

Fig. 1. Liberation of ammonia when heparin, chondroitin sulfuric acid and glucosamine are treated with N NaOH at $100^{\circ}C$. Distilled nitrogen in per cent of total nitrogen is plotted against time in minutes.

Curve I. Glucosamine hydrochloride.

Curve II. Sodium salt of chondroitin sulfuric acid.

Curve III. Sodium salt of heparin.

Curve IV. The same salt of heparin with about 60 per cent of the amino group free after 8 hours hydrolysis at $100^{\circ}C$ with $0.04 N$ HCl.

In glucosamine (curve I) where the amino group is free, the formation of ammonia took place rapidly. After 135 minutes 90 per cent of the total nitrogen had distilled over as ammonia.

In chondroitin sulfuric acid (curve II) where the amino group is acetylated, the formation of ammonia was also remarkably rapid. After 135 minutes 55 per cent of the total nitrogen had distilled over.

In heparin (curve III) the formation of ammonia was very poor. After 135 minutes only about 10 per cent of the total nitrogen had distilled over as ammonia.

If the amino group in heparin, however, had been partly liberated by means of slightly acid hydrolysis with $0.04 N$ HCl the formation of ammonia was quite considerable (curve IV). After 135 minutes 38 per cent of the total nitrogen had distilled over as ammonia.

Consequently the linkage of the amino group in heparin is of another type than in the chondroitin sulfuric acid. The high resistance to alkaline hydrolysis may be considered as a further support for the assumption that the amino group in heparin is linked to sulfuric acid.

This investigation was aided by grants from the Wallenberg Foundation and the Vitrum Company, Stockholm.

1. Jorpes, E., Boström, H., and Mutt, V. *J. Biol. Chem.* **183** (1950) 607.
2. Berglund, E. *J. Chem. Soc.* **34** (1878) 643.

Received January 29, 1952.

Surface Balance Studies of the Multimolecular Layers of Isodextropimaric Acid

HENRIK BRUUN

Institute of Physical Chemistry, Abo Akademi, Abo, Finland

The properties of isodextropimaric acid monolayers on water have been recently studied with a surface balance^{1,*}. It was found that the surface pressure in the isodextropimaric acid monolayer began to increase on compression when the area per molecule was reduced to 54.1 \AA^2 , and the monolayer collapsed when the area was 42.6 \AA^2 per molecule. After this an equilibrium surface pressure equal to 19.7 dynes per cm was established, the layer remained liquid.

* A paper read at the VII Nordiska kemistmötet in Helsingfors, August, 1950.

When this liquid collapsed layer is further compressed until its area is approximately one half of the area at collapse, it is observed that the layer becomes solid within a narrow compression region. The surface balance curve for this phenomenon including also the monolayer compression range is of the form shown in Fig. 1. The monolayer collapses at the point marked a. In the range a—b the layer is liquid and the surface pressure remains practically constant. After the point b the surface pressure begins to increase and the layer becomes gradually more rigid in appearance. At c the layer has become solid. Further compression is accompanied by a pronounced pressure increase and it seems that the layer undergoes collapse at d, where the curve shows an inflexion. The surface pressure at d is about 37 dynes per cm.

The phenomenon is reversible between a and d. The curve shown in Fig. 1 was taken at a temperature of 20° C, but similar curves were obtained also at other temperatures between 5° and 40° C. The influence of the pH of the substrate was also investigated, whereupon it was found that the solidification of the isodextropimaric layer no longer takes place when the pH of the substrate exceeds 6. Between pH 4.2 and 5.5 the collapse pressure at d increases and attains its highest value, about 48 dynes per cm, at pH 5.5.

It is highly improbable that the molecules of isodextropimaric acid can be compressed in a monolayer to an area of only 21 Å² per molecule (at point b). Calculation of the size of the molecule indicates that the packing can not be much closer than that corresponding to the area, 42.6 Å² per molecule, observed at the collapse point a of the monolayer. If it is assumed that each molecule takes up in the region between a and b an area which is equal to the collapse area we come to the conclusion that at point b the layer corresponds to a complete di-

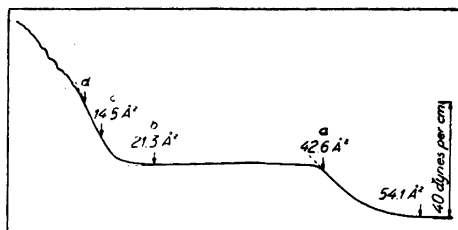


Fig. 1 The surface pressure-area curve for isodextropimaric acid on 0.001 M hydrochloric acid. Temperature 20° C.

layer. The area at point c, 14–15 Å², corresponds well with the value 14.2 Å² calculated for a complete trilayer. Since the transition of isodextropimaric layer from a liquid to a solid occurs gradually on compression between b and c, it appears that the formation of the third molecular layer brings about the solidification of the layer. The process taking place between b and d resembles to some extent that generally observed for monolayers on compression. There first occurs a closer packing of the molecules in the layer and then the layer collapses. It seems possible that a corresponding process takes place also in the isodextropimaric trilayer and that collapse of the trilayer occurs at d.

