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179. Masaaki Horiguchi, Nobuyuki Higosaki, Tadahiro Iwashige, and Issei Iwai : Gas Liquid Partition Chromatography of 2,3-Anhydro-D-ribofuranoside and 2,3-Anhydro-D-lyxofuranoside.

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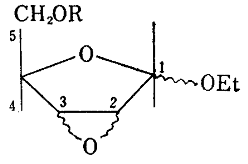
Recent and rapid development of gas chromatographic procedures of great efficiency and sensitivity, have made the separation possible for a wide variety of less volatile compounds which have rather high molecular weights of polar substituents.

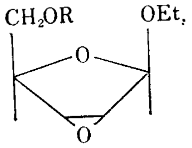
After the first application of Bishop1) to carbohydrate compounds, several reports were found which have been classified into the following substituted derivatives : i) acylated,2~4) ii) alkylated,5~11) iii) isopropylidene,12,13) iv) trimethylsilylated sugars.14,15) Moreover, it has been reported16) recently that even unsubstituted monosaccharides can be separated.

Now, anhydrosugars (epoxysugars) would be the interesting intermediates for the conversion to heterosugars.

Regarding the configuration of 2,3-anhydropentofuranoside (I), four isomers of each optical series are theoretically required, due to the stereochemical relation between $C_{2,3}$ epoxy ring and C_1-anomeric substituent. Namely, ethyl 2,3-anhydro-β-D-ribofuranoside (II), ethyl 2,3-anhydro-α-D-ribofuranoside (III), ethyl 2,3-anhydro-β-D-lyxofuranoside (IV) and ethyl 2,3-anhydro-α-D-lyxofuranoside (V) exist for D-series.



I



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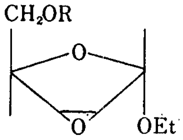

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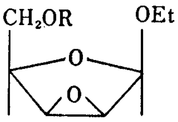

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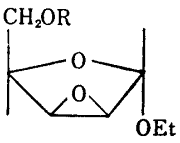
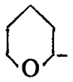


V

a : R=H b : R=Ac c : R=Tp Tp=



In this report, twelve derivatives, II_{a-c}, III_{a-c}, IV_{a-c}, V_{a-c}, were applied to gas chromatography to study the relationship between their retention times and the differences

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in structures and substituents, and also the thermal stability of epoxy ring under several operating conditions.

Column packings used in this study were i) 1% polydiethyleneglycol succinate on 80~100 mesh Chromosorb-W (DEGS), ii) 1% polyneopentylglycol succinate on 80~100 mesh Chromosorb-W (NPGS), iii) 3% Carbowax 6000 on 40~60 mesh Chromosorb-W (CW 6000), iv) 1% FS-1265 (QF-1) on 80~100 mesh Chromosorb-W (FS-1265), v) 1% SE-30 on 80~100 mesh Chromosorb-W (SE-30). 1~2 μl. of each sample was taken as 0.5% acetone solution.

The 5-OH compounds (II_a, III_a, IV_a, V_a) were synthesized from D-xylose, according to Baker[17] and Percival's[18] procedures and their purities were confirmed. Some of their gas chromatograms are shown in Fig. 1. Then, 5-O-acetyl and 5-O-(tetrahydro-2-pyranyl) derivatives have been prepared from the corresponding 5-OH compounds.*2 Their purities have been likewise confirmed before this experiment.

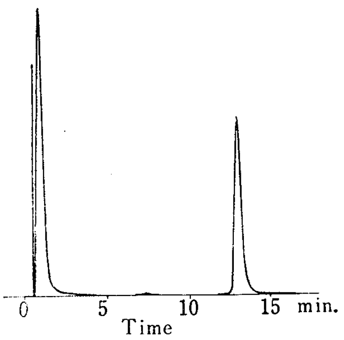

Fig. 1-A. Gas Chromatogram of Ethyl 2,3-Anhydro-α-D-ribofuranoside (IIIa) on NPGS

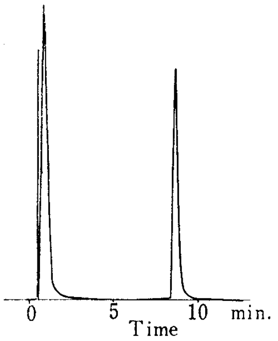

Fig. 1-B. Gas Chromatogram of Ethyl 2,3-Anhydro-β-D-lyxofuranoside (IVa) on NPGS

The gas chromatograms on packings DEGS and NPGS are shown in Figs. 2 and 3. Separation of V_b-II_b, V_c-II_c-IV_a on DEGS and II_a-V_b-V_a, IV_a-IV_b, V_c-III_a on NPGS could not be achieved. However, no tailing was observed and symmetrical single sharp peaks were obtained.

