The probable error in the density determinations is less than 0.05%; with the aid of a cathetometer it can be reduced to 0.01%.

McGill University.

[Contribution from the Bureau of Chemistry, U. S. Department of Agriculture.]

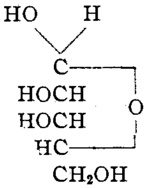
CRYSTALLOGRAPHY AND OPTICAL PROPERTIES OF THREE ALDOPENTOSES.

By Edgar T. Wherry.

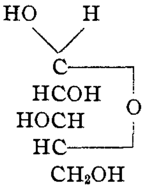
Received September 6, 1918.

The aldopentoses, of which the general formula is $C_5H_{10}O_5$, have each a *d*- and an *l*-form, and each of these in turn exists in an α- and a β-modification, as brought out by the following formulas:

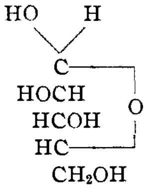
d-lyxose.



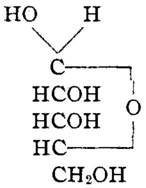
d-xylose.[1]



d-arabinose.



d-ribose.



The arrangement used is the conventional method of representing the *d*-forms; the *l*-forms would have the positions of all the groups along either side of the carbon chain reversed. The lactone structure is adopted because it is the only one which makes it possible to bring out the difference between the α- and β-modifications. These differ in the relative positions of the uppermost H and OH groups, although it has not yet been ascertained which position corresponds to each.

The crystallographic and optical properties of *d*- and *l*-forms are necessarily the same, except that the positions of (*hkl*) faces would be toward the right and toward the left of the crystal in the two cases. It would seem probable that the α- and β-isomerism has a more fundamental effect on the crystallization, and the following studies were undertaken to ascertain the extent of this effect, as well as to compare the properties of as many of the members of the group as possible. Three were obtainable in crystals of sufficient size for measurement of their angles, and one additional isomer in a form suitable for optical examination under the microscope.

The identities of the isomers measured were established by the following specific rotations $[\alpha]_D^{20}$:

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[1] In the case of xylose, Fischer regarded the formula given as belonging to the *l*-form, but Rosanoff (This Journal, **28**, 114 (1906)) pointed out that this conclusion was based on erroneous assumptions, and Hudson (*Ibid.*, **31**, 70 (1909)) has fully confirmed this view.

α-*d*-lyxoses: initial, + 5; final, —14;
α-*d*-xylose: initial, + 92; final, + 19;
β-*d*-arabinose: initial, —175; final, —105.

I. Crystallography.

Lyxose.

Crystals of synthetic α-*d*-lyxose have been measured by Sachs;[1] recalculated into angle-table form, his results are as follows:

LE I.—ANGLE-TABLE FOR α-*d*-LYXOSE.

System, Monoclinic; Class, seemingly prismatic, but probably sphenoidal.

$a:b:c = 1.608:1:1.828$; $\beta = 62°\ 10'$ or $117°\ 50'$.

		Symbols.			Observed.		Calculated.	
No.	Letter.	Gdt.	Mill.	Description.	φ.	ρ.	φ.	ρ.
1......	*c*	0	001	Larger terminal faces	90° 00′	28° 05′	90° 00′	27° 50′
2......	*a*	∞0	100	Narrow but definite	90° 00′	90° 00′	90° 00′	90° 00′
3......	*m*	∞	110	Dominant form in prism zone	35° 08′	90° 00′	35° 08′	90° 00′
4......	*d*	$\bar{1}0$	$\bar{1}01$	Smaller terminal faces	90° 00′	36° 40′	90° 00′	37° 09′

The calculated angles given correspond to the axial values obtained by Sachs, using angles $m:m'$, $c:m$ and $d:m$ as fundamental. The divergence between these and the results of observation is due to the rather poor quality of the crystals measured. Under these circumstances the axial values can not be regarded as established beyond the second decimal place.

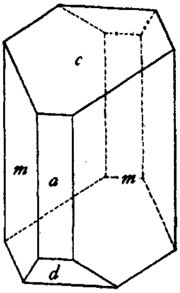

Fig. 1.—α-Lyxose (after Sachs).

Xylose.