It was found that under the same conditions as used for isodextropimaric acid the monolayers of dextropimaric acid and the abietic acids (abietic, dehydroabietic, dihydroabietic and tetrahydroabietic acids) remain liquid on compression to very small areas per molecule and do not undergo a solidification process of the type described. Experiments conducted with isodextropimaric acid and dextropimaric acid mixtures and isodextropimaric and abietic acid mixtures showed that the solidification will not occur if the layer contains more than 20–30 per cent of the second component.

I am indebted to Professor Per Ekwall, the Head of the Institute for the opportunity

of using the facilities of the Institute and for discussions.

I am grateful to Dr. C. G. Harris of Hercules Powder Company, Wilmington, USA, for the sample of isodextropimaric acid received by the Institute.

1. Bruun, H. *Acta Chem. Scand.* **6** (1952).

Received February 5, 1952.

Identification of Galactose and Rhamnose in Birchwood and Aspenwood

K. J. BJÖRKQVIST and L. JÖRGENSEN

*Research Laboratory, Billeruds AB,
Säffle, Sweden*

In our last communication¹ we gave the carbohydrate composition of birch and spruce holocelluloses. In continuing our work on the hemicelluloses we have found the previous results to be incomplete, partly due to destruction of easily hydrolyzed sugars, when the standard quantitative saccharification method² is used. Better results have been obtained by employing a milder partial hydrolysis, followed by quantitative saccharification of the residue. The finely divided wood or holocellulose was heated for 15 hours at 95° C with dilute (0.5–1.0 N) sulfuric acid. The hydrolyzate was filtered through a sintered glass filter, and the residue was washed with water. The filtrate and washings were passed through a column of Amberlite IR 4 B anion-exchange resin, then concentrated *in vacuo* and examined by means of paper-partition chromatography. The residue from the partial hydrolysis was hydrolyzed by the standard method.

Applying this method we have found galactose to be present in birch — *Betula*

pubescens and *Betula verrucosa* — and aspen — *Populus tremula* — to the extent of about one per cent. No variations in galactose content could be noticed in birch grown in widely different areas. Our results confirm the work of Gustafsson *et al.*³, who also detected galactose in the same species, but found, however, that the amount varied. On the other hand, Jensen and Nuotio⁴, using Schorger's method for determination of sugars, found galactose in *Betula pubescens* only.

Rhamnose was also detected in these partial hydrolyzates of the two birch species and the aspen. The two birches contained 0.3–0.4 per cent of rhamnose, and the aspen probably somewhat less. Recently Jones and Schoettler⁵ identified L-rhamnose in aspenwood using a similar mild hydrolysis procedure. Up to now the presence of rhamnose as a constituent building unit in the wood hemicelluloses has not been proved⁶. Rhamnose has, however, long been known to be present in gums and mucilages of various origin^{7,8}. Holocellulose contains the same amount of rhamnose as the original wood. It belongs to the easily hydrolyzable part of the hemicellulose.

1. Björkqvist, K. J., and Jörgensen, L. *Acta Chem. Scand.* **5** (1951) 978.
2. Saeman, J. F., Bubl, J. L., and Harris, E. E. *Ind. Eng. Chem., Anal. Ed.* **17** (1945) 35.
3. Gustafsson, Ch., Sundman, J., Pettersson, S., and Lindh, T. *Paper and Timber (Finland)* **33** (1951) 300.
4. Jensen, W., and Nuotio, J. *Paper and Timber (Finland)* **33** (1951) 33.
5. Jones, J. K. N., and Schoettler, J. R. *Tappi* **35** (1952) 102 A.
6. Hägglund, E. *Chemistry of Wood*. (1951) 356. New York, Academic Press.
7. Jones, J. K. N., and Smith, F. *Advances in Carbohydrate Chemistry* **4** (1949) 243.
8. Pigman, W.W., and Goepf, R. M. Jr. *Chemistry of the Carbohydrates* (1948) 429. New York, Academic Press.

Received April 18, 1952.