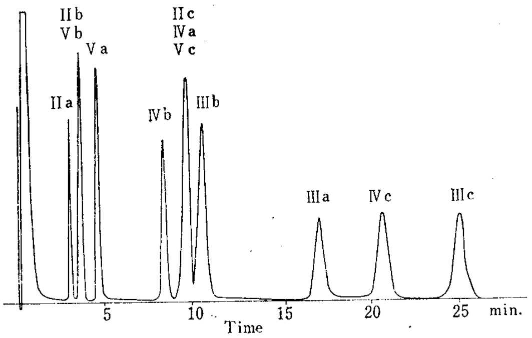

Fig. 2. 1% Polydiethyleneglycol Succinate on 80~100 mesh Chromosorb-W

Column temp, 129°, argon flow rate 64 ml./min.

The chromatogram on CW-6000 is shown in Fig. 4. The separation of IV_a-III_b, V_c-II_c could not be affected. In this case, also no tailing was observed and single sharp peaks were recognized as by DEGS and NPGS, and with this column, the best separation was achieved in this experiment.

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*2 Details of syntheses will be published later.

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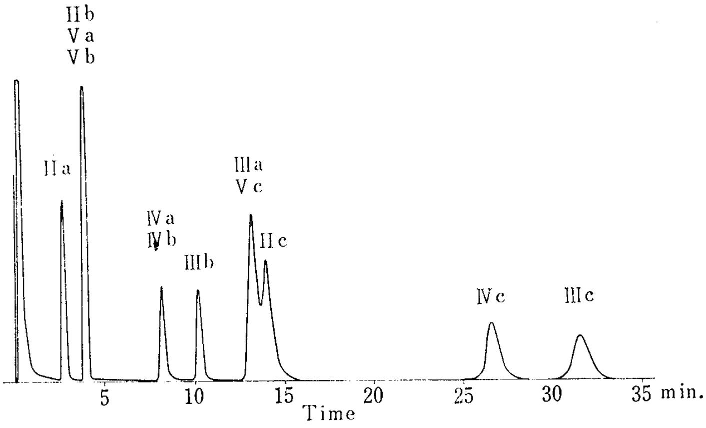

Fig. 3. 1% Polyneopentylglycol Succinate on 80～100 Mesh Chromosorb-W

Column temp. 125°, argon flow rate 67.5 ml./min.

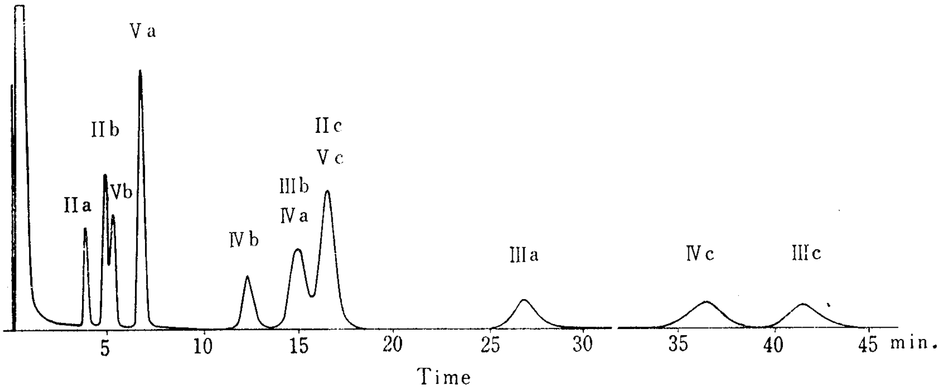

Fig. 4. 3% Carbowax 6000 on 40～60 Mesh Chromosorb-W
Column temp. 104°, argon flow rate 60 ml./min.

FS-1265 (QF-1) was used as polar liquid phase besides DEGS, NPGS, CW-6000. It has been reported[2] that this liquid phase gives effective separations for polyacetate derivatives. However, a few splitted peaks which might have resulted due to thermal decomposition in column, and also the intensive tailings were observed for several derivatives applied. Therefore, this column packing has been proved unsuitable.

Finally, separations on the column packing, using SE-30 as nonpolar liquid phase, are shown in Fig. 5. This liquid phase tends to cause a little tailing, contrary to DEGS, NPGS, CW-6000 and also the inversion of the order of elution was observed in some derivatives.

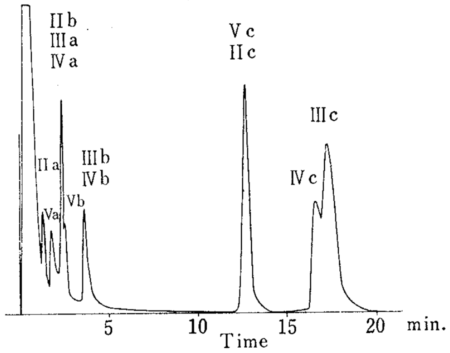

Fig. 5. 1% SE-30 on 80～100 Mesh Chromosorb-W

Column temp. 120°, argon flow rate 66 ml./min.

