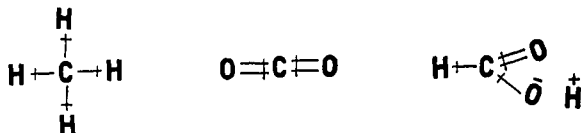


The method of notation illustrated herewith, which uses a cross line at one end of a bond line has the advantage of simplicity in writing, inasmuch as the valences in an ordinary structural formula can be changed to show a definite polarity by one stroke of the crayon, and there is no chance



for confusion of the negative sign with the valence sign. Valences in which the polarity is not known or need not be considered can be left in the original form. A distinctly non-polar valence can if desired be indicated by writing the cross mark across the center of the valence sign. One of the main advantages of the method suggested is that it gives a notation for a small difference in polarity, different from the notation customarily used to indicate ionization. It is possible to indicate mere differences of polarity and ionization in the same formula without confusion.

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A REVISION OF ROSANOFF'S DIAGRAM OF THE ALDOSE SUGARS^{1,2}

By J. J. WILLAMAN AND CLARENCE A. MORROW

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In 1906 M. A. Rosanoff³ published a critique of Fischer's classification of stereo-isomers in the sugar group. He pointed out that, although the latter's system of grouping into one family all the sugars which are genetically related, and all the enantiomorphs of these sugars into an opposite family is excellent in principle, it contains several gross errors. These errors are partly due to the order of discovery of certain members of the group, and partly to a false premise regarding the bases for genetic relationships among stereo-isomers. Rosanoff proposed a modified system of classification which would eliminate the discrepancies. He supported his argument by a diagram, which showed by means of symbols the rational

¹ Published with the approval of the Director as Paper No. 279, Journal Series, Minnesota Agricultural Experiment Station.

² Presented at the meeting of the American Chemical Society, Sept. 9, 1921.

³ Rosanoff, *THIS JOURNAL*, 28, 114 (1906).

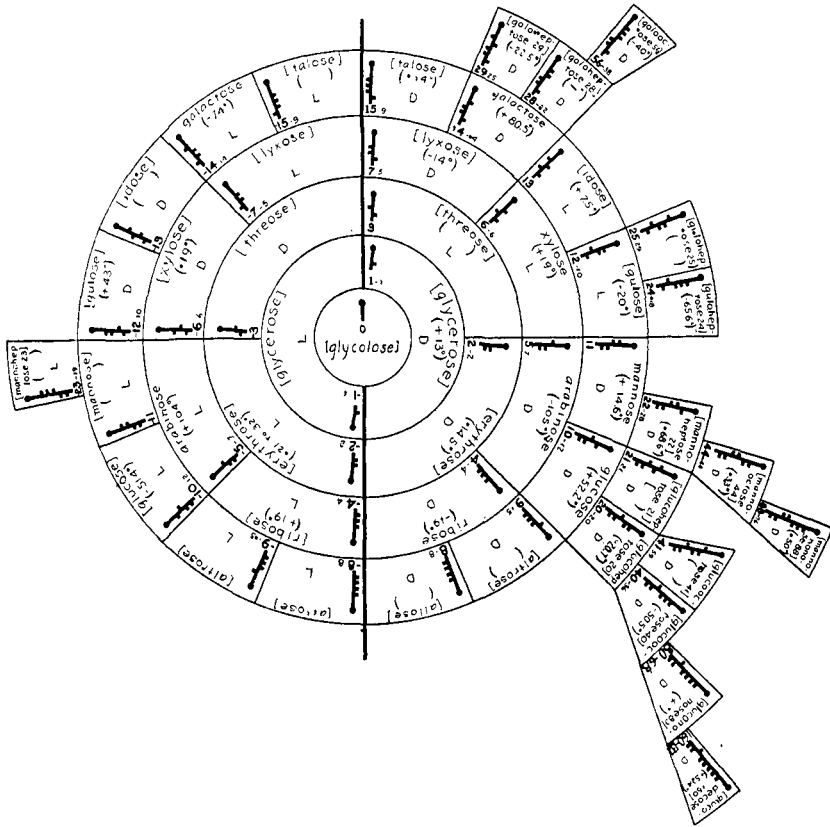


Fig. 1.—The structural relationships among the aldose sugars, together with data concerning their specific rotation, occurrence and Fischer classification.

