETATE BY PAPER PARTITION CHROMATOGRAPHY – PART I

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Commercial cellulose triacetate samples derived from wood pulp have shown a separate peak or shoulder on the high molecular weight side of the GPC distribution curve. Material isolated from this region by fractional precipitation was found to be highly enriched in mannose and xylose, attributed to the presence of a hemicellulose derivative. Cellulose triacetate from cotton linters did not show this behaviour.

The wood pulp and shoulder material after acid hydrolysis were analysed by paper partition chromatography against known calibration standards of glucose, mannose and xylose. Both wood pulp and shoulder material were found to contain mannose and xylose, resulting from the presence of hemicellulose derivative.

INTRODUCTION

Paper partition chromatography (PPC) has been widely applied to the identification and estimation of various constituents in fruit juices. Lewis *et al* [1] identified sugars present in the Java plum. Sugars in some fruits were identified by Srivastava [2]. One of us (FM) has made extensive studies on the identification of sugars in juices of 18 fruits by paper chromatography [3].

This paper describes the use of PPC for the qualitative identification of component sugars present in the hydrolytes of wood pulp, shoulder material [4] and unfractionated cellulose triacetate samples.

The commercial importance of cellulose derivatives for a variety of purposes naturally derives from cellulose itself. Cellulose as a naturally occurring high polymer has been used for years in timbers, textiles and paper. The high cellulose content, i.e. 97 to 99%, is found in cotton, ramie and flax, [5] whereas the cellulose content of wood species [6] amounts to 41-53%. In Europe and the United States, wood pulp is primarily used for the manufacture of paper and commercially important cellulose derivatives. These include nitrates, acetates and butyrates.

British Celanese (Courtauld's Ltd.) employ wood pulp for the manufacture of both primary and secondary cellulose acetates, which are mainly used for the production of acetate

yarns, photographic films, magnetic sound recording tapes, transparent and pigmented sheets, insulating cables and cigarette filters.

Wood pulp is subjected to repeated chemical treatment in aqueous sodium hydroxide solution in order to isolate hemicellulose and other non-cellulosic materials.

Gel permeation chromatography (GPC) has established [4] the presence of hemicellulose in commercial cellulose triacetates as a small peak or shoulder on the high D_p side of GPC distribution curve. The shoulder material (hemicellulose) was isolated by both fractional precipitation and preparative GPC. Segal [7], Brewer *et al* [8] and Brookshaw *et al* [9] have also reported similar results for wood pulp-based cellulose derivatives.

A number of solvents were used for the development of the chromatogram but n-butanol: acetic acid (glacial): water (4:1:5 V/V) gave better resolution of the various sugars present in the hydrolysates in question.

The presence of glucose, mannose and xylose was established by comparing the R_f -values* of the unknown sugars to those of the synthetic known sugars mixture.

* R_f = value is defined as:

$$R_f = \frac{\text{distance moved by the substance}}{\text{distance moved by the solvent front}}$$

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EXPERIMENTAL

Materials. All chemicals and solvents used in this study were analytical grade materials.

Solvent. n-Butanol: acetic acid (glacial): water (4:1:5 V/V).

Paper. Whatman paper No. 1 (0.16 mm thick).

Spray Reagent Silver nitrate in acetone/0.50 mol/lit alcoholic sodium hydroxide.

Sample Application Device: Micropipette.

Acid hydrolysis of wood pulp, shoulder material and unfractionated cellulose triacetate. One g. of wood pulp was dissolved in 100 ml of 72% (V/V) sulphuric acid and the dark solution was left for one week at room temperature with frequent shaking. The acid solution was diluted to one litre with distilled water and boiled under reflux for 16 hr. using a heating mantle. The filtered solution was neutralized to litmus paper with barium carbonate and the white precipitate of barium sulphate was moved by filtration. The filtrate, which was still slightly turbid, was finally centrifuged for 15 min. at 6000 r.p.m. Since alkalinity develops during solution concentration, the solution was made slightly acidic using 0.10 mol/lit sulphuric acid. The residue from distillation was extracted with AnalR methanol under reflux and the lightly coloured solution was decolourized with 200 mg charcoal. The clear alcoholic extract was evaporated under vacuum (12 mm Hg) at low temperature and the residue which looked like brown sugar, used for subsequent analysis.

The shoulder material [4] was hydrolysed following the above procedure with a slight modification as stated below.

The sample was first refluxed with concentrated ammonia (sp. gr. 0.91 (25% NH₃)) for 2 hr. until the product was insoluble in both acetone and dichloromethane. It was washed thoroughly with six 25 ml portions of distilled water, dried under vacuum (at 80-90°C) for 30 min. and then hydrolysed in the same way as above.

The unfractionated cellulose triacetate sample was hydrolysed by the same procedure described above for the shoulder material.

