[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Distillation of Sugar Propionates at Low Pressures

BY CHARLES D. HURD, R. W. LIGGETT[1] AND K. M. GORDON[2]

Work in this Laboratory for some time has been directed toward the separation and identification of sugars in mixtures. A promising approach has been the conversion of sugars to volatile derivatives to achieve separation by distillation. Separation by means of methylated derivatives has been developed into a satisfactory analytical procedure[3] for mixtures of monosaccharides, disaccharides and trisaccharides, or even pentoses and hexoses.

The methylation approach suffers distinct limitations, however, in the identification of sugars in mixtures. One drawback is the fact that so many of the methylated sugars are liquids or sirups. Another major limitation, perhaps the chief one, is the fact that it is impossible to hydrolyze off the methyl groups of di- or trisaccharides without concurrent rupture of the carbohydrate itself.

Attention was turned, therefore, to other possible volatile derivatives. Esters were selected because if they were found to be distillable they would possess several advantageous features, namely, the simplicity of preparation, the excellence of the yields and the ease of removal of the ester groups if desired without disturbing the carbohydrate linkages otherwise.

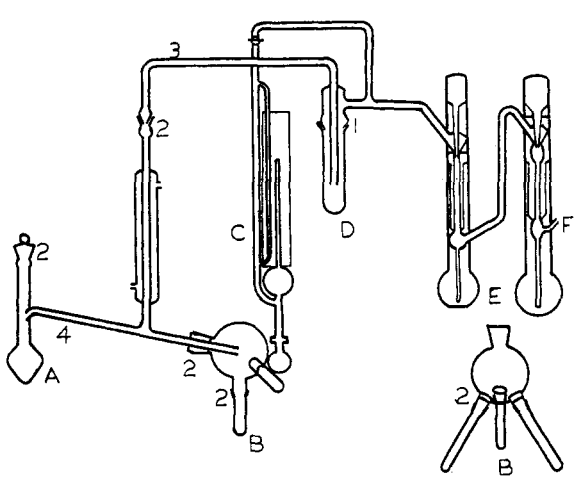

Fig. 1.—A, Distillation flask, 50 cc.; B, fraction cutter; C, McLeod gage; D, cold trap; E, mercury pumps; F, outlet to oil pump; 1, standard taper 40/50; 2, standard taper 24/40; 3, tubing 22 mm.; 4, tubing 15 mm.

Distillation of acetic esters was found to be possible if sufficiently low pressure was used, but it was found that propionic esters were much easier to distil. It was established that the propionates of not only the mono- and disaccharides but also the trisaccharides were distillable, and this paper concerns itself with the distillation technique which is involved. The two succeeding papers deal with the chemistry of these propionates.

The apparatus is sketched in Fig. 1. The distillation bulb shown is of 50-cc. capacity but larger bulbs (100 and 200-cc.) were used also. A water condenser is shown in the figure but it was omitted ordinarily since it was established that the vertical tube cooled by air alone was equally satisfactory. When very low pressures were desired, liquid nitrogen was used to chill the cold trap, otherwise a mixture of dry-ice and acetone was satisfactory. The two mercury pumps were supported by an oil pump.

The tendency to bump during distillation was lessened by sintering a small amount of powdered glass into the bottom of the distillation flask and by placing a few glass helices in it. The uptilted, inset side arm simplified the problem of obtaining a clear distillate. The wide-bore tubes were incorporated to assist in obtaining good vacua. The temperature of the oil-bath (or salt-bath) was recorded but no provision was made to take the distillation temperature inside the flask. The slow distillation rate would make such temperatures meaningless.

The propionates of the monosaccharides were of sufficiently low viscosity that they flowed readily into the receiver. Those from the disaccharides were more viscous and frequently required warming to maintain a flow through the side arm. The material remaining in the side arm was rinsed out with ether at the end of the distillation.

If it is possible to do so, the propionic esters should be transferred to the distilling flask without the use of a solvent. This lessens the tendency for bumping. The material is poured directly into the flask after heating it to 100° on the steam-bath. If a solvent is already present it is removed at 100° and 20 mm. in a larger flask. The flask in Fig. 1 should not be more than three-fourths full, and for quantitative work not over half full.

Heavy vacuum grease which is soft at room temperature is adequate for all the joints except the one in the distillation flask. For the latter a grease is selected which softens at about 100°.

To start the distillation, the bath temperature around the distillation flask must be sufficiently high to lower the viscosity of the substance in the flask to a point where frothing does not occur when the pumping is started and

(1) Corn Products Fellow, 1938–1941.
(2) Pabst Fellow, 1938–1941.
(3) Hurd and Cantor, THIS JOURNAL, **60**, 2677 (1938).

degassing occurs. As most substances have a decomposition point not far above this, an optimum temperature must be discovered. The pressure should be lowered gradually with the oil pump and, when its full capacity is reached, pumping should progress for about five minutes before the mercury pumps are started, the temperature being raised gradually until the substance is about 10 to 20° below the boiling point as the mercury pumps take hold. The temperature is then raised until distillation commences. If no decomposition appears to be taking place, the temperature may be raised until a steady distillation occurs.

