THREE NEW DERIVATIVES OF *d*-GLUCOHEPTULOSE[1]

BY W. C. AUSTIN

In 1930 the writer,[2] in association with Hudson, described the preparation of a new crystalline ketoheptose, *d*-glucoheptulose, from *d*-α-glucoheptose following rearrangement of the latter with dilute alkali. The *d*-glucoheptulose was reported to have a rotation of $[\alpha]_D^{20}$ +67.5°, without mutarotation. In order to determine whether the *d*-glucoheptulose exists in the alpha or beta form it became necessary to prepare the methyl-*d*-glucoheptuloside from it. By heating *d*-glucoheptulose in methyl alcohol containing 1% of dry hydrogen chloride there was formed the crystalline α-methyl-*d*-glucoheptuloside, of $[\alpha]_D^{20-25}$ +108.5° in water, melting at 138–140°. It will be shown later in this article that the rotation of this derivative proves that the *d*-glucoheptulose exists in the alpha form.

By acetylating the α-methyl-*d*-glucoheptuloside with acetic anhydride and sodium acetate, the α-methyl-*d*-glucoheptuloside pentaacetate has been prepared in crystalline form. This second new derivative of *d*-glucoheptulose has been recrystallized to constant specific rotation, $[\alpha]_D^{20-25}$ +78.5°, in chloroform, with m. p. 110°.

The acetylation of *d*-glucoheptulose with acetic anhydride and sodium acetate has given the crystalline *d*-glucoheptulose α-hexaacetate, which has been purified to constant specific rotation, $[\alpha]_D^{20-25}$ +87.0°, in chloroform, with m. p. 112°.

Calculation of the Rotations of the Beta Forms of the above Derivatives of *d*-Glucoheptulose.—The rotations of the above alpha forms of the three derivatives of *d*-glucoheptulose will now be examined in connection with those of α-methyl-*d*-fructoside and its tetraacetate, recently described by Schlubach and Schröter.[3] These workers have called attention to the fact that the values of the rotations of the end asymmetric carbon atoms may now be calculated for these derivatives of *d*-fructose by the application of the rule of Hudson,[4] taking one-half the difference between the molecular rotations of the alpha and beta isomers. The β-methyl-*d*-fructoside and its tetraacetate, beta isomers of the two alpha compounds recently prepared by Schlubach and Schröter, were made in 1916 by Hudson and Brauns.[5a] The alpha and beta forms of *d*-fructose penta-

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² Austin, THIS JOURNAL, **52**, 2106 (1930).

³ Schlubach and Schröter, *Ber.*, **61**, 1216 (1928); **63**, 363 (1930).

⁴ Hudson, THIS JOURNAL, **31**, 66 (1909).

⁵ (a) Hudson and Brauns, *ibid.*, **38**, 1216 (1916); (b) **37**, 1283, 2736 (1915).

acetate were also prepared by Hudson and Brauns[5b] and furnish values of rotations for determining the value of the end asymmetric carbon atom in the d-fructose pentaacetate. The determinations on the three pairs of isomers are shown in Table I for these fructose derivatives. For purposes of comparison the corresponding values given by Hudson[6] for the aldoses are also given in the tabulation.

TABLE I

VALUES OF THE COEFFICIENT a_{Me}, A_{Me} AND A_{Ac} IN THE FRUCTOSE SERIES

Substance	Mol. wt.	$[\alpha]_D^{20}$ in water	$[M]_D$	Rotation of end Carbon, A	A for corresponding derivatives of aldoses
α-Methyl-d-fructoside	194	$+ 46.0°$	$+ 8,900$	$a_{Me} = 21,200$	$a_{Me} = 18,700$
β-Methyl-d-fructoside	194	$-172.7°$	$-33,500$		
Tetraacetates of		$[\alpha]_D^{20}$, in CHCl$_3$			
α-Methyl-d-fructoside	362	$+ 45.5°$	$+16,850$	$A_{Me} = 31,050$	$A_{Me} = 26,900$
β-Methyl-d-fructoside	362	$-125.0°$	$-45,250$		
Pentaacetates of					
α-d-Fructose	390	$+ 34.7°$	$+13,533$	$A_{Ac} = 30,458$	$A_{Ac} = 19,100$
β-d-Fructose	390	$-121.5°$	$-47,384$		

