D-MANNOKETOHEPTOSE, A NEW SUGAR FROM THE AVOCADO.*

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This article describes the isolation of a new ketose sugar, containing seven carbon atoms, from the fruit of *Persea gratissima*[1] commonly known as avocado or alligator pear. The sugar exists in the free state in the fruit and this fact is noteworthy because there is thus added another monosaccharide to the small number of such substances which have been found to occur in a free state in nature. It is striking that only two monosaccharides, namely, glucose and fructose, have been found widely distributed in any considerable quantity in the free state among all the numerous natural substances that have been investigated; the occurrence of other sugars in nature seems to be usually in combined forms, such as the complex sugars, polysaccharides and glucosides. The new sugar is both a ketose and a heptose and is accordingly the fourth natural ketose to be isolated, the other three being fructose, sorbose, and ketoxylose,[2] and is the first heptose to be found in nature, the previously known heptoses having all been prepared synthetically from hexoses.

The plant in which the new sugar occurs is also the source of the long known *d*-perseite,[3] a heptahydroxy alcohol which has been shown by Fischer[4] to be the alcohol obtained by the

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* Published with the permission of the Secretary of Agriculture.

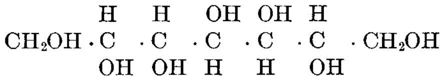
[1] My attention was first called to the presence of an unfermentable sugar in this fruit by Dr. E. E. Butterfield, then of Bellevue Hospital, New York.

[2] Levene, P. A., and La Forge, F. B., *J. Biol. Chem.*, 1914, xviii, 319.

[3] Avequin, *Ann. chem. med. Ph. et Toxic*, 1831, vii, 464. Maquenne, *Compt. rend. Acad.*, 1888, cvii, 583.

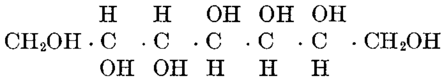
[4] Fischer, E., and Passmore, F., *Ber. chem. Ges.*, 1890, xxiii, 2226.

reduction of α-mannoheptose. The occurrence in the same fruit of these two similar and rare seven carbon members of the sugar group suggests that there may be some biological relationship between them, and this view receives support from the fact that the new heptose can be transformed into *d*-perseite by reduction with sodium amalgam, as will be described later. There is also produced by this reduction a second crystalline alcohol which appears to be identical with *d*-β-mannoheptite which Peirce[5] has lately prepared from *d*-β-mannoheptose. In Peirce's article conclusive proof is advanced that *d*-perseite (*i.e.*, *d*-α-mannoheptite) has the configuration



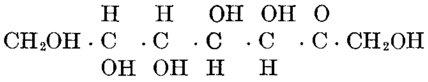
$$\mathrm{CH_2OH}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\mathrm{CH_2OH} \qquad \text{(I)}$$

and the corresponding *d*-β-mannoheptite the configuration



$$\mathrm{CH_2OH}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\mathrm{CH_2OH} \qquad \text{(II)}$$

While the formation from the new heptose of two alcohols having these space formulas may be taken to indicate that it has the configuration



$$\mathrm{CH_2OH}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\overset{\mathrm{O}}{\mathrm{C}}\cdot\mathrm{CH_2OH} \qquad \text{(III)}$$

it is to be remembered that the various alcohols of the sugar group are nearly impossible to distinguish by analysis, and in many cases have such similar properties that positive identification of them is a matter of considerable difficulty. It has, however, been possible to prove conclusively by other means that the avocado sugar has the configuration (III).

Proof That the Avocado Sugar Is d-Mannoketoheptose, of Configuration (III).

The *p*-bromophenylhydrazone of the new sugar was found to contain 20.8 per cent bromine, as an average of three closely

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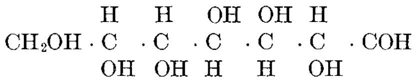
[5] Peirce, G., *J. Biol. Chem.*, 1915, xxiii, 327.