Pressures as low as 10^{-5} mm. were obtained if a liquid nitrogen trap was used and if the temperature of the distillation flask was held reasonably low. Most of the compounds studied, however, do not require such low pressures. With many of the propionates, good results were obtained if the pressures were 0.01 mm. Some distilled even up to 0.1 mm., whereas others required pressures below 0.001 mm. Usually the latter pressure could be reached when the cold trap was at −78° but it could always be reached without difficulty when cooled by liquid nitrogen.

With pressures below 0.05 mm., as read on the gage, the bath temperatures around the distillation flask do not correlate well with the pressure. If a mixture is being distilled it is usually necessary to maintain a higher bath temperature than if the corresponding pure substance was being distilled. The place to make a cut, therefore, must be decided from the character of the distillate, particularly its color and viscosity, and the rate of distillation. In separating monosaccharide and disaccharide derivatives, for example, the distillate becomes darker as the disaccharide starts to distil. Receivers are changed when the distillate ceases to drop freely and starts to string. The approximate time to take a cut can be told by the stopping of distillation at a given pot temperature if the pressure remains constant.

It is possible to distil as complex a compound as raffinose hendecapropionate in the apparatus shown in Fig. 1, but the molecular still of Fig. 2 makes this operation easier to perform. The molecular still is attached directly to the cold trap (Fig. 1) by means of the standard taper joint. The design of this type of molecular still was suggested to one of us by Dr. K. C. D. Hickman.

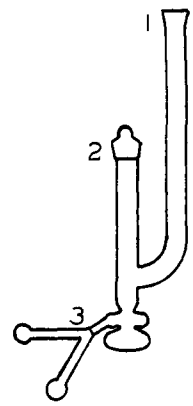

Fig. 2.—1, Standard taper 24/40; 2, standard taper 29/42; 3, standard taper 14/35.

Summary

An apparatus is described and the procedure outlined for the distillation of propionates of mono-, di- and trisaccharides.

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Propionyl Derivatives of Sugars

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Only one propionyl derivative of a monosaccharide is reported in the literature and there are none for di- or trisaccharides. α-D-Glucose pentapropionate was reported by Hess and Messmer[2] to be a colorless sirup boiling at 205° (2 mm.).

Sixteen new propionates have been prepared in the present investigation. The carbohydrates from which these were derived may be grouped as follows: two pentoses, one methylpentose, two aldohexoses, two ketohexoses, eight disaccharides, one trisaccharide. All were completely propionylated, the general method being to leave a mixture of the sugar, propionic anhydride and dry pyridine at room temperature for several days. A summary of data concerning these compounds is given in Table I.

Most of these propionates were purified by distillation at low pressures. No decomposition was apparent when appropriate conditions were maintained. Propionates of the monosaccharides and disaccharides distilled at pressures of 0.07–0.001 mm., when the bath temperature was 160–280°. The propionates from sorbose or fructose were less stable than the others, hence lower bath temperatures were used for them, namely, 160 to

TABLE I

PROPIONATES OF MONO-, DI- AND TRISACCHARIDES

	M. p., °C.	$[\alpha]^{20}D$	Anal., % Found	C_2H_5CO Calcd.
L-Rhamnose tetrapropionate	Sirup	−43	58.3	58.8
L-Arabinose tetrapropionate	80	116	60.6	61.0
D-Xylose tetrapropionate	42–43	43	61.1	61.0
D-Fructose pentapropionate	Sirup	24	62.2	62.0
D-Mannose pentapropionate	Sirup	24	62.5	62.0
D-Galactose pentapropionate	Sirup	54	62.0	62.0
L-Sorbose pentapropionate	Sirup	−17	62.1	62.0
Maltose octapropionate	144	55	57.7	57.7
Cellobiose octapropionate	170	8.0	57.7	57.7
Lactose octapropionate	Sirup	32	57.1	57.7
Sucrose octapropionate	45–46	53	57.6	57.7
Gentiobiose octapropionate	151–152	− 3.3	58.6	57.7
Trehalose octapropionate	52–53	144	57.5	57.7
Melibiose octapropionate	Sirup	92		
Neolactose octapropionate	Sirup	−4.5		
Raffinose hendecapropionate	Sirup	95	55.8	56.0

(1) Holder of Pabst Research Fellowship, 1938–1941.

(2) Hess and Messmer, *Ber.*, **54**, 511 (1921).