Schlubach and Schröter have called attention to the fact that the values of a_{Me} and A_{Me} are greater for the derivatives of fructose than for the corresponding derivatives of aldoses. Differences of the same nature are observed in comparison of the value A_{Ac} from derivatives of fructose with that from derivatives of aldoses. The reason for these differences between the corresponding coefficients of fructose and the aldoses is not definitely known. The differences may be due to the fact that the end asymmetric carbon atom in fructose is attached to $-CH_2OH$ or to $-CH_2OR$ instead of to $-H$, as in the aldoses and their derivatives. The attachment of additional weight to the end asymmetric carbon in the fructose series may cause its rotation to be larger than in the aldose series; this explanation would lead one to expect that the rotation coefficients of the fructose series will be found to apply in other 2-ketose series. For the present it is assumed that the values of a_{Me}, A_{Me} and A_{Ac} are the same in the fructose and glucoheptulose series on account of the like groups attached to carbon 2 in these ketoses.[7] The values of the rotations of the unknown beta isomers of the three known alpha derivatives of d-glucoheptulose may now be calculated by deducting from the molecular rotation of the alpha isomer twice the value of the rotation of the end asymmetric carbon atom for the corresponding derivative of fructose and dividing the difference so obtained by the molecular weight of the beta isomer.

The value of the $[M]_D$ of α-methyl-d-glucoheptuloside is $(+108.5°)$

[6] Hudson, THIS JOURNAL, **48**, 1428 (1926).

[7] I am indebted to Dr. C. S. Hudson for the suggestion that the coefficients of the fructose series may apply to the series of the 2-ketose sugars in general.

$(224) = +24,300$. The value of $2a_{Me}$ from the fructose series is $+42,400$, and the difference is $-18,100$, which is the calculated $[M]_D$ for β-methyl-d-glucoheptuloside. The corresponding specific rotation is $[\alpha]_D = -18,100/224 = -81.0°$.

The value of the $[M]_D$ of α-methyl-d-glucoheptuloside pentaacetate is $(+78.5°)$ $(434) = +34,069$. The value of $2A_{Me}$ from the fructose series is $+62,100$, and the difference is $-28,031$, which is the calculated $[M]_D$ for β-methyl-d-glucoheptuloside pentaacetate. The corresponding specific rotation is $[\alpha]_D = -28,031/434 = -64.6°$.

The value of the $[M]_D$ of d-glucoheptulose α-hexaacetate is $(+87.5°)$ $(462) = +40,424$. The value of $2A_{Ac}$ from the fructose series is $+60,917$, and the difference is $-20,493$, which is the calculated $[M]_D$ for d-glucoheptulose β-hexaacetate. The corresponding specific rotation is $-20,493/462 = -44.3°$.

On page 1928 the rotation of the unknown beta form of d-glucoheptulose is calculated by a slightly different method.

The Ring Structure of the Derivatives of d-Glucoheptulose.—In the article describing the preparation of d-glucoheptulose, shown as structure I, evidence was given that the new sugar contained the 2,5 ring. Proof may now be advanced that the ring structure of the derivatives of d-glucoheptulose is also 2,5, and that the structures of the new derivatives are those represented in II, III and IV.
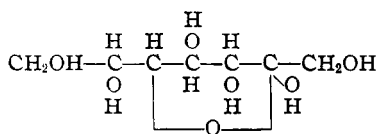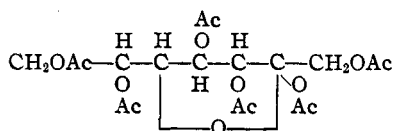