No measurements appear to have been made on this sugar heretofore. A sample of pure precipitated α-*d*-xylose (in the collection of the Carbohydrate Laboratory) was dissolved in hot water, filtered into a crystallizing dish, and allowed to stand loosely covered in a room kept at approximately constant temperature for several days. Numerous minute crystals separated, of which a few of the largest were removed; the solution was then brought to boiling, so as to dissolve all of the crystals remaining in it, and again allowed to cool. When cold the crystals which had previously been picked out were dropped in, and the dish was closely covered and allowed to stand overnight. Crystals about 5 mm. long were obtained; they were rod-shaped and doubly terminated, although because of sub-parallel intergrowth they showed curvature and bulging toward their centers. All of the faces were, in fact, somewhat rounded, and gave rather poor

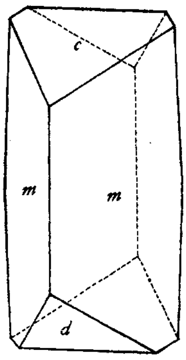

Fig. 2.—α-Xylose. Showing central bulging.

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[1] *Z. Kryst. Min.*, **34**, 158 (1901).

reflections of the goniometer signal, but as no better crystals could be obtained in spite of repeated trials, the measurements obtained upon these are here recorded. The orientation adopted is that which brings this sugar into correspondence with lyxose, as described above.

TABLE II.—ANGLE-TABLE FOR *α-d*-XYLOSE.

System, Monoclinic; Class, seemingly prismatic, but probably sphenoidal.

$a:b:c = 1.655:1:1.776$; $\beta = 62° 55'$ or $117° 05'$.

		Symbols.			Observed.	
No.	Letter.	Gdt.	Mill.	Description.	φ.	ρ.
1...........	*c*	0	001	One set of terminal faces	90° 00'	27° 05'
2...........	*m*	∞	110	Only form in prism zone	34° 10'	90° 00'
3...........	*d*	$\bar{1}0$	$\bar{1}01$	The other set of terminal faces	90° 00'	34° 45'

Arabinose.

Minute and rather poorly developed prismatic crystals of *l*-arabinose have been measured by Groth and Hintze,[1] and somewhat better crystals of the *d*-form by Traube.[2] The axial values obtained by the latter are adopted by Groth[3] as characteristic of the sugar, although the value of axis *a* given does not agree with the angles; it should be 0.6686 (tan. 33° 46'). As no relationship between these crystals and those of the other two members of the group is evident from the data given by these authors, it was decided to study arabinose further. A sample of *β-d*-arabinose prepared by Dr. E. Yanovsky was available for this purpose; it consisted of needle-like crystals several millimeters in length, many of which showed brilliant faces, yielding good reflections. A slight bulging toward the center, (less than in xylose), prevented great accuracy in the measurement of the angles, but the errors probably do not exceed 15'.

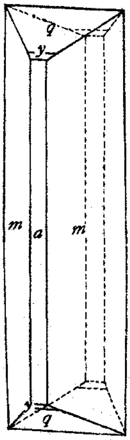

Fig. 3.—*β*-Arabinose. Simple crystal.

The crystal system is in this case rhombic, but if the orientation adopted by the writers above cited be changed so as to make their axis *a* the right-left axis *b*, several points of similarity with the other two pentose sugars may be brought out. The first two indices of all the forms are, correspondingly, to be transposed. The results of the measurements are given in Table III; they are reasonably close to those of the previous authors.

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[1] *Ber.*, **6**, 615 (1873).

[2] *Ibid.*, **26**, 741 (1893).

[3] *Chem. Kryst.*, **3**, 380 (1910).

TABLE III.—ANGLE-TABLE FOR β-ARABINOSE.

System, Rhombic; Class, seemingly prismatic, but probably bisphenoidal.

$a:b:c = 1.497:1:0.738$.

No.	Letter.	Symbols.		Description.	Observed.		Calculated.	
		Gdt.	Mill.		φ.	ρ.	φ.	ρ.
1....	*a*	∞0	100	Narrow but distinct	90° 00′	90° 00′	90° 00′	90° 00′
2....	*n*	3∞	310	(Groth and Hintze)	...	...	63° 29′	90° 00′
3....	*m*	∞	110	Dominant prism form	33° 45′	90° 00′	...	90° 00′
4....	*l*	∞2	120	Narrow but fair	18° 30′	90° 00′	18° 28′	90° 00′
5....	*x*	$^5/_2$ 0	502	(Groth and Hintze)	...	...	90° 00′	11° 10′
6....	*q*	10	101	Dominant terminal form	90° 00′	26° 15′	90° 00′	...
7....	*y*	$^2/_3$ 0	203	New; a narrow terminal form	90° 00′	37 ±	90° 00′	36° 30′

The striking similarities between the three sugars of this group are shown by the angles listed in Table IV.

TABLE IV.—COMPARATIVE ANGLES OF THREE SUGARS.

