Since the same mixture is obtained by pyrolysis of any of these three compounds, the isomerization is reversible. It is suggested that isomerizations of other indene derivatives under similar conditions are likewise reversible, and that an apparently complete isomerization is a result of an equilibrium very favorable for one product.

Other hydrocarbons whose pyrolyses are reported are 1,1,3-triphenylindene, 3-phenyl-*spiro*-[fluorene - 9, 1 - indene], 1 - methyl - 1,3 - diphenylindene, 1,1 - dimethyl - 3 - phenylindene, 2,3 - dimethyl - 1 - phenylindene, 1,1 - dimethyl - 2-phenylindene, 2-methylindene, and 2-methylindene. All of these substances except the last two yielded the rearrangement products expected. In some cases the isomerization products were isolated and in others their presence was shown by oxidative degradation of inseparable mixtures.

An interpretation of the migration is given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Synthesis of an Epimeric Pair of Trisaccharides Containing Mannose Units[1]

BY EUGENE A. TALLEY AND WM. LLOYD EVANS

The preparation of acetobromomannosidoglucose,[2] led to the synthesis of a trisaccharide of the type proposed by Nishida and Hashima[3] as a unit in the structure of the mannan from the tubers of *Amorphophallus konjac.* Condensation of the acetobromo compound with β-D-glucose-1, 2,3,4-tetraacetate and with β-D-mannose-1,2,3, 4-tetraacetate by the Koenigs and Knorr reaction gave the two epimeric trisaccharides, 12-β-D-mannosido-β-gentiobiose hendecaacetate and 12-β-D-mannosido-β-*epi*-gentiobiose hendecaacetate, respectively. The trisaccharide acetates do not contain an orthoester grouping as shown by the fact that all eleven acetyl groups are removed by an alkaline deacetylating agent in both cases.

Although 12-mannosido-*epi*-β-gentiobiose hendecaacetate is made up of two mannose units and one glucose unit, it was not thought that the compound would be identical with the trisaccharide of Nashida and Hashima[3] as pointed out in another contribution from this Laboratory.[4] Nashida and Hashima reported that their trihexose could be broken down to give two disaccharides, of which one (mannosido-mannose) was hydrolyzed only to mannose and the other (mannosido-glucose) was hydrolyzed into one molecule of mannose and one molecule of glucose. Such a result could not be obtained from our mannosido-*epi*-gentiobiose. But after preparing it, the properties found for 12-mannosido-*epi*-β-gentiobiose hendecaacetate did seem to be comparable with those of two fractions reported by the Japanese workers.[3] The properties are given in Table I.

TABLE I

Material	M. p., °C.	Acetic acid, %	$[\alpha]_D$ in $CHCl_3$	Molecular weight (in benzene)
10-B[a]	105–115	68.69	+10.8°	1134
11-B[a]	102–115	68.76	+12.3°	1413
MGM[b]	113–114	68.0, 67.0 (68.3 calcd.)	+11.2°	1015, 1005 (967 calcd.)

[a] Sample numbers of Nashida and Hashima.[3] [b] MGM = Synthetic 12-mannosido-*epi*-β-gentiobiose hendecaacetate.

The synthetic compound and these fractions were all insoluble in ethyl ether. The properties given by Nashida and Hashima[3] for what they thought was the best fraction of their trisaccharide acetate were as follows: m. p. 95–110°, $[\alpha]^{20}$D in chloroform +18° and in benzene +6°. The molecular weight and acetic acid content of this particular fraction were not given but other fractions were listed which were found to have similar specific rotations. In every case the acetic acid content given was higher than the values in Table I and the molecular weights were lower, indicating that these latter fractions may have contained a larger percentage of a disaccharide octaacetate. In addition most of these fractions were ether soluble. Also it is of interest to point out that β-D-mannosido-β-D-glucose octaacetate[2] is ether soluble and its $[\alpha]^{19}$D +38.9° ($CHCl_3$).

On the basis of the above-mentioned observa-

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(1) Abstracted from a thesis presented by Eugene A. Talley to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) E. A. Talley, D. D. Reynolds and W. L. Evans, THIS JOURNAL, **65**, 575 (1943).

(3) Kitsuji Nishida and Hideo Hashima, *J. Dept. Agr. Kyushu Imp. Univ.*, **2**, 277–360 (1930).

(4) To be published.

tions, it seemed that the glucomannan hendecaacetate of Nashida and Hashima, and 12-mannosido-*epi*-β-gentiobiose hendecaacetate were identical. But a determination of the specific rotation of the latter compound in benzene, ($[\alpha]^{23}\mathrm{D}+14.3°$ to be compared with $[\alpha]^{20}\mathrm{D} + 6°$) showed that this property was not identical. The difference might be explained on the basis of impurities in the benzene used by Nashida and Hashima but it does not seem likely that the difference would be as great in magnitude as it is. Hence, we cannot definitely show whether the synthetic compound is identical with the compound from natural sources since no samples of the latter are at present available.

