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VPC Analysis of Pyrolysis Products of Saccharides

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Chem 80 done under Dr. Niemann, 1963-64

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abstract

The pyrolysis products formed from the decomposition on a hot platinum coil of a number of saccharides were analyzed with a high-sensitivity vapor-phase chromatograph. Reproducibility was erratic, but the chromatographs of the pyrolysis products of mannose, dextrose, galactose, xylose, sucrose, levulose, maltose, lactose and cellobiose were indistinguishable. Rhamnose and sorbitol behaved unlike any of the other saccharides, and alpha-methylglucoside behaved similarly only to alpha-methylmannoside.

Purpose: To investigate the possibility of the applicability of vapor-phase chromatographic analysis of pyrolysis products of saccharides as a semi-qualitative analytic tool.

Procedure

Sample saccharide solutions were prepared by dissolving 0.25g saccharide in 10ml distilled water, and kept in rubber-stoppered pyrex flasks. Although after a few weeks, a cottony mold would appear in the solutions, comparison pyrolysis analyses with the chromatograph failed to show any difference between fresh and old solutions. The sample size was 25 micrograms (one microlitre) and was placed on the platinum coil with a one microlitre syringe. The water was boiled off by heating the coil to just

above the boiling point for 30 seconds.

Most of the samples were pyrolyzed by heating the platinum coil to an orange-red heat for eight seconds. In any series of runs, the current through the coil was controlled and constant, but ageing effects on the coil caused the necessary current to vary from 8 to 10 amperes. A few samples were pyrolyzed at a just-visible dull-red heat, requiring 5.4 amperes, for 15 seconds. The pyrolysis chamber was continually swept with a nitrogen flow of 20 ml/second which was used as a carrier gas through the chromatographic column.

Two chromatographic columns were used, both 5 feet by 1/8 inch. They were a 5% SE-30 on 60/80 chromosorb W column and a 15% Hallcomid M-18 on 60/80 firebrick column. The Chromatograph employed was an Aerograph Hi-Fi using a hydrogen flame ionization detector. The platinum coils were periodically cleaned in hot, concentrated nitric acid, since after many pyrolyses, firings were noticed to yield products having retention times corresponding to those of the saccharides even when no sample had been placed on the coil.

RESULTS

Although conditions were kept as constant as possible, long-term reproducibility of pyrolysis analyses was difficult. The most frequent variable was an unexplained occasional lack of resolution of peaks occarring closer than about seven seconds, however such a condition was readily recognized. More disturbing was the both short and long-term vari-

ability of relative peak heights of the several produced by the pyrolysis of one saccharide. Retention times of identifiable peaks were constant only to about plus or minus three seconds in twenty five.

Thus for meaningful comparison of the pyrolysis products of two saccharides, their pyrolyses have to be run consecutively, preferably at least four pairs of runs, to make evident random variations in relative peak heights and retention times.

Following Dr. Niemann's suggestion, dextrose, mannose and galactose were studied in the greatest detail and variety of conditions. The chromatographs of their pyrolysis products were compared at 35, 50, 60 and 100 degrees (C) column temperature with both the SE-30 and Hallcomid columns and were the only saccharides compared with low-temperature pyrolysis. In all conditions, the chromatographs of the pyrolysis products of the saccharides and their mixtures were indistinguishable.

In addition, at a 50 degree column temperature (the only temperature used for studies of all the saccharides studied in consecutive runs), mannose, dextrose, galactose, sucrose, levulose, maltose, xylose, lactose and cellobiose were found to be indistinguishable. However, the chromatographs of the pyrolysis products of Rhamnose and sorbitol were unique, and those of alpha-methylglucoside and alpha-methylmannoside resembled only each other.

Under high-temperature (orange-red heat) pyrolysis, mannose, dextrose galactose, etc. were characterized by four "analytical" peaks (that is, with more or less predictable and reproducible retention times, half-widths and relative peak heights). Rhamnose was characterized by a single dominant peak and one auxiliary with a much less area. This dominant peak served as a good standard when comparing retention times of peaks

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of pyrolyses run on different days, since a rough additive correction factor for retention time could be gotten by comparing the retention times of the unmistakeable rhamnose peak. Sorbitol appeared similar to dextrose except for the consistent presence of a unique peak. Alpha-methylglucoside and alpha-methylmannoside were characterized by three peaks of much less area than those of dextrose.