agreeing determinations. Since this hydrazone in the case of a hexose would contain 22.9 per cent bromine, in the case of a heptose 21.1 per cent, and in that of an octose 18.9 per cent, it is evident that the sugar is a heptose. This is in agreement with the fact previously mentioned that the reduction of the sugar yields a heptite, namely, perseite. The percentages of nitrogen and carbon in the *p*-bromophenylhydrazone, as recorded in the experimental part, also point to the same conclusion, which is further corroborated by the estimation of these elements in the phenylosazone of the new sugar. Its nitrogen content was 14.4 per cent as an average of several determinations, and the calculated value for a hexose osazone is 15.6, for that of a heptose 14.4, and in the case of an octose only 13.4. The carbon content was 59.2, and the corresponding values for the osazones of a hexose, heptose, and octose are 60.3, 58.8, and 57.4. This phenylosazone was found to melt at 200° and on comparing this value with the melting points of such of the heptose osazones as are known, it seemed probable that the substance might be identical with *d*-mannoheptose osazone, which Fischer[4] found to melt at about 200°. However, *l*-mannoheptose osazone would of course melt at the same temperature. Since the osazones of the *d* and *l* forms of mannoheptose must have rotations of equal magnitude but opposite sign, a measurement of this property can serve to distinguish the two forms and can also serve as additional evidence that the osazone of one of them is identical with that of the avocado sugar. The osazone of *d*-mannoheptose was prepared and found to rotate in the same direction (right) as the osazone of the avocado sugar, and solutions of the two substances, of equal strengths, in a mixture of pyridine and alcohol, gave the respective values, 0.35 and 0.48°, which do not differ beyond the limits of error. Dr. F. E. Wright in the following article has compared crystals of the two osazones by petrographic-microscopic methods, and finds the substances to be identical. It is, therefore, accepted that the osazone of the avocado heptose is identical with that from *d*-mannoheptose.

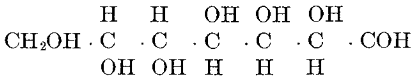
According to considerations of structure, *d*-mannoheptose osazone can be derived from three heptoses just as glucose osazone can be prepared from three hexoses, glucose, mannose, and fructose. One of these heptoses is, of course, *d*-α-mannoheptose which Peirce[5] has shown to have the configuration



$$\begin{array}{lllllll} & \mathrm{H} & \mathrm{H} & \mathrm{OH} & \mathrm{OH} & \mathrm{H} & \\ \mathrm{CH_2OH}\cdot & \mathrm{C} & \cdot\mathrm{C} & \cdot\mathrm{C} & \cdot\mathrm{C} & \cdot\mathrm{C} & \cdot\mathrm{COH} \\ & \mathrm{OH} & \mathrm{OH} & \mathrm{H} & \mathrm{H} & \mathrm{OH} & \end{array}$$

(IV)

A second would be *d*-β-mannoheptose, of configuration



$$\begin{array}{lllllll} & \mathrm{H} & \mathrm{H} & \mathrm{OH} & \mathrm{OH} & \mathrm{OH} & \\ \mathrm{CH_2OH}\cdot & \mathrm{C} & \cdot\mathrm{C} & \cdot\mathrm{C} & \cdot\mathrm{C} & \cdot\mathrm{C} & \cdot\mathrm{COH} \\ & \mathrm{OH} & \mathrm{OH} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \end{array}$$

(V)

and the third would be a ketose having the configuration already given as (III). To distinguish among these three possible configurations for the avocado heptose, it was noted in the first place that its *p*-bromophenylhydrazone was entirely different in melting point and solubility from the *p*-bromophenylhydrazone of *d*-α-mannoheptose, a fact which excludes configuration (IV). Regarding *d*-β-mannoheptose, configuration (V), Peirce records that he was unable to crystallize its *p*-bromophenylhydrazone, whereas the avocado heptose yielded this derivative readily. Since configuration (V) is thus excluded, the new sugar can only be represented by the ketose formula (III), and must accordingly be named *d-mannoketoheptose.*

Further proof of its ketose nature was obtained from the fact that bromine in aqueous solution was without action upon it, corresponding to the general observation[6] that bromine oxidizes aldoses readily but does not affect ketoses.

Considerations on the Configuration of Perseulose.