ALCOHOL AND DICARBOXYLIC ACID DERIVATIVES OF THE ALDOSE SUGARS			
Space in diagram	Sugars	Dicarboxylic acids	Alcohols
0	Glycolose	Oxalic	Ethylene glycol
1, -1	Glycerose	Tartronic	Glycerol
2, -2	Erythrose	Mesotartaric	Meso-erythrol
3	Threose ^a	δ-Tartaric ^a	δ-Erythrol ^a
-3	Threose ^a	λ-Tartaric ^a	λ-Erythrol ^a
4, -4	Ribose	Ribotrihydroxyglutaric	Adonitol
5, 7	Arabinose	δ-Arabortrihydroxyglutaric	δ-Arabitol
-5, -7	Arabinose	λ-Arabortrihydroxyglutaric	λ-Arabitol
6, -6	Xylose ^a	Xylotrihydroxyglutaric	Xylitol
7, 5	Lyxose	= 5, 7	= 5, 7
8, -8	Allose	Allomucic	(Allitol)
9, 15	Altrose	δ-Talomucic	δ-Talitol
-9, -15	Altrose	λ-Talomucic	λ-Talitol
10, -12	Glucose	δ-Saccharic	δ-Sorbitol
-10, 12	Glucose	λ-Saccharic	λ-Sorbitol
11	Mannose	δ-Mannosaccharic	δ-Mannitol
-11	Mannose	λ-Mannosaccharic	λ-Mannitol
12, -10	Gulose ^a	= -10, 12	= -10, 12
-12, 10	Gulose ^a	= 10, -12	= 10, -12

13	Idose ^a	δ -Idosaccharic ^a	δ -Iditol ^a
-13	Idose ^a	λ -Idosaccharic ^a	λ -Iditol ^a
14, -14	Galactose	Mucic	Dulcitol
15, 9	Talose	= 9, 15	= 9, 15
-15, -9	Talose	= -9, -15	= -9, -15
20, -20	Glucuheptose 20	Glucuheptonic	Glucuheptitol
21, 27	Glucuheptose 21	Glucuheptonic	Glucuheptitol
22, -28	Mannoheptose 22	Mannoheptonic	Perseitol
-23, -19	Mannoheptose 23	Mannoheptonic	Mannoheptitol
24, -18	Guloheptose 24	Guloheptonic	Guloheptitol
25, 29	Guloheptose 25	Guloheptonic	Guloheptitol
28, -22	Galaheptose 28	Galaheptonic	Galaheptitol
29, 25	Galaheptose 29	= 25, 29	= 25, 29
40, -36	Gluco-octose 40	(Gluco-octonic)	Gluco-octitol
41, 59	Gluco-octose 41	(Gluco-octonic)	(Gluco-octitol)
44, -44	Manno-octose 44	(Manno-octonic)	Manno-octitol
56, -38	Gala-octose 56	(Gala-octonic)	Gala-octitol
80, -68	Glucononose 80	(Gluconononic)	Glucononitol
88, -76	Mannononose 88	(Mannonononic)	(Mannononitol)
160, -132	Glucodecose 160	(Glucodeconic)	Glucodecitol

^a Compounds whose family designation is the reverse of that assigned by Fischer.

structural relationships among, and logical classification of, the aldose sugars and their derivatives. In this diagram all aldoses derivable from Fischer's *d*-glycerose are in the right semicircle, and all those from *l*-glycerose in the left. Rosanoff named them, respectively, the δ and λ families. They are arranged on the basis of accepted projection-formulas, all of which were proposed by Fischer himself. This results in placing four sugars, threose, xylose, gulose and idose, which Fischer had designated as *l*-compounds, in the right half of the circle, with an obvious clash in nomenclature. This gives rise to the question: shall we accept Fischer's nomenclature because of its historical significance, or shall we reject it in favor of a rational system? Fischer's prestige has naturally been such as to cause hesitancy in changing his designations of these 4 sugars. Hudson,⁴ however, has adopted the new classification; and Armstrong, in the third edition of his monograph on the carbohydrates,⁵ announces his acceptance of it. Fischer's designations still appear throughout the German literature, and to a great extent in the English. The above writers reverse the family designations of these 4 sugars, but do not use the symbols δ and λ . Since the more often the rational system has attention called to it the quicker will the irrational disappear from the literature, and since the writers believe that certain modifications of Rosanoff's diagram make it more useful in the study of the sugars, they present herewith a revision of it.

Objects of the Revision.—1. Since the original diagram was published, several of the theoretically possible aldoses, unknown at that time, have been prepared, and are now included in the diagram. Diagrams have also been prepared which contain the ketoses and the methylaldoses that are now known.