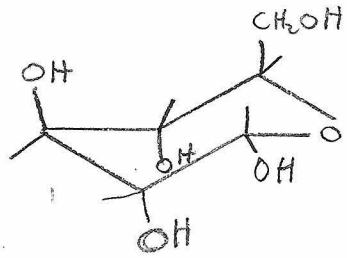
The few low-temperature (dull-red heat) pyrolyses done of dextrose, galactose and mannose show six "analytical" peaks each of which, as expected, is of lesser area than the peaks of the high-temperature pyrolyses.

CONCLUSIONS

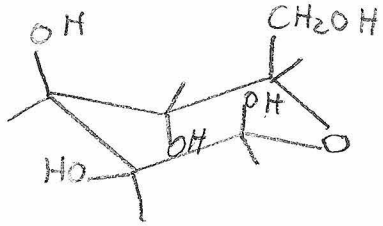
It appears that conformational effects on pyrolysis are only evidenced when the difference is very great - such as the difference between a straight chain carbohydrate like sorbitol, and the cyclic conformations of mannose, sucrose, etc. The stereochemistry of the hydroxyls has no effect. Also, whether the saccharide forms a five or six membered linked-ring conformation did not affect the pyrolysis products. However, the substitution of a $-CH_3$ group for a $-CH_2OH$ as in Rhamnose and a substitution of a methoxyl for a hydroxly as in alpha-methylglucoside produced marked differences.

Thus, although the technique is able to distinguish between two substitutional effects , it appears of little value in the distinguishing of the common saccharides, even though their structure is markedly different (as in glucose and sucrose).

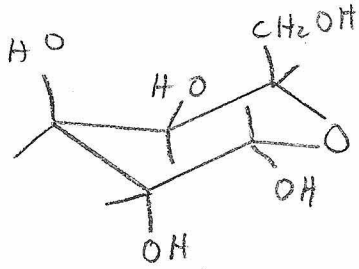
D Glucose (Dextrose)



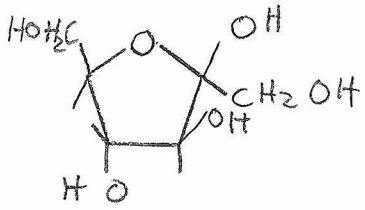
β-D mannose



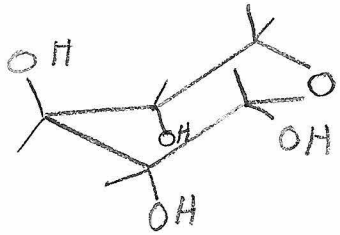
-D Galactose



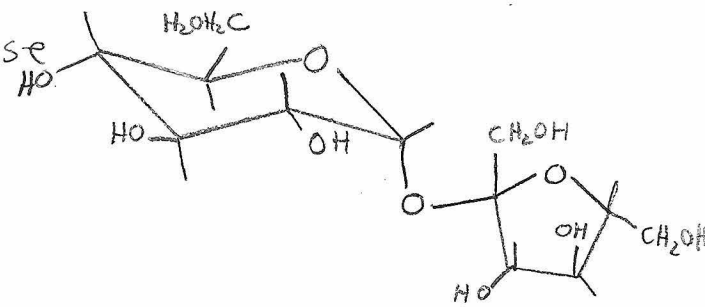
β-D Fructose (Levulose)