Bertrand[7] has obtained from *d*-perseite, through the action of *Bacterium xylinum*, a seven carbon sugar, perseulose, which he records as having the following properties: melting point 110–115°, $[\alpha]_D$ initial value -90 mutarotating to $-80°$, and yielding an osazone of melting point 230°. These properties are sufficient to differentiate it from the avocado sugar, nor can it be identical with either of the mannoaldoheptoses which yield the same osazone as the avocado sugar. While these data are sufficient to prove that the avocado sugar is not perseulose and that perseulose

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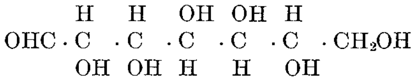
[6] Votoček, E., and Němečk, J., *Z. Zuckerind. Böhmen,* 1910, xxxiv, 399. Nef, J. U., *Ann. Chem.,* 1914, cdiii, 204.

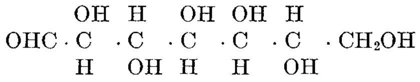
[7] Bertrand, G., *Compt. rend. Acad.,* 1908, cxlvii, 201; 1909, cxlix, 225.

is not one of the mannoaldoheptoses, they do not show positively the configuration of perseulose. It appears, however, from the following additional evidence that its configuration can be established with a fair degree of certainty. Referring back to the configuration of *d*-perseite (I) from which perseulose is derived, it has just been proved that the oxidation to the sugar does not take place at the carbon atom at the extreme right in the formula nor at the carbon atom in the α position to it, because perseulose osazone is not identical with that from the sugars having the structures (III), (IV), and (V), as mentioned above. If it should be that the oxidation takes place at the carbon atom at the extreme left or at the carbon atom in the α position to it, a sugar would be obtained which should yield an osazone identical with that from the two *l*-galaheptoses



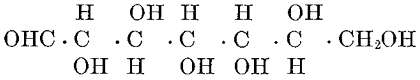
$$\mathrm{OHC}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\mathrm{CH_2OH} \qquad \text{(VI)}$$

and



$$\mathrm{OHC}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\mathrm{CH_2OH} \qquad \text{(VII)}$$

The melting point of perseulose osazone was found to be 230° by Bertrand, and Fischer[8] records the melting point of *d*-galaheptose osazone as 224°, and the melting point of *l*-galaheptose osazone would of course be the same. I have prepared the osazone of *d*-galaheptose and found it to melt at 222°, which agrees with Fischer's determination and is sufficiently close to the value found by Bertrand, when it is remembered that the melting points of the osazones depend considerably on the rate of heating, to indicate with a fair degree of certainty that perseulose osazone is identical either with *d*- or *l*-galaheptose osazone. Peirce has proved that crystalline *d*-β-galaheptose has the configuration



$$\mathrm{OHC}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}\cdot\underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}}\cdot\mathrm{CH_2OH} \qquad \text{(VIII)}$$

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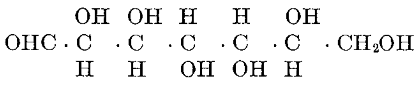
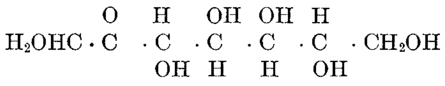
[8] Fischer, *Ann. Chem.*, 1895, cclxxxviii, 139.

which is the antipode of (VII). Neither (VII) nor (VIII) can be the configuration of perseulose because neither can give the configuration of *d*-perseite by reduction. The other *d*-β-galaheptose of configuration



$$OHC\cdot\underset{H}{\overset{OH}{C}}\cdot\underset{H}{\overset{OH}{C}}\cdot\underset{OH}{\overset{H}{C}}\cdot\underset{OH}{\overset{H}{C}}\cdot\underset{H}{\overset{OH}{C}}\cdot CH_2OH \qquad (IX)$$

the antipode of (VI), was obtained by Fischer as an uncrystallizable sirup, whereas perseulose crystallizes readily. Hence, perseulose cannot be identical with either of these sugars and there remains the configuration



$$H_2OHC\cdot\overset{O}{C}\cdot\underset{OH}{\overset{H}{C}}\cdot\underset{H}{\overset{OH}{C}}\cdot\underset{H}{\overset{OH}{C}}\cdot\underset{OH}{\overset{H}{C}}\cdot CH_2OH \qquad (X)$$

This conclusion is supported by Bertrand's generalization that the oxidation of the alcohols of the sugar group by *Bacterium xylinum* only takes place at the carbon atom in an α position, and only then in case the hydroxyl on the β carbon atom is on the same side of the configuration as that on the α carbon.