⁴ Hudson, THIS JOURNAL, 31, 66 (1909); 39, 1013 (1917); 40, 997 (1918).

⁵ E. F. Armstrong, "The Simple Carbohydrates and the Glucosides," Longmans, Green and Co., London, 1919, 3rd ed., pp. 34-38.

2. The original diagram included only the aldoses through 6 carbon atoms. It is now made to include all those known at the present time beyond 6 carbon atoms.

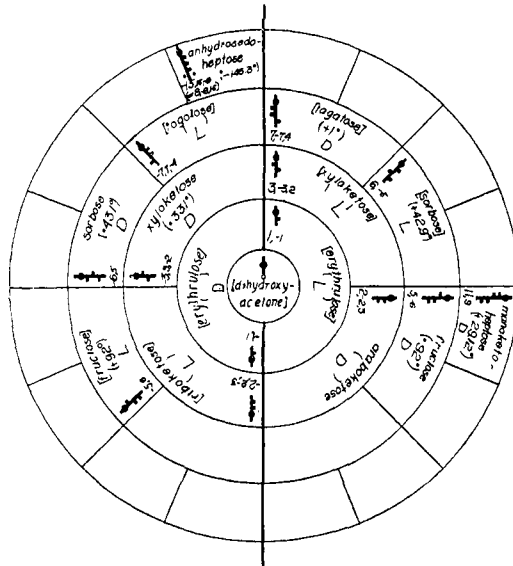


Fig. 2.—The structural relationships among the ketose sugars, together with data concerning their specific rotation, occurrence and Fischer classification.

ALCOHOL DERIVATIVES OF THE KETOSE SUGARS					
Sugars	Space in diagram	Alcohols	Sugars	Space in diagram	Alcohols
Dihydroxyacetone	0	Glycerol	Sorbose	6	λ-sorbitol δ-iditol ^a
Erythrulose	1	δ-erythrol ^a meso-erythrol		-6	δ-sorbitol λ-iditol ^a
	-1	λ-erythrol ^a	Tagatose	7	δ-talitol
Riboketose	2	δ-arabitol adonitol		-7	dulcitol λ-talitol
	-2	λ-arabitol	Mannoketoheptose	11	δ-perseitol δ-mannoheptitol 23 taloheptitol 30 (sedoheptitol) volemitol
Xyloketose	3	δ-arabitol xylytol	Sedoheptose	15	
	-3	λ-arabitol			
Fructose	5	δ-sorbitol δ-mannitol λ-sorbitol λ-mannitol			
	-5				

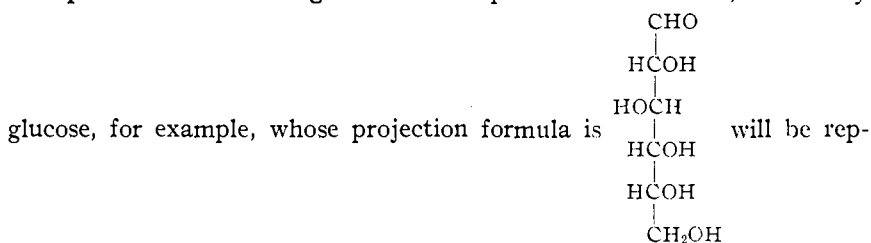
^a Compounds whose family designation is the reverse of that assigned by Fischer.

3. To make such a diagram of the greatest use, it should contain as much information as possible without being crowded. Therefore, in each space in the diagram the following facts have been included, which were not included by Rosanoff: (a) the name of the sugar; (b) its specific rotatory power; (c) an indication as to whether it occurs in nature. The facts included by Rosanoff are retained as well. They are: (d) the projection formula by means of a symbol; (e) the original Fischer designation

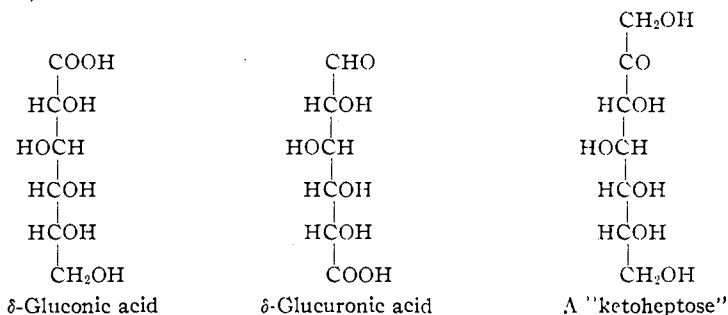
of family relationship, as *d* or *l*; (*f*) an index number or numbers, which, referred to a legend, gives the name of the sugar and that of its corresponding acid and alcohol.