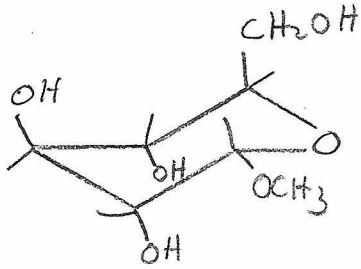
-D -Xylose



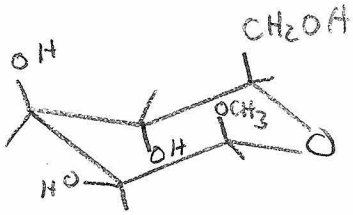
Sucrose



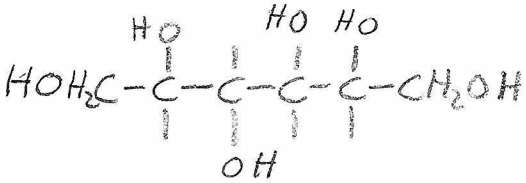
methyl glucoside



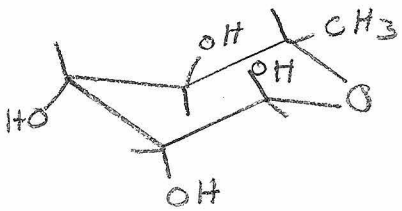
α-methyl mannoside



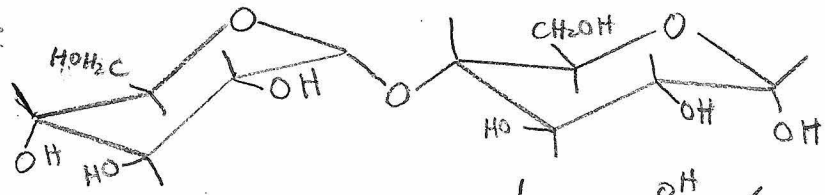
orbitol



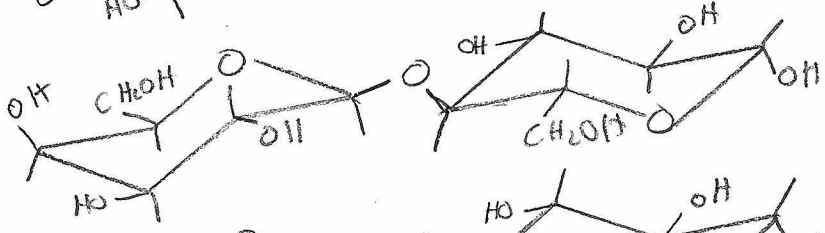
α-L Rhamnose



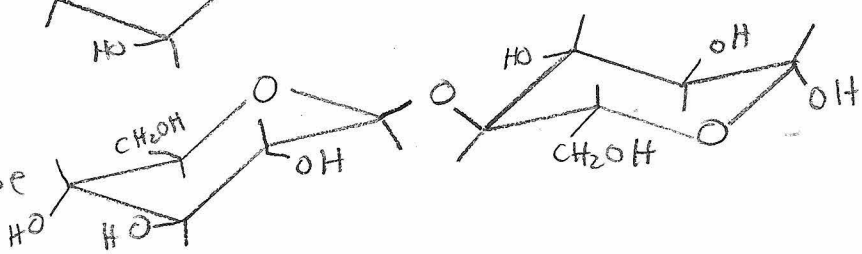
altose



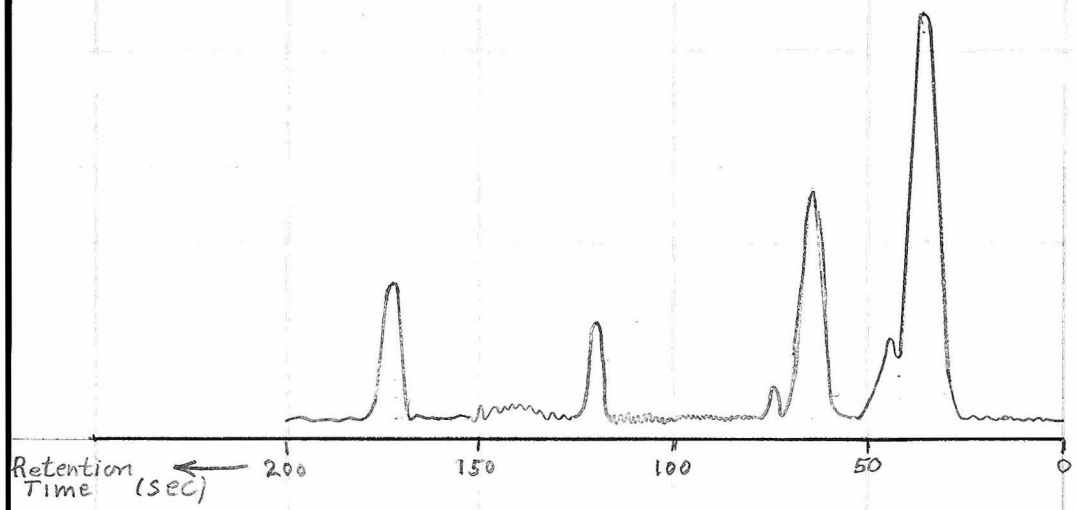
ctose