I
d-Glucoheptulose(2,5)
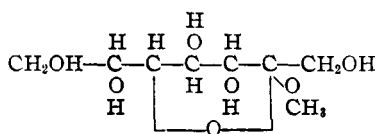
II
α-Methyl-d-glucoheptuloside(2,5)
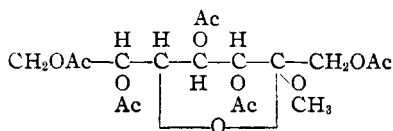
III
α-Methyl-d-glucoheptuloside
pentaacetate(2,5)

IV
d-Glucoheptulose α-hexaacetate(2,5)

In each of the structures shown the asymmetric carbon atoms (Nos. 3, 4, 5 and 6) have the same configurations as the corresponding asymmetric carbon atoms (Nos. 2, 3, 4 and 5) of d-glucose, or the corresponding derivative of this sugar with the 1,4 ring. The rotations of d-glucose and its derivatives with this ring have not been measured because the substances are not known, but the values of the rotations have been calculated by Hudson.[8] Using the values for the corresponding derivatives of d-glucose-

[8] Hudson, THIS JOURNAL, **48**, 1434 (1926); **52**, 1680 (1930).

(1,4) it should be possible to calculate the rotations of the derivatives of d-glucoheptulose, with the same type of ring(2,5).

Hudson has calculated for the α-methyl-d-glucoside(1,4) the rotation $[\alpha]_D$ +114°, or $[M]_D$ (+114°) (194) = +22,120. By subtracting from the $[M]_D$ of this compound the value of a_{Me} for aldoses, +18,700, there is obtained the value of $B_{d\text{-glucose}(1,4)}$ = +3420. The $[M]_D$ for α-methyl-d-glucoheptuloside(2,5) should be the value $B_{d\text{-glucose}(1,4)}$ plus a_{Me} from the fructose series, +21,200, giving +24,620. The corresponding $[\alpha]_D$ value is +24,620/224 = +110°. This calculated value is so near the observed value of +108.5° that it may be safely concluded that the α-methyl-d-glucoheptuloside is an alpha form and has the 2,5 ring.

Haworth and Porter[9] have prepared α-ethyl-d-glucoside(1,4) and β-ethyl-d-glucoside(1,4), with $[\alpha]_D$ values of +98 and −86°, respectively. By taking one-half the sum of the values of the $[M]_D$ of these compounds, +20,384 and −17,888, the value of $B_{d\text{-glucose}(1,4)}$ is obtained = +1248. The $[M]_D$ of α-methyl-d-glucoheptuloside(2,5) should be the value of $B_{d\text{-glucose}(1,4)}$ plus a_{Me} from the fructose series, +21,200, giving +22,448, which corresponds to the $[\alpha]_D$ value of +100°. By subtracting from the value of $B_{d\text{-glucose}(1,4)}$ the value of a_{Me} from the fructose series the $[M]_D$ of β-methyl-d-glucoheptuloside(2,5) is found to be −19,952, corresponding to the $[\alpha]_D$ value of −89°. The differences of 8° between the values calculated by this method and the values found for the α-methyl-d-glucoheptuloside(2,5), or calculated for the β-methyl-d-glucoheptuloside-(2,5) by the method on page 1926, are not in conflict with the conclusions from the calculations in the preceding paragraph and are due to the slight differences in the values of $B_{d\text{-glucose}(1,4)}$ as calculated from the data of Hudson or from the observations of Haworth and Porter.