	ρ of prominent terminal form.	ρ of another terminal form.	φ of dominant prism.
Lyxose........................	27° 50′	37° 09′	35° 08′
Xylose........................	27° 05′	34° 45′	34° 10′
Arabinose.....................	26° 15′	36° 30′	33° 45′

The crystallization of arabinose in another system than the other two sugars is evidently due to the fact that the β- rather than the α-form is represented. But in spite of this difference, its angles are closely related to those shown by the others, and the group is thus essentially isomorphous. The α-form could not be isolated in measurable crystals, but optical study suggested it to be monoclinic like the others.

II. Optical Properties.

Observations upon the optical properties of these sugars were made by the methods recently outlined by the writer,[1] with certain modifications, as follows:

Since sugars are soluble in aqueous liquids, it becomes necessary to use oils for the determination of the refractive indices by the immersion method. The three liquids best suited to this purpose are turpentine oil, with $n = 1.47$, clove oil with $n = 1.53$, and α-monobromonaphthalene, with $n = 1.66$. Mixtures of these in the proportions calculated so that each will differ in n from the next by 0.003 are then prepared, and their exact ns determined on a refractometer. In addition to making observations on the crystals in yellow light, it is well to match each index for several different wave-lengths, and to find the n for the D line by interpolation.

Lyxose.

A small sample of synthetic α-*d*-lyxose in the collection of the Carbohydrate Laboratory was available for optical study. It proved to consist

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[1] U. S. Dept. Agr., *Bull.* 679, 1918.

of minute but well crystallized grains, and the following results were obtained upon it:

In ordinary light: colorless; grains mostly six-sided and but little elongated in any direction.

Refractive indices for D: $\alpha = 1.532$, $\beta = 1.541$, $\gamma = 1.549$, $\gamma - \alpha = 0.017$, all ± 0.001; α is usually shown in one direction, and γ in the other.

In parallel polarized light: Extinction inclined, the angle being, however, very small; double refraction moderate, colors being mostly first or second order.

In convergent polarized light: Interference figures rarely seen, but occasionally part of a negative biaxial figure with very large axial angle is obtained.

Xylose.

The optical properties of the pure recrystallized *α-d*-xylose were found to be as follows:

In ordinary light: colorless; crystals rod-like, with oblique terminations, breaking o irregular fragments.

Refractive indices for D: $\alpha = 1.517$, $\beta = 1.544$, $\gamma = 1.546$, $\gamma - \alpha = 0.029$, all ± 0.001; α is usually shown horizontally, and γ vertically.

In parallel polarized light: Extinction inclined, but angle very small; double refraction strong, the colors being mostly of third order; elongation of crystals negative.

In convergent polarized light: partial interference figures are frequently obtained; they are biaxial with a moderately large axial angle, $2E = 50°$, and negative sign.

Arabinose.

The crystallized *β-d*-arabinose above described showed the following optical properties:

In ordinary light: colorless; crystals rod-like, showing cleavage lengthwise, parallel to the face taken as *a* (100), and splitting into fragments bounded in part by this cleavage.

Refractive indices for D: $\alpha = 1.555$, $\beta = 1.573$, $\gamma = 1.577$, $\gamma - \alpha = 0.022$, all ± 0.001; α is usually shown horizontally, and γ vertically.

In parallel polarized light: Extinction straight; double refraction moderately strong, colors being mostly of second order; elongation negative.

In convergent polarized light: partial interference figures are sometimes obtained; they are biaxial with a large axial angle, $2E = 80°$, and the sign is negative.

A specimen of natural *l*-arabinose was also examined; it consisted of a mixture of the α- and β-forms of the sugar; the latter agreed in properties with the synthetic material above described; the former was in small rod-shaped crystals with the following properties:

In ordinary light: colorless; habit rod-like, with prominent oblique terminations, the rods being often collected in stellate groups or twins.

Refractive indices for D: $\alpha = 1.551$, $\beta = 1.567$, $\gamma = 1.571$, $\gamma - \alpha = 0.020$, all ± 0.001; α is usually shown horizontally, and γ vertically.[1]

In parallel polarized light: Extinction apparently inclined, but angle small; double refraction moderately strong, the colors being mostly first order; elongation negative.

In convergent polarized light; only traces of negative biaxial figures with large axial angle (90°?) obtainable.

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[1] Bolland, *Monatsh.*, 31, 408 (1910) gave $\alpha = 1.545$ and $\gamma = 1.560$ for this sugar; be used, however, white light, and his measurements appear to have been only approximate.

The results of refractive index measurement in light of different wave-lengths are summarized in Table V.

TABLE V.—DISPERSIONS OF THE ALDOPENTOSES.