The conclusion that configuration (X) applies to perseulose requires that perseulose osazone be identical with *l*-galaheptose osazone, rather than with that from *d*-galaheptose, a deduction which is not obtainable alone from the identity of the melting points of the osazones. The osazone of *d*-galaheptose which melted at 222°, as mentioned, was found to rotate to the right. Hence, it must be concluded that *l*-galaheptose osazone, which seems to be identical with perseulose osazone, rotates to the left. The osazone of the avocado sugar rotates to the right, thus completing the evidence that the sugar itself cannot be identical with perseulose or with either of the *l*-galaheptoses.

In addition to *d*-mannoketoheptose and *d*-perseite the pulp of the avocado yielded another carbohydrate; namely, a gum insoluble in aqueous alcohol which gave on hydrolysis *l*-arabinose. The pentose was isolated in the form of its benzylphenylhydrazone.

It should be mentioned that no starch was found in the ripe fruit of the avocado.

In the following article are given crystallographic and optical measurements of mannoketoheptose and an optical comparison of the osazones of mannoketoheptose and mannoaldoheptose.[9]

EXPERIMENTAL.

Preparation of d-Mannoketoheptose from the Avocado.

The pulp of twelve avocados (Trapp variety), the aggregate weight of which was 3,500 gm., was passed through a sieve, mixed with about 6 liters of water, and filtered over night on folded filters. The residue was again extracted with the same amount of water and the combined filtrates were concentrated in a large dish on the steam bath to about 4 liters. The separated protein was removed by filtration and the solution concentrated under diminished pressure, with the addition of amyl alcohol to prevent foaming, to about 1.5 liters. 6 liters of about 98 per cent alcohol were added and the separated gum was filtered off with suction. The filtrate was then concentrated under diminished pressure to 250 to 300 cc. and sufficient absolute alcohol added to cause a permanent turbidity. After standing over night in the ice box, the perseite that had crystallized out was filtered off and the alcoholic solution was concentrated under diminished pressure to a thick sirup. It may be stated at this point that the first crystals of the sugar were obtained by preparing from such a sirup the crystalline *p*-bromophenylhydrazone, decomposing it with benzaldehyde and allowing the concentrated solution of the regenerated sugar to crystallize spontaneously. In later preparations it was found simpler to use the following procedure after crystals of the sugar had become available for seeding. The sirup referred to above was mixed with an equal volume of glacial acetic acid,[10] seeded with a few crystals of the sugar, and allowed

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[9] These were made by Dr. F. E. Wright of the Geophysical Laboratory of this city, to whom I wish to express my thanks. I also wish to thank Dr. C. S. Hudson for revising the manuscript of this article and for helpful suggestions during the course of the work.

[10] According to the method of A. Wernicke, for crystallizing cane sugar (*Ber. chem. Ges.*, 1882, xv, 3105), and U. S. Patent No. 260,340 of June 27, 1882. Dr. I. K. Phelps was the first to use this method in the Bureau of Chemistry.

to stand 3 or 4 days in a desiccator. The crystals which had formed were filtered from the sirupy mother liquor with suction, washed with glacial acetic acid, and finally with alcohol. The yield was about 50 gm. The sugar was recrystallized by dissolving in a very small amount of water and adding several volumes of absolute alcohol. Often, when solutions of the sugar were allowed to evaporate slowly, crystals of 1 to 2 mm. diameter were formed, which appeared as six-sided prisms. The pure sugar melts at 152° uncorrected, without decomposition. Like other heptoses and like the pentoses, it gives a color reaction with orcin and hydrochloric acid. In aqueous solution it showed a dextrorotation as follows:

$$\text{I.}\quad [\alpha]_{\text{D}}^{20} = \frac{+\,2.8° \times 5.5243}{1 \times 1.036 \times 0.5083} = +\,29.37°$$

$$\text{II.}\quad [\alpha]_{\text{D}}^{20} = \frac{+\,2.76° \times 5.5013}{1 \times 1.034 \times 0.5069} = +\,28.97°$$

No mutarotation was observed.

0.1445 gm. substance gave 0.2127 gm. CO_2 and 0.0868 gm. H_2O.