The specific rotation of the α-methyl-d-glucoheptuloside pentaacetate-(2,5) may be calculated similarly. The $[M]_D$ of the corresponding compound of d-glucose(1,4) is (+83°) (362) = +30,046. From this value of +30,046 the value of A_{Me} for aldoses, +26,900, is subtracted to give the value $B_{d\text{-glucose}(1,4), \, Ac}$ = +3146. By adding the value of A_{Me} for ketoses, +31,050, to the value of +3146 there is obtained the $[M]_D$ value for the α-methyl-d-glucoheptuloside pentaacetate(2,5) = +34,196. The corresponding $[\alpha]_D$ value is +34,196/434 = +78.8°. This calculated value for the derivative with the 2,5 ring is so near the observed value of +78.5° that the 2,5 ring is also assigned to the α-methyl-d-glucoheptuloside pentaacetate.

The specific rotation of the d-glucoheptulose α-hexaacetate(2,5) may be calculated in the following manner. The $[M]_D$ of d-glucose pentaacetate is obtained, (+55°) (390) = +21,450. From this value of +21,-450 is subtracted the value of A_{Ac} for aldoses, +19,100, giving the value of $B_{d\text{-glucose}(1,4), \, Ac}$ = +2350. Adding to the value of +2350 the value

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[9] Haworth and Porter, *J. Chem. Soc.*, 2796 (1929).

of A_{Ac} from the fructose series, $+30,458$, there is obtained the value of $+32,808$, the calculated $[M]_D$ for d-glucoheptulose α-hexaacetate-2,5. The corresponding $[\alpha]_D$ value is $+32,808/462 = +71°$. This value of $+71°$ is lower than the observed value of $+87.5°$, but not sufficiently different to indicate any ring but the 2,5 type in the hexaacetate. In consideration of the values of the rotations of the basal acetylated chains in derivatives of d-fructose and of d-glucoheptulose the observation has been made that the values are larger in the pentaacetates of fructose and in the hexaacetates of d-glucoheptulose than in the methylfructoside tetraacetates and methyl-d-glucoheptuloside pentaacetates by 2725 and 6896. At present no valid explanation can be given for the abnormally large value calculated for $B'_{d\text{-glucoheptulose(2,5), Ac}}$ from the hexaacetates. The question of the differences in the values of the basal acetylated chains is one peculiar to the 2-ketose sugars and can only be solved by the preparation and study of corresponding derivatives of other 2-ketoses. It is interesting to note that, using the value $B_{d\text{-glucoheptulose(2,5), Ac}} = +3019$ (one-half the sum of the values of $[M]_D$ from the methyl-d-glucoheptuloside pentaacetates), one may calculate the value of the specific rotation of the α-d-glucose pentaacetate(1,4) by adding the value of A_{Ac} for aldoses and dividing by the molecular weight, 390, of the compound of d-glucose. The value calculated is $[\alpha]_D +56.1°$, which is so near the value of $+55°$ calculated for this substance by Hudson, from other rotations, as to warrant the suggestion that the normal value of $B_{d\text{-glucoheptulose(2,5), Ac}}$ is found by consideration of the methyl-d-glucoheptuloside pentaacetates rather than the hexaacetates of the ketose. The use of the value $B'_{d\text{-glucoheptulose(2,5), Ac}} = +9915$ in a similar calculation leads to the value $[\alpha]_D +74.4°$ for the α-d-glucose pentaacetate(1,4). As there is no other evidence for the existence of an acetate of d-glucose of such rotation, the value of $B'_{d\text{-glucoheptulose(2,5), Ac}}$ must be considered abnormal, pending the preparation of similar acetates of other ketoses.