Substance.	Index.	Wave-lengths.					
		450.	500.	550.	D. 589.	600.	650.
α-Xylose.......	α	1.525	1.521	1.518+	1.517	1.516+	1.515
	β	1.553	1.549	1.546	1.544	1.543+	1.542
	γ	1.555	1.551	1.548	1.546	1.545	1.543+
	γ — α	0.030	0.030	0.030	0.029	0.029	0.028
α-Lyxose.......	α	1.541	1.537	1.534	1.532	1.531+	1.530
	β	1.550	1.546	1.543	1.541	1.540	1.538+
	γ	1.559	1.554+	1.551	1.549	1.548	1.547
	γ — α	0.018	0.017	0.017	0.017	0.017	0.017
α-Arabinose....	α	1.560	1.556	1.552+	1.551	1.550	1.549
	β	1.576	1.572	1.569	1.567	1.566	1.565
	γ	1.581	1.577	1.573	1.571	1.570	1.569
	γ — α	0.021	0.021	0.021	0.020	0.020	0.020
β-Arabinose....	α	1.565	1.561	1.559	1.555	1.554	1.553
	β	1.584	1.579	1.576	1.573	1.572	1.571
	γ	1.588	1.583	1.579	1.577	1.576	1.574
	γ — α	0.023	0.022	0.022	0.022	0.022	0.021

Other Physical Properties.

The much higher refractive indices shown by arabinose than by either of the other sugars of the group made a determination of the specific gravity of the several members seem desirable. This was accomplished by suspending a few crystals of each in carbon tetrachloride, and adding benzene until the crystals neither floated nor sank on being stirred up. The specific gravities of the mixtures were then taken by means of a Westphal balance at 20°. From these data the refractivities could be calculated, by the formula $M = n^2 - 1/n^2 + 2 \, . \, W/\rho$. The results are presented in Table VI, and show the close physical relationship between these sugars:

TABLE VI.—PHYSICAL PROPERTIES OF ALDOPENTOSE SUGARS ($W = 150.1$).

	Refractive indices. D.								
	α.	β.	γ.	γ — α.	Mean n.	2 E.	Sign.	Sp. gr. (ρ).	Refractivity (M).
Lyxose......	1.532	1.541	1.549	0.017	1.541	Large	—	1.545	30.60
Xylose......	1.517	1.544	1.546	0.029	1.536	50°	—	1.525	30.67
α-Arabinose.	1.551	1.567	1.571	0.020	1.563	Large	—	1.585	30.76
β-Arabinose.	1.555	1.573	1.577	0.022	1.568	80°	—	1.605	30.61

The theoretical value of the refractivity, based on C = 2.4, H = 1.1, O′ = 1.5, and O″ = 2.2, is 31.2; the observed values on all the members of the group are somewhat less than this, probably because of some influence of their configuration upon this property, the exact nature of which cannot, however, be determined.

The sugars of this group may be readily distinguished by their optical properties, for which purpose the following determinative table may be used:

TABLE VII.—DETERMINATIVE TABLE FOR THE ALDOPENTOSES.

Immerse a few grains in an oily liquid with refractive index n = 1.53 and examine with polarizing nicol in and diaphragm partly closed.

One refractive index decidedly lower than that of the liquid; between crossed nicols shows 2nd or 3rd order colors; in convergent light frequently yields interference figures...α-XYLOSE.

One index about equal to that of liquid; between crossed nicols shows first or second order colors; in convergent light rarely yields figures.........α-LYXOSE.

All indices decidedly higher than that of liquid; between crossed nicols shows mostly 2nd order colors; in convergent light rarely yields figures..ARABINOSE.

(Lowest index of α-form less, of β-form greater, than 1.553).

Identification should be confirmed in each case by the measurement of one other refractive index, according to data previously given.

Summary.

The crystallography and optical properties of three aldopentose sugars are described in detail, and the close resemblances existing among them pointed out. The usefulness of optical properties for distinguishing these substances is indicated, a determinative table being given.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON.]

CALORIMETRIC LAG.

BY WALTER P. WHITE.

Received September 8, 1918.

This paper makes an addition to the mathematical treatment of lag effects in calorimetry, and also derives therefrom several suggestions for advantageous experimental arrangements.

Calorimetry is a subject in which a very simple measurement, that of a temperature change, is considerably complicated by the tendency of heat to leak to or from the apparatus. The complication is three-fold: there is first the necessity of calculating the loss or gain of heat; then in order to make any definite temperature measurements possible the irregularity produced by the leakage must be overcome, usually by employing a liquid that can be stirred, which brings in errors from fluid friction and evaporation; finally, in spite of this procedure there still are some uncorrected irregularities, or lags. These lags, with one partial exception, the lag from insufficient stirring, depend on the spontaneous flow of heat, that is, on conduction and radiation. Exact data regarding these processes are nearly always hard to get, hence experimenters, whenever they have recognized a lag, have usually felt safer at first in eliminating or abolishing it as far as possible. On the other hand, the fundamental laws of