The specific rotation of 12-β-D-mannosido-β-gentiobiose hendecaacetate (A) was calculated using Hudson's isorotation rules, according to the method described previously.[5] The calculation was based on the known values for 12-β-D-mannosido-β-*epi*-gentiobiose hendecaacetate (B), β-D-glucose pentaacetate (A′)[6] and β-D-mannose pentaacetate (B′).[6] Thus

$$[\alpha_{\mathrm{A}}]M_{\mathrm{A}}{}^{7} = [\alpha_{\mathrm{A'}}]M_{\mathrm{A'}} - [\alpha_{\mathrm{B'}}]M_{\mathrm{B'}} + [\alpha_{\mathrm{B}}]M_{\mathrm{B}}$$

$$\begin{aligned}[\alpha_{\mathrm{A}}]M_{\mathrm{A}} &= (+1480) - (-9830) + (10830)\\ &= 22{,}140\\ [\alpha_{\mathrm{A}}] &= +22.9° \text{ (The observed value is } +20.2°\text{)}\end{aligned}$$

Experimental Part

12-β-D-Mannosido-*epi*-β-gentiobiose Hendecaacetate.—The following materials were used: 6.3 g. of β-D-mannose-1,2,3,4-tetraacetate (1.2 mol), 11.25 g. of silver oxide, 31.5 g. of "Drierite," 95 ml. of purified chloroform, 2 g. of iodine, and 10.48 g. (1 mol) of acetobromo-6-β-D-mannosido-D-glucose.[2] The apparatus and procedure used were similar to those for the preparation of the mannosidoglucose octaacetates.[2] The sirup from the chloroform solution was treated with 500 ml. of boiling distilled water with vigorous stirring. The gum separating out on cooling with ice was taken up in 75 ml. of absolute ethanol. Thin platelets of 12-β-D-mannosido-*epi*-β-gentiobiose hendecaacetate (6.62 g.) separated out in the refrigerator; m. p. 111–113° and $[\alpha]^{26}\mathrm{D}$ +11° ($CHCl_3$), moderately soluble in benzene and warm ethyl alcohol, insoluble in ethyl ether and water; yield 46%. The substance was recrystallized from alcohol, and from chloroform and ethyl ether. The crystals are rather difficult to dry completely free from solvent. The pure compound melts at 112–113° (cor.) to a highly viscous liquid which becomes clear of air bubbles 50–60° higher; $[\alpha]^{23}\mathrm{D}$ (+1.66)(15.00)/(0.8689)(2) = +14.3° in purified benzene; $[\alpha]^{23}\mathrm{D}$ (+1.00)(15.00)/(0.669)(2) = +11.2° (constant) in purified chloroform.

Anal. Calcd. for $C_{18}H_{21}O_{16}(COCH_3)_{11}$: (a) acetyl, 11.38 ml. of 0.1 *N* NaOH for 100-mg. sample. Found[8]: 11. 32 ml. and 11.15 ml. (b) Molecular weight, 966.83. Found cryoscopically in benzene: 1015 and 1005; in camphor, 982.

12-β-D-Mannosido-β-gentiobiose Hendecaacetate.—12-β-D-Mannosido-β-gentiobiose hendecaacetate was prepared in the same manner as its epimer except that β-D-glucose-1,2,3,4-tetraacetate was used instead of β-D-mannose-1,2,3,4-tetraacetate and the method used for working up the product was slightly different. The residue from the distilled water treatment was dried, then taken up in 45 ml. of absolute alcohol, and decolorized with "Darco," and after standing overnight at −7°, the brittle, amorphous residue separating out was filtered off. The residue was again dissolved in absolute alcohol. After standing at 50° about half an hour, it began to crystallize in very fine white needles. If cooled too quickly, the material comes out as an oil. After three recrystallizations, 3.2 g. of 12-β-D-mannosido-β-gentiobiose hendecaacetate was obtained from 4 g. of acetobromomannosidoglucose (58%). The crystals melted at 117–119° and the specific rotation was +19.7° in chloroform. The material is soluble in warm alcohol, moderately soluble in benzene, very soluble in chloroform and very slightly in ethyl ether. It appears to be slightly more soluble in benzene and ether than its epimer. Recrystallized to constant rotation, the melting point from chloroform and ether was 118–119° (cor.) and $[\alpha]^{24}\mathrm{D}$ (+2.27)(15.00)/(0.8421)(2) = +20.2° (purified chloroform).

Anal. Calcd. for $C_{18}H_{21}O_{16}(COCH_3)_{11}$: (a) acetyl, 11.38 of 0.1 *N* NaOH for 100-mg. sample. Found[8]: 11.40 ml. and 11.44 ml. (b) Molecular weight, 966.83. Found cryoscopically in benzene, 960.

Summary

1. Crystalline 12-β-D-mannosido-β-*epi*-gentiobiose hendecaacetate (m. p. 112–113° (cor.); $[\alpha]^{23}\mathrm{D} + 11.2°$ ($CHCl_3$)) has been prepared and its properties compared with those of the trisaccharide acetate obtained from *konjac* mannan.

2. Crystalline 12-β-D-mannosido-β-gentiobiose hendecaacetate (m. p. 118–119° (cor.), $[\alpha]^{24}\mathrm{D} + 20.2°$ ($CHCl_3$)) has been prepared.

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[5] Delbert D. Reynolds and Wm. Lloyd Evans, THIS JOURNAL, **62**, 68 (1940).

[6] C. S. Hudson, "Relations Between Rotatory Power and Structure in the Sugar Group," *Scientific Papers of the Bureau of Standards*, No. 533, p. 379, Government Printing Office, Washington, D. C., 1926.

[7] M = Molecular weight

$[\alpha_{\mathrm{A}}]M_{\mathrm{A}}$ = Molecular rotation of 12-mannosido-β-gentiobiose hendecaacetate

$[\alpha_{\mathrm{B}}]M_{\mathrm{B}}$ = Molecular rotation of 12-mannosido-*epi*-β-gentiobiose hendecaacetate

$[\alpha_{\mathrm{A}}']M_{\mathrm{A}}'$ = Molecular rotation of β-glucose pentaacetate

$[\alpha_{\mathrm{B}}']M_{\mathrm{B}}'$ = Molecular rotation of β-mannose pentaacetate

[8] The method used was that described by Alfons Kunz and C. S. Hudson, THIS JOURNAL, **48**, 1982 (1926).