The retention times of the derivatives applied on the several column packings described above are listed in Table I.

From these experimental results, i) the structure which has shown to be independent of a kind of liquid phase used for a column packing, affects to increase the

TABLE I. Retention Times[a] (min.) of Twelve Derivatives

Sample	Column			
	(SE-30)	(DEGS)	(NPGS)	(CW-6000)
Ethyl 2,3-anhydro-β-D-ribofuranoside (IIa)	2.6	2.9	2.7	3.9
Ethyl 2,3-anhydro-α-D-ribofuranoside (IIIa)	5.4	16.7	12.7	28.1
Ethyl 2,3-anhydro-β-D-lyxofuranoside (IVa)	5.4	9.4	8.1	15.9
Ethyl 2,3-anhydro-α-D-lyxofuranoside (Va)	3.8	4.4	3.8	7.1
Ethyl 5-O-acetyl-2,3-anhydro-β-D-ribofuranoside (IIb)	5.9	3.5	3.9	5.1
Ethyl 5-O-acetyl-2,3-anhydro-α-D-ribofuranoside (IIIb)	9.0	10.2	10.2	15.1
Ethyl 5-O-acetyl-2,3-anhydro-β-D-lyxofuranoside (IVb)	8.9	7.8	8.0	12.9
Ethyl 5-O-acetyl-2,3-anhydro-α-D-lyxofuranoside (Vb)	6.3	3.6	3.9	5.5
Ethyl 5-O-(tetrahydro-2-pyranyl)-2,3-anhydro-β-D-ribofuranoside (IIc)	11.9[b]	9.5	13.8	17.1
Ethyl 5-O-(tetrahydro-2-pyranyl)-2,3-anhydro-α-D-ribofuranoside (IIIc)	16.7[b]	24.6	31.2	43.5
Ethyl 5-O-(tetrahydro-2-pyranyl)-2,3-anhydro-β-D-lyxofuranoside (IVc)	15.7[b]	20.2	26.3	38.0
Ethyl 5-O-(tetrahydro-2-pyranyl)-2,3-anhydro-α-D-lyxofuranoside (Vc)	11.9[b]	9.4	13.0	17.5
Column temp. (°C)	102	129	125	104
Carrier gas flow rate ml./min.	62.0	64.0	67.5	60.0

a) Gas hold up adjusted

b) Column temp. 120°, argon flow rate 66 ml./min.

retention time in the order of ethyl 2,3-anhydro-β-D-ribofuranoside (II) <ethyl 2,3-anhydro-α-D-lyxofuranoside (V) <ethyl 2,3-anhydro-β-D-lyxofuranoside (IV) <ethyl 2,3-anhydro-α-D-ribofuranoside (III), although the difference of retention time between two corresponding derivatives with same substituent for (II) and (V) was smaller in most cases. This order of retention time is especially apparent in polar liquid phases. ii) Next, the nature of 5-O-substituent tends to increase the retention time in the order of Ac<OH<Tp for the polar liquid phases, while non polar liquid phase (SE-30) affects the enhancement in the order of OH<Ac<Tp. However, only IIa is excluded from those orders, since it always eluates first in all cases. Also as shown in Fig. 5, the rather high boiling 5-O-(tetrahydro-2-pyranyl) derivatives are clearly divided from 5-O-acetyl and 5-OH type derivatives when non polar liquid phase (SE-30) is used.

Consequently, it becomes apparent that, at least, the series of isomer with same substituent can be separated and the separation of the mixture of some other derivatives is also possible by a suitable selection of column packing.

Experimental

Apparatus and Column Packings——A Barber Colman Model 10 gaschromatograph equipped with a tritium argon ionization detector was used in this investigation. The column was a U-shaped Pyrex glass tube, 6 mm. i.d. and 2 m. long filled with a solid support of acid washed Chromosorb-W, treated with dimethyldichlorosilane and coated with a liquid phase. The liquid phases used are as follows:

1% SE-30 (G.E. methyl substituted type silicone gum)
1% Polydiethyleneglycol succinate (Craig's polyester succinate)
1% Polyneopentylglycol succinate
3% Carbowax 6000
1% FS-1265 (QF-1 Dow Corning, fluoro alkyl silicone polymer).

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Summary

Gas liquid partition chromatography has been applied to twelve derivatives to separate the anomeric mixtures of 2,3-anhydro-D-ribofuranoside and 2,3-anhydro-D-lyxofuranoside under several operating conditions. The relation between retention times, their structures and substituents were observed.

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