	Calculated for $C_7H_{14}O_7$:	Found:
C	40.00	40.14
H	6.66	6.66

It is not fermentable with yeast nor is the aqueous extract of the fruit.

p-Bromophenylhydrazone.—16 gm. of the thick crude sugar sirup, already referred to, were dissolved in 8 cc. of H_2O, and a solution of 12 gm. of *p*-bromophenylhydrazine in 125 cc. of absolute alcohol was added. The mixture was warmed a few minutes on the steam bath until all was dissolved and was then allowed to stand 24 hours at room temperature.. The solvents were distilled off under diminished pressure and the resulting light brown sirup was mixed with about two volumes of cold water. Crystallization of the hydrazone began at once and was complete after standing for a few hours in the ice box. After filtering with suction and washing with water and then with ether until colored material was no longer removed, the hydrazone was recrystallized from the least possible amount of hot water. The product thus obtained was recrystallized from alcohol, of which about the same amount was necessary for solution as was used of water in the first instance. For a final purification it was again recrystallized from absolute alcohol, of which about five times the above amount was necessary for solution of the purified material. The yield was 10 to 12 gm. The hydrazone crystallizes in thin plates which are usually slightly yellow. It melts at 179° uncorrected.

0.1348 gm. substance gave 0.0662 gm. AgBr.
0.2777 " " " 0.1366 " "
0.2390 " " " 0.1166 " "
0.1479 " " " 10.1 cc. N_2 at 767 mm. and 24°.
0.1316 " " " 0.1985 gm. CO_2 and 0.0579 H_2O.

	Calculated for $C_{13}H_{19}N_2BrO_6$:	Found:
C	41.16	41.13
H	5.01	4.88
N	7.39	7.69
Br	21.10	I. 20.89
		II. 20.75
		III. 20.94

Cleavage of Bromophenylhydrazone.—5.75 gm. of hydrazone were suspended in 250 cc. of 30 per cent alcohol, 4.5 gm. of benzaldehyde added, and the solution was boiled over a free flame until the alcohol was expelled. The *p*-bromophenylhydrazone of benzaldehyde separated out oily at first, but crystallized on cooling. This was filtered off and the filtrate extracted repeatedly with ether and concentrated to a thick sirup under diminished pressure. This was stirred up with very little absolute alcohol and allowed to stand in a desiccator. Crystallization took place after about a week. The yield of the sugar was almost quantitative.

The Phenylosazone of d-Mannoketoheptose.—This was prepared in the usual way from a 1 per cent solution of the pure sugar. It was recrystallized from dilute alcohol and washed with absolute alcohol. It melted at about 200° with rapid heating and the substance mixed with the osazone of mannoaldoheptose melted simultaneously with the separate samples.

0.1375 gm. substance gave 0.2987 gm. CO_2 and 0.0771 H_2O.
0.1485 " " " 19.9 cc. N_2 at 756 mm. and 18°.
0.1457 " " " 18.4 " " " 768 " " 22°.

	Calculated for $C_{19}H_{24}O_6N_2$:	Found:
C	58.76	59.24
H	6.19	6.23
N	14.43	I. 14.55 II. 14.38

A solution of 0.1000 gm. of osazone from the avocado sugar in 5 cc. of pyridine alcohol mixture rotated with sodium light in a 0.5 dm. tube after about 15 minutes + 0.74°, to the right, and after 24 hours + 0.35°.

A solution of 0.1000 gm. of osazone from mannoaldoheptose under the same conditions rotated after 15 minutes + 0.78°, to the right, and after 24 hours + 0.48°.

Attempt to Oxidize the Avocado Sugar with Bromine.—An aqueous solution of the sugar, 5 cc. of which corresponded to (I) 0.0964 gm. of Cu_2O, (II) 0.0954 gm. of Cu_2O, was allowed to stand for 4 days with an excess of bromine. After this time 5 cc. were boiled to remove the bromine and corresponded to 0.0952 gm. of Cu_2O, which shows that no appreciable oxidation had taken place.