4. A fourth, but minor, change from the original is in the arrangement of the sugars in the semicircle, depending upon the position of the new secondary alcohol group introduced by the cyanohydrin synthesis when passing to a series containing one more carbon atom. This is explained in Paragraph 3 below.

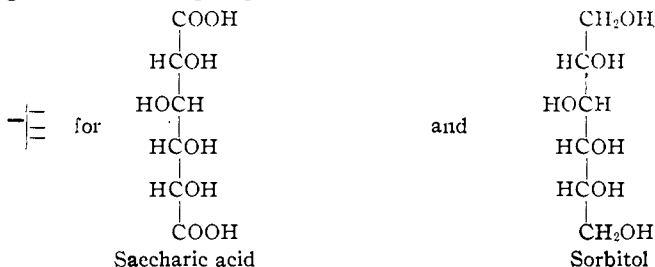
Explanation of the Diagram.—1. To quote from Rosanoff, "Ordinary



and the same symbol will stand for all other compounds with different terminal groups and stereochemically similar to glucose, such as



Since in the present paper monocarboxylic acids are not discussed, the symbol has been modified so that the dot signifies the aldehyde or ketone group. When the dot is removed, the symbol represents a compound having like terminal groups, as



Thus the flags represent the hydroxyl groups of the secondary alcohol groups, and thus also such groups as affect the stereochemical properties of the compound. In Fig. 3 the hollow circle represents the methyl group.

2. δ -Glycerose is represented as having its hydroxyl group to the right; λ -glycerose, to the left. Hence, all the derivatives of δ -glycerose fall in the right semicircle of the diagram, all have the basal hydroxyl group on the right, and all belong to the δ -family of sugars.

3. When, by means of the cyanohydrin synthesis, a sugar has one more carbon atom added to its chain, 2 epimeric sugars result, one having the

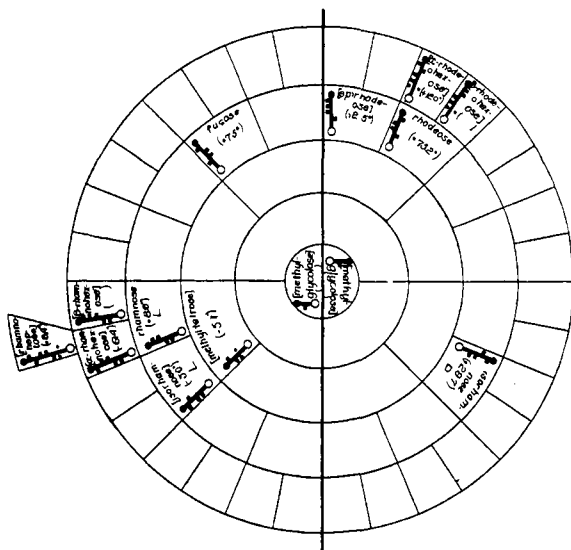


Fig. 3.—The relationships among the methyl aldoses, together with data concerning their specific rotation, occurrence and Fischer classification.

hydroxyl group of the new α -carbon atom on the right, the other on the left. In the diagram, the sugar with it on the right is placed in the right of the two corresponding sections; the one with it on the left, in the left section. The reverse arrangement was used by Rosanoff, for no apparent reason. The new arrangement adds to the geometrical perfection of the diagram. The sugars bear the same index numbers, however, as in the original with the exception of the correction of a few obvious errors in signs.

4. The two semicircles are, of course, the mirror images of each other.

5. The index numbers under the symbols indicate the derivation of alcohols and dicarboxylic acids from the aldoses. To quote again from Rosanoff: "Thus aldose 11 (δ -mannose) leads to an acid and an alcohol not derivable from any other aldose. The designation 5₇ [or 7₅] shows that two different aldoses, 5 and 7, the lyxose and arabinose of the same

δ -family, yield the same (active) acid and alcohol. The designation 14-₁₄ shows that the two enantiomorphous galactoses, 14 and -14, yield the same (hence optically inactive) acid and alcohol. Finally, the designation 10-₁₂ indicates that two aldoses belonging to the opposite families yield the same saccharic acid and sorbite; the aldoses not being enantiomorphous, the acid and alcohol must obviously be optically active. The antipodal acid and alcohol are derived from the aldoses -12 and 10, as indicated by the designation -12₁₀.⁶ The legends to the diagrams give the names both of the acid and of the alcohol derivatives of the aldoses, but only of the alcohol derivatives of the ketoses, and neither one in the case of the methyl aldoses.