The above methods of allocation of ring structure in the derivatives of d-glucoheptulose may be applied to a determination of the ring in d-glucoheptulose itself. From one-half the sum of the $[M]_D$ values of the two forms of methyl-d-fructoside the value of $B_{d\text{-fructose}}$ is obtained, $-12,300$. If this value is subtracted from the $[M]_D$ value of β-d-fructose, $-24,000$, there is obtained the value A_{OH} for fructose, $-11,700$. The $[M]_D$ value of α-d-glucose(1,4), calculated by Hudson, is $(+66°)$ $(180) = +11,880$. From this value of $+11,880$ the value of $B_{d\text{-glucose(1,4)}} = +3380$ is obtained by subtraction of the value of A_{OH} for aldoses, $+8500$. Adding the values of $+3380$ and $+11,700$ there is obtained the calculated $[M]_D$ of α-d-glucoheptulose(2,5) $= +15,080$. The corresponding $[\alpha]_D$ value is $+15,080/210 = +72°$. This is so near the observed rotation, $[\alpha]_D^{20} +67.5°$, as to constitute further proof, independent of

that in the previous paper by the writer, that the d-glucoheptulose which has been synthesized is of the alpha form and contains the 2,5 ring.

The specific rotation of the β-d-glucoheptulose may now be calculated. The value of the $[M]_D$ of α-d-glucoheptulose(2,5) is $(+67.5°)$ (210) = $+14,175$. The value of $2A_{OH}$ from the fructose series, as derived in the preceding paragraph, is $+23,400$, and the difference is -9225, which is the calculated $[M]_D$ for β-d-glucoheptulose(2,5). The corresponding specific rotation is $[\alpha]_D = -9225/210 = -44.0°$.

Experimental Part

Preparation of α-Methyl-d-glucoheptuloside.—This substance was prepared by the method used by Fischer[10] in the preparation of α-methyl-d-glucoheptoside. d-Glucoheptulose, 8.4 g. of $[\alpha]_D^{20}$ $+67.3°$, was finely powdered and dissolved, with heating, in 100 cc. of methyl alcohol containing 1 g. of dry hydrogen chloride. The solution of the sugar was accomplished in twenty minutes of heating on the steam-bath. The reaction mixture was allowed to stand at room temperature for twelve to fourteen hours and was then freed of hydrogen chloride by warming with an excess of silver carbonate and filtering. The filtrate was diluted to 150 cc. with methyl alcohol. A quantitative copper reduction test on a 5-cc. portion of this solution showed that only 3.2% of the used ketose remained uncombined. The remaining 145 cc. of solution was concentrated to a thin sirup by evaporation under reduced pressure. After holding this sirup for several days in a desiccator over calcium chloride crystal tufts appeared. On stirring these into the sirup the entire mass became semi-crystalline. This mass was dissolved in 35 cc. of warm methyl alcohol and 500 cc. of warm acetone was added. The solution was cooled to zero, decanted from an impurity of sirup and refrigerated overnight. The next day the crop of crystals, which formed as tufts of prisms, was filtered out and dried at 37°. The precipitated sirup was worked over twice by solution in methyl alcohol and dilution with acetone, followed by cooling to zero, decantation of the cleared solution, and crystallization of more of the substance by refrigeration. The three crops of material were united to give 5.5 g., 63% of the theoretical yield. This fraction was found to have $[\alpha]_D^{20-25}$ $+109.38°$ (0.6342 g. of substance in water to 25.0 cc. read $\alpha = +5.55°$, using a 2-dm. tube). The material softened at 135° and melted at 138–140°. The remaining 4.9 g. was recrystallized from 20 cc. of warm methyl alcohol by the addition of 250 cc. of acetone, followed by refrigeration overnight. No sirup separated and the next day the mother liquor was decanted and the crystals washed with acetone by decantation and dried at 37° to 4.2 g. of substance, melting at 138–140° of $[\alpha]_D^{20-25}$ $+108.78°$ (0.5890 g. substance in solution with water to 25.0 cc. read $\alpha = +5.13°$, using a 2-dm. tube). These values did not change on further recrystallization and the $[\alpha]_D^{20-25}$ $+108.5 \pm 0.5°$, with melting point 138–140°, are accepted as constants for the pure substance.

Anal. Estimations of OCH_3 were made on 0.3089 and 0.2160 g. samples of the substance and gave 0.3216 and 0.2295 g. of AgI, corresponding to 13.76 and 14.04% OCH_3. Calcd. for $C_8H_{16}O_7$: mol. wt., 224.12; OCH_3 13.84%.