Reduction of Heptose.—6.5 gm. of the avocado sugar were reduced with sodium amalgam in the usual way. The solution was kept at about 0° for the first 4 hours and neutralized with sulfuric acid frequently throughout the reaction. After about 8 hours' action of the amalgam, the solution which then showed no reduction with Fehling's solution was concentrated under diminished pressure until a large part of the sodium sulfate had crystallized out. It was then poured into 1.5 liters of 95 per cent alcohol and the alcoholic solution concentrated to about 15 cc. and diluted with about 200 cc. of absolute methyl alcohol. On standing 24 hours, 1.25 gm. of *d*-perseite crystallized out. This was once recrystallized from dilute methyl alcohol and it melted then at 188°. It rotated in saturated aqueous borax solution as follows:

$$[\alpha]_D^{20} = \frac{+0.41° \times 5.6062}{1 \times 0.5069} = +4.53°$$

The characteristic heptacetate of *d*-perseite was obtained by warming one part of the crystals with ten parts of acetic anhydride in the presence of a trace of zinc chloride. The reaction mixture was poured into water and after the oil which first separated out had crystallized, the product was filtered off and purified by recrystallization from 70 per cent alcohol. It melted at 119°.

0.1526 gm. substance gave 0.0831 gm. H_2O and 0.2806 gm. CO_2.

	Calculated for $C_{21}H_{30}O_{14}$:	Found:
C	49.80	50.14
H	5.92	6.05

From the filtrate from perseite the second heptite was obtained on evaporation as a sirup which crystallized on slow addition of alcohol and stirring. After washing with 95 per cent alcohol and drying, the yield amounted to 2.6 gm. This second hexite was recrystallized three times from fifteen to twenty parts of 95 per cent alcohol, and it melted at about 140° to a turbid viscous liquid which did not become clear until the temperature was raised to about 215°. It was, therefore, sublimed in a high vacuum and was then found to melt simultaneously with a sample of *d*-β-mannoheptite prepared by Peirce, at 149–155°, uncorrected.

0.1425 gm. substance gave 0.0952 gm. H_2O and 0.2071 gm. CO_2.

	Calculated for $C_7H_{16}O_7$:	Found:
C	39.60	39.63
H	7.64	7.42

In aqueous solution it showed a dextrorotation as follows:

$$[\alpha]_{D}^{20} = \frac{+0.24^\circ \times 5.4987}{1 \times 0.5174} = +2.55^\circ$$

0.4994 gm. in 5 cc. of saturated aqueous borax solution rotated in a 1 dm. tube + 0.93°.

d-Galaheptose Osazone.—This was prepared in the usual way from *d*-α-galaheptose.[8] It crystallized from methyl alcohol in long needles which melted at 216° (222° corrected). A solution of 0.1 gm. of substance in 10 cc. of pyridine alcohol mixture rotated in a 1 dm. tube and D-light + 0.60°, to the right, and after 48 hours + 0.40°.

p-Bromophenylhydrazone of d-Mannoaldoheptose.—Equal parts of α-mannoaldoheptose and *p*-bromophenylhydrazine were dissolved on the steam bath in thirty parts of 75 per cent alcohol, and the solution was allowed to stand for 24 hours at room temperature. The yield was quantitative. The substance is difficultly soluble in water. It was recrystallized from a large volume of alcohol, in which it is also extremely difficultly soluble. It melted at 207–208° uncorrected.

0.2020 gm. substance gave 13.60 cc. N_2 at 768 mm. and 25°.

	Calculated for $C_{13}H_{19}N_2BrO_6$:	Found:
N	7.39	7.55

Hydrolysis of the Gum from the Avocado.—100 gm. of gum which had been purified by dissolving in a small amount of water, filtering, and precipitating with alcohol were hydrolyzed for 3 hours with 1 liter of about 9 per cent sulfuric acid. The acid was removed with barium carbonate and the filtrate concentrated to a sirup which was extracted with hot alcohol. The alcoholic solution was concentrated under diminished pressure to a small volume and the benzylphenylhydrazone of *l*-arabinose prepared by adding to the warm solution the calculated amount of benzylphenylhydrazine. After recrystallization from alcohol, it melted at 174° uncorrected.

0.2044 gm. substance gave 15.8 cc. N_2 at 772 mm. and 25°.

	Calculated for $C_{18}H_{22}N_2O_4$:	Found:
N	8.48	8.72

l-Arabinose Osazone.—This derivative was prepared from the hydrolytic product from the gum in the usual way. It was recrystallized three times from water and melted then at 158° uncorrected.

0.1000 gm. of substance in 10 cc. of pyridine alcohol mixture rotated in a 1 dm. tube with sodium light after 10 minutes, + 0.60°, to the right, and after 6 hours + 0.30° in the same direction.