Analysis of hydrolysates of wood pulp, shoulder material and unfractionated cellulose triacetate by paper chromatography. A 1% (m/V) solution of all the unknown samples was prepared separately using methanol as solvent and were then applied individually to previously marked spots on a Whatman paper No. 1, having 0.16 mm thickness. Similarly, a 0.5% (m/V) mixture of the reference sugars having glucose, mannose and xylose as well as the individual

pure sugars in methanol were also applied to the same paper for comparison as shown in Fig. 1. n-Butanol: acetic acid (glacial): water (4:1:5 V/V) was used as a solvent system for

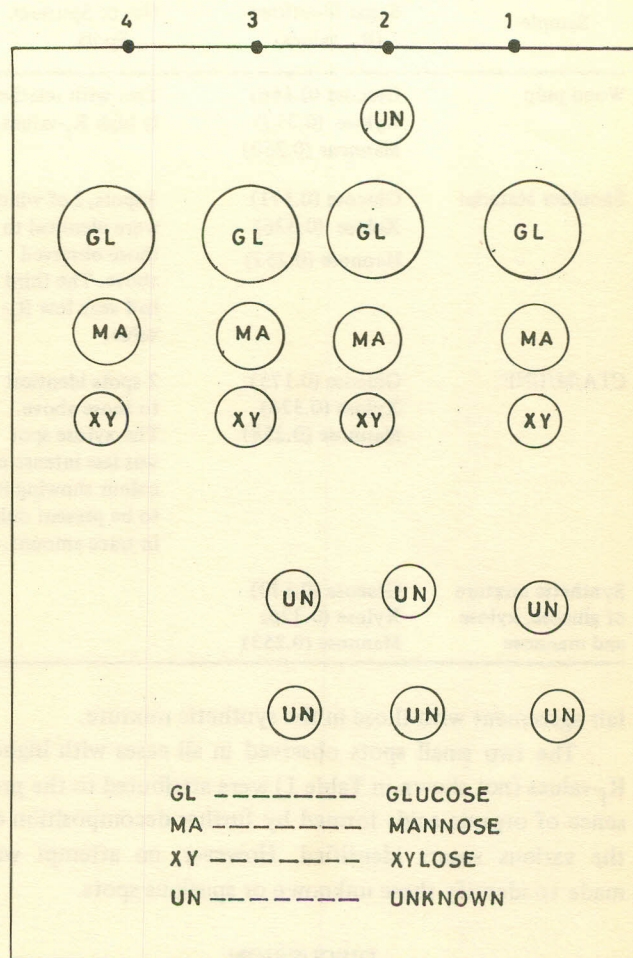


Fig. 1. Chromatogram of hydrolysate of (1). Wood pulp. (2). Shoulder Material. (3). CTA/M/UNF. (4). Synthetic Sugar mixture.

the development of the chromatogram in the present studies. The spots were located by dipping the dried developed paper consecutively into solutions of silver nitrate in acetone, 0.50 mol/lit alcoholic sodium hydroxide, and 1% (m/V) sodium thiosulphate.

The presence of the three sugars (glucose, mannose and xylose) was established by comparing the R_f -values of the unknown sugars to those of the synthetic known sugars mixture as shown in Table 1.

RESULTS

Paper chromatography of sugars present in the hydrolysate of wood pulp, shoulder material and unfractionated cellulose triacetate. The R_f -values of the unknown sugars in the hydrolysates of the various samples given in Table 1, show a

Table 1. R_f -Values of Sugars Identified in the Hydrolysates of Wood Pulp Shoulder Material and Unfractionated Cellulose Triacetate

Sample	Sugar Identified (R_f values)	No. of Spurious Spots
Wood pulp	Glucose (0.166) Xylose (0.317) Mannose (0.250)	Two with relatively high R_f -values
Shoulder Material	Glucose (0.171) Xylose (0.326) Mannose (0.252)	3 spots, 2 of which were identical to those observed above. The third had very low R_f -value.
CTA/M/UNF	Glucose (0.175) Xylose (0.326) Mannose (0.258)	2 spots identical to those above. The xylose spot was less intense in colour showing it to be present only in trace amount.
Synthetic mixture of glucose, xylose and mannose	Glucose (0.170) Xylose (0.326) Mannose (0.253)	

fair agreement with those in the synthetic mixture.

The two small spots observed in all cases with higher R_f -values (not shown in Table 1) were attributed to the presence of organic acids formed by further decomposition of the various sugars identified. However, no attempt was made to identify these unknown or spurious spots.

DISCUSSION

Fig. 1 shows the chromatogram of the hydrolysates of wood pulp, shoulder material, unfractionated cellulose triacetate, and a synthetic mixture of known sugars. On examining the chromatogram with reference to the synthetic mixture, it was seen that glucose, mannose and xylose were the common sugars present in the samples in question.

Further comparison of the density of the spots of various sugars on the chromatogram revealed that glucose was present in greater amount than mannose and xylose in all cases.

The R_f -values of the various sugars identified in the samples in question show slight variation from those in the synthetic mixture. This is probably due both to temperature changes and non-uniform drop size.

No attempt has been made to identify the two spurious spots observed in all samples. The high R_f -values and low spot densities for these spots suggest that they are probably due to the organic acids formed by further decomposition of the sugars mentioned above.

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