The combustions[11] of 0.15 to 0.23 g. samples showed C, 42.93, 42.30; H, 7.57, 7.17; calcd.: C, 42.83; H, 7.19.

[10] Fischer, *Ber.*, **28**, 1157 (1895).

[11] All of the combustions reported herein were made by the writer in the Chemical Laboratory of the College of Liberal Arts, Northwestern University, by the kind permission of Dr. C. D. Hurd.

Preparation of α-Methyl-d-glucoheptuloside Pentaacetate.—A mixture of 2.3 g. of pure α-methyl-d-glucoheptuloside, 15 cc. of acetic anhydride, and 1.5 g. of anhydrous sodium acetate was heated for one and one-half hours on the steam-bath with frequent shaking. The solution was then poured into a mixture of ice and water, 100 g. of each. The acidity of the mixture was reduced with additions of solid sodium bicarbonate. The sirup which immediately separated hardened and crystallized in thirty minutes. The next day the crystalline material was filtered out and dried at 37° to 3.5 g. Extraction of the filtrate with chloroform resulted in the recovery of 0.2 g. more of the substance, making a yield of 87% of the theoretical. The 3.5 g. of substance was recrystallized three times from solution in 10–15 cc. of absolute alcohol by the addition of 5 volumes of water to give 2 g. of substance with a melting point of 110° and a rotation of $[\alpha]_D^{20-25}$ +78.44° (0.5466 g. substance in chloroform to 25.0 cc. read α = +3.43°, using a 2-dm. tube). A fourth recrystallization did not alter the value of the rotation or the melting point. Accordingly, the constants, $[\alpha]_D^{20-25}$ +78.5 ± 0.5°, and m. p. 110°, are accepted for the pure α-methyl-d-glucoheptuloside pentaacetate.

Anal. Estimations of OCH_3 were made on 0.4120 and 0.3103 g. samples of the substance, and gave 0.2337 and 0.1749 g. AgI, corresponding to 7.50 and 7.45% OCH_3. Calcd. for $C_{18}H_{26}O_{12}$: mol. wt., 434.2; OCH_3, 7.14. The combustions[11] of 0.15 g. samples of the substance showed C, 49.67, 49.58; H, 6.12, 6.30; calcd.: C, 49.75; H, 6.04. By the directions of Kunz[12] 0.3840 and 0.4081 g. samples of the substance were equivalent to 44.04 and 46.74 cc. of 0.1 N KOH. Calcd., 44.23, 46.99 cc.

Preparation of d-Glucoheptulose α-Hexaacetate.—A mixture of 10 g. of finely powdered d-glucoheptulose with 70 cc. of acetic anhydride and 6 g. of anhydrous sodium acetate was heated for one and one-half hours on the steam-bath with frequent shaking. The dark colored reaction mixture was then poured into a mixture of ice and water, 200 g. of each. The acidity of the mixture was reduced with additions of solid sodium bicarbonate. The dark sirup which separated slowly crystallized overnight. The soft dark mass was then filtered out and dried at 50° to 10 g. This crude product was recrystallized from solution in 15 cc. of alcohol by the addition of 7 cc. of water to give 5.5 g. of material. This material was combined with 16.0 g. of similar material made from 30 g. more of the d-glucoheptulose. The average yield of recrystallized acetate was approximately 25% of the theoretical, much lower than the customary yield of 60% in acetylating d-α-glucoheptose. Extraction of all mother liquors with chloroform and carbon tetrachloride has given no evidence of the formation of isomeric acetates. The continued darkening during the acetylation by heating the reaction mixture is indicative of decomposition of the acetate. In future preparations it is hoped that shortening the period of heating will result in a larger yield of pure product. The 21.5 g. of material was recrystallized twice from solution in three times its weight of alcohol by the addition of its weight of water, and gave 20.0 g. of hexaacetate, of $[\alpha]_D^{20-25}$ +87.8° (0.4907 g. substance in chloroform to 25.0 cc. read α = +3.45°, using a 2-dm. tube). The substance melted at 112°. A third recrystallization gave 17.5 g. of substance of $[\alpha]_D^{20-25}$ +87.08° (0.4923 g. of substance in chloroform to 25.0 cc. read α = 3.43°, using a 2-dm. tube). The melting point was unchanged, at 112°. The values $[\alpha]_D^{20-25}$ +87.0 ± 0.5°, m. p. 112°, are accepted for the pure crystalline d-glucoheptulose α-hexaacetate. The substance crystallizes from alcohol by the addition of water in very slender, interlaced and silky prisms. It was found that recrystallized preparations must be dried in vacuum over calcium chloride at room temperature to avoid decomposition, which is slight but detectable at 50°.

