

have as the second substituent a hydrogen atom. The basis for this statement, as well as the basis for the structure assigned to the free radical formed in step 3, will be presented in our next publication dealing with this interesting reaction.

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CHROMATOGRAPHY OF CARBOHYDRATES AND SOME RELATED COMPOUNDS

Sir:

We wish to report that we have developed a method for the chromatography of the carbohydrates and related polyhydroxy compounds. Columns of adsorptive clays were used as adsorbents; an example is a Florida clay sold by the Floridin Co. of Warren, Pennsylvania, under the name Florex XXX. As developer we have used various low molecular weight hydrophilic solvents such as the alcohols, hydroxylic ethers, ether, dioxane, ketones, acids, pyridine, and water, either singly or in admixture.

Streak reagents that have been used on the exuded columns to detect the zones are alkaline permanganate, 2,6-dichlorophenolindophenol and acid-base indicators. Water was the eluting agent.

By the use of this method we have arranged a large number of the members of this class of compounds in an adsorption series. This chromatographic sequence shows the position each compound occupies on the adsorption column in relation to the other members. We have included in this series three pentoses, nine hexoses, two heptoses, six disaccharides, two trisaccharides, one tetrasaccharide, two other oligosaccharides, four glycosides, twenty polyhydric alcohols, seven polyhydric alcohol inner ethers, and ten acids, lactones or salts. Several positions in the sequence are occupied by more than one compound with the degree of resolution currently in use.

As examples of the applicability of this method the following are given. On chromatographing a mixture containing equal amounts of sorbitol and D-glucose, the separated D-glucose zone showed the presence of 100% of the added sugar by a reducing sugar determination, and the sorbitol zone showed 99.7% of the sorbitol by periodic acid oxidation. The sorbitol zone gave a negative reaction toward Fehling solution. A mixture containing 98% sorbitol and 2% D-mannitol was chromatographed to exhibit the presence of two zones. A mixture of equal amounts of D-mannitol and dulcitol was chromatographed and each component eluted and crystallized. The first crop of D-mannitol gave a recovery of 90% with m. p. 166–167°; a second crop gave a further 6% with the same melting point. The accepted value for the m. p. of D-mannitol is

166°. The first crop of dulcitol gave 95% recovery with m. p. 187–188° (accepted value 188°). A mixture, in disproportionate amounts, of 1,4:3,6-dianhydrosorbitol, 1,4:3,6-dianhydro-D-mannitol, and 1,4:3,6-dianhydro-L-iditol was chromatographed to show three zones. The rate of lactonization and delactonization of D-gluconic acid was followed qualitatively since the acid and the lactones occupied different positions on the column. Lemon juice was chromatographed and the ascorbic acid content was concentrated into a zone detectable by 2,6-dichlorophenolindophenol.

Work is being continued on this method and details will be communicated at a later date.

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THE CONFIGURATION OF THE PYRANOSE RINGS IN POLYSACCHARIDES

Sir:

If one accepts the assumption that the C–C and C–O bond angles and distances occurring in polysaccharides are those found in simple molecules, then two *trans* configurations are possible for a pyranose ring. The important difference between these two *trans* configurations is the angle which the C₁- and C₄-to-glycosidic-oxygen bond makes with the "plane" of the pyranose ring.

In the present discussion we are concerned only with those polysaccharides in which the glycosidic oxygens are *trans* to one another. This includes polymers of β-glucose (cellulose), β-mannuronic acid (alginic acid) and α-galacturonic acid (pectic acid). With this restriction it follows, then, that in one *trans* configuration of the pyranose ring (I) the two carbon-glycosidic bonds make an angle of about 20° with the "plane" of the pyranose ring. In the other *trans* configuration (II) this angle is about 90°. This difference in angle results in a difference in the fiber identity period when units of the same configuration are joined together to make a long chain. A chain made with I has a projection per pyranose unit in the direction of the fiber axis equal to 5.15 Å., while the projection for a chain made from II is 4.37 Å.

It is now generally accepted that the pyranose rings in cellulose are I.¹ Recent X-ray studies on fibers of sodium pectate² and alginic acid³

(1) Astbury and Davies, *Nature*, **154**, 84 (1944); Cox, *ibid.*, **154**, 84 (1944).

(2) Palmer and Lotzkar, *THIS JOURNAL*, **67**, 883 (1945); Palmer and Hartzog, *ibid.*, in press.

(3) Astbury, *Nature*, **155**, 667 (1945). We wish to express our thanks to Dr. Astbury for kindly sending us a copy of this paper before publication.