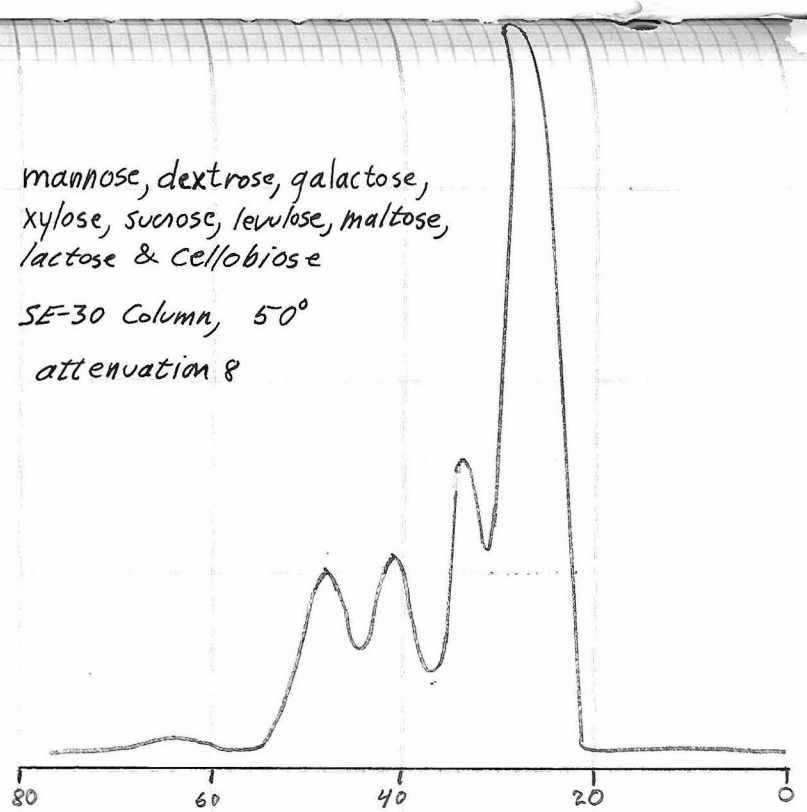
obiose



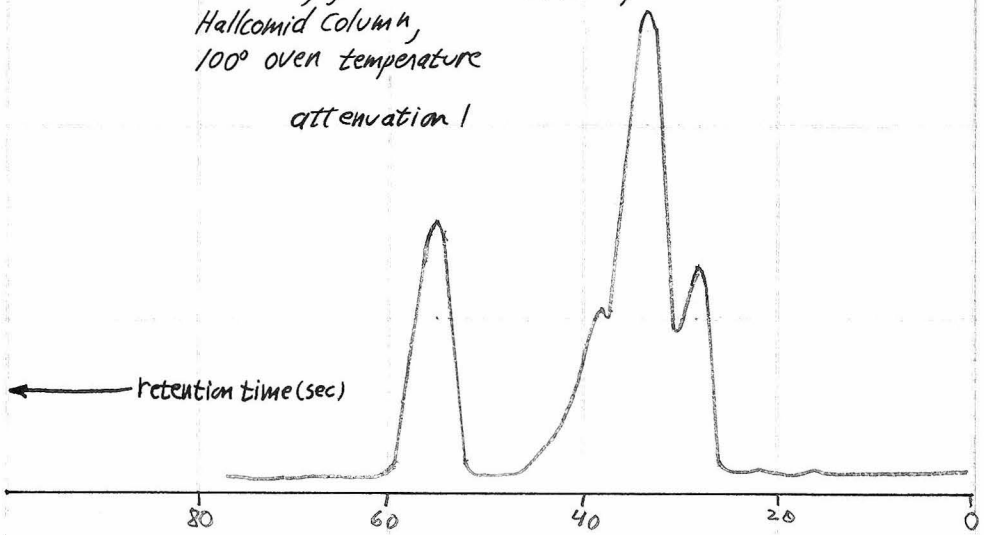
Galactose, Mannose
38° oven Temperature
low temperature pyrolysis
attenuation 1



mannose, dextrose, galactose,
xylose, sucrose, levulose, maltose,
lactose & cellobiose
SE-30 Column, 50°
attenuation 8



α-methylglucoside and α-methylmannoside
Hallcomid Column,
100° oven temperature
attenuation 1



attenuation 16

Rhamnose
SE-30 Column
50° Column Temp.