6. The *d*'s and *l*'s indicate Fischer's classification. The four discrepancies mentioned above will be noticed in each semicircle, in the case of the threoses, xyloses, guloses and idoses. It is obvious that the individuals of these pairs, designated *l* by Fischer, belong in the right semicircle because of their structure; and this is the basis for Rosanoff's contention that the old designations for these 4 sugars should be reversed.⁶ The proposed rational system has already been adopted by Hudson and by Armstrong and the writers urge its general acceptance. The letters are omitted in the diagram in the case of the sugars not designated by Fischer and his colleagues.

7. It should be noted that the family designations, δ and λ , show genetic relationships, and have nothing to do with the direction of rotation of polarized light. Several schemes for indicating both the rotatory power and the family name have been suggested, but none has been generally adopted.

8. Brackets around the name of a sugar show that it does not occur in nature. Thus δ -glucose occurs naturally, but λ -glucose does not; whereas both δ - and λ -gulose are synthetic, and both δ - and λ -arabinose are naturally occurring.

9. The specific rotation of the sugar is placed under the name in parentheses. Where no value is given, it indicates that the specific rotation is not known. When no parentheses are used, it indicates that the sugar has not yet been prepared. Thus δ -allose has been prepared, but its specific rotation has not been determined; and λ -allose is still unknown to science. Parentheses in the legend of the diagram indicate compounds not yet prepared.

10. It is usually considered that the members of any enantiomorphous pair have rotations which are equal, but opposite in character. Several exceptions to this appear in the diagram, as in the galactoses and erythroses. These discrepancies may be due to (1) inaccuracies in the determinations, (2) to impurity of the preparations, or (3) to a different point of equilibrium

⁶ For an explanation of Fischer's errors, the reader is referred to Rosanoff's paper.

attained by the α and β forms of the 2 enantiomorphs. Whatever the cause we are not justified in assuming a value where it has not been determined, as in the case of λ -idose.

11. Fischer named the aldoses having more than 6 carbon atoms after the hexoses from which they originated, as *d*-glucoheptose, *d*-manno-octose. In the case of epimers, the one with the α -hydroxyl group to the right was called the α form, the one with it to the left the β form. Thus he had α -*d*-glucoheptose and β -*d*-glucoheptose. This system of designation is undesirable, since Greek letters are already in common use to designate the isomeric modifications of the mutarotating sugars, as α -*d*-glucose, β -*d*-glucose. As similar modifications of the above *d*-glucoheptoses exist, confusion in nomenclature occurs. A system of double Greek letters is sometimes used, as α , α -*d*-glucoheptose for the α modification and β , α -*d*-glucoheptose for the β modification. This system becomes very awkward, however, in the sugars of 8 or more carbon atoms; as α or β , α - α -*d*-gluco-octose.

Since the present diagram is geometrically perfect, and since there is a space in it for all possible aldoses of any number of carbon atoms, it is proposed that each space be given a number, and that, when an aldose does not bear a specific name it be designated by the genetic hexose and by the number of the space in which it occurs in the diagram. Thus Fischer's α -*d*-glucoheptose becomes δ -glucoheptose 20; β -*d*-glucoheptose becomes δ -glucoheptose 21. In like manner there will be 4 δ -gluco-octoses, 8 δ -gluco-nonoses, and so on. In each case the aldose with the α -hydroxyl group on the right will bear an even index number throughout the δ -family; in the λ -family the reverse will obtain. Also, the sign of the number will indicate the family, without the δ or λ . Although the above system of nomenclature is specific and descriptive, it will no doubt be found desirable to coin other names for these sugars, as has been done for all those of 6 carbon atoms and less.

It is hoped that the above diagrams and explanation will prove as useful to others as it has to the writers in teaching stereoisomerism, and that it will promote the gospel of rationality in nomenclature in the sugar group. Suggestions for improving the diagrams will be gratefully received.

Summary

Rosanoff's diagram of the aldoses has been modified in such ways as (1) to make it include all of the known sugars, and (2) to make it include more facts about these sugars. Also, diagrams have been constructed for the known ketoses and for the methyl aldoses.

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