Anal. The combustions[11] of 0.15 to 0.22 g. samples of the substance showed C,

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[12] Kunz and Hudson, THIS JOURNAL, **48**, 1982 (1926)

48.94, 48.99; H, 5.72, 5.77; calcd.: C, 49.32; H, 5.67. By the directions of Kunz[12] 0.5285 and 0.4592 g. samples of the substance were equivalent to 70.18 and 61.01 cc. of 0.1 N KOH. Calcd., 70.20 and 61.00 cc.

The author desires to thank Dr. C. S. Hudson for his helpful interest and many valuable suggestions in connection with the above contribution.

Summary

The following three new crystalline derivatives of the ketoheptose, d-glucoheptulose, have been prepared and purified to constant rotation and melting point: α-methyl-d-glucoheptuloside, $[\alpha]_D^{20-25}$ +108.5°, in water, m. p. 138–140°; α-methyl-d-glucoheptuloside pentaacetate, $[\alpha]_D^{20-25}$ +78.5°, in chloroform, m. p. 110°; and d-glucoheptulose α-hexaacetate, $[\alpha]_D^{20-25}$ +87.0°, in chloroform, m. p. 112°.

d-Glucoheptulose and d-fructose are alike in configuration about carbon atoms No. 1 and 2, and d-glucoheptulose contains about carbon atoms 3, 4, 5 and 6 the same configurations as carbon atoms 2, 3, 4 and 5 of d-glucose. By applying to the above-mentioned rotations and those of the corresponding derivatives of d-glucose the rotation coefficients of the 2-ketose series (given in large part by Schlubach and Schröter from the fructose series) and of aldoses (given by Hudson) it has been shown that the new derivatives of d-glucoheptulose are alpha forms and contain the 2,5 ring.

The rotations of the corresponding unknown beta forms of this sugar and its derivatives have been calculated from those of the known alpha forms by applying the rotation coefficients of the 2-ketose series.

By the use of the above rotation coefficients in connection with the rotation of d-glucose (1,4 ring), predicted by Hudson, the rotation of the alpha form of d-glucoheptulose has been calculated; the fair agreement with the observed value lends further support to the conclusion in the previous paper that the ring in the known form of this ketoheptose is 2,5. Conversely, the rotations of d-glucoheptulose and its derivatives, containing the 2,5 ring, lend added support to the values given by Hudson for d-glucose and its corresponding derivatives of the 1,4 ring.

The rotations of the alpha and beta forms of methyl-d-glucoheptuloside-(2,5) have also been calculated by considering the rotation coefficients of the 2-ketose series in connection with the rotations of the alpha and beta forms of ethyl-d-glucoside(1,4), recently prepared by Haworth and Porter. These calculated rotations agree so closely with the values found, or calculated by the other methods, that they are accepted as added confirmation that the ring in these derivatives of d-glucoheptulose is 2,5 and corresponds to the 1,4 ring in the new ethyl glucosides of Haworth and Porter.