another carbon atom (change from C to B) and a simultaneous shifting of an acetyl group from B to C. In other words, this reaction involves a migration of an acetyl group and a shifting of a ring. It may serve to illustrate what remarkable changes some of the sugar structures can undergo with great ease. Irvine and Burt[20] have observed that tetramethyl-γ-methyl mannoside readily rearranges to tetramethyl-α-methyl mannoside, which seems likewise to involve a shifting of the ring and a migration of a methoxy group.

Summary

A review of the experimental data shows that while many pairs of substances in the mannose, rhamnose and lyxose series exhibit comparative rotation differences that are abnormal with respect to the similar differences in the glucose series, which are regarded as the normal values, many other pairs in these series show quite normal comparative rotations. These facts lead to the hypothesis that *among the known derivatives of mannose and rhamnose there occur substances of various ring types* (which accounts for the observed exceptional comparative rotations) *and that substances belonging to the same ring type show normal comparative rotations* (which accounts for the normal values). Through this hypothesis it becomes possible to allocate most of the known forms and derivatives of mannose and rhamnose to three types of ring structure which are here provisionally designated 1,A, 1,B and 1,C, respectively. The proof of the precise position of these rings, which involves considerations that are not necessary to the present proof of the classifications according to ring types, follows in the next article.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE POLARIMETRY SECTION OF THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE][1]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. XIV.[2] THE DETERMINATION OF RING STRUCTURES IN THE GLUCOSE, MANNOSE AND RHAMNOSE SERIES

BY C. S. HUDSON

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The classifications according to ring types in the mannose and rhamnose series that have been shown in the preceding article can be extended to other sugar series. It has resulted that the correlations which can be established when the members of the glucose series are brought into the classification furnish a clear proof that the structural positions of the rings which have been provisionally designated 1,A, 1,B and 1,C are 1,5, 1,4

[1] Published by permission of the Director of the Bureau of Standards.

[2] Article XIII immediately precedes this.

and 1,3, respectively. This proof is dependent upon the proof, which will now be made, that the α- and β-methyl glucosides possess a 1,4-ring structure and the latter proof is dependent in turn upon the recent proof from methylation studies that methyl xyloside,[3] arabinoside[4] and galactoside[5] possess 1,5-ring structures.

Proof of the 1,4-Ring Structure of the Alpha and Beta Forms of Methyl Glucoside

Purdie and Irvine[6] have methylated α-methyl *d*-glucoside (+158) and obtained the tetramethyl derivative in reasonably pure though uncrystallized condition by distillation. By hydrolyzing this substance they have produced tetramethyl glucose (+83, final, in water) in pure crystalline form. In similar manner Irvine and Cameron[7] have methylated β-methyl *d*-glucoside (—32.5), obtained its tetramethyl derivative (—17 in water) in pure crystalline state, and by hydrolysis of the latter have produced the tetramethyl glucose (+83) just mentioned. They have remarked that these results clearly prove that the ring is the same in the two methyl glucosides and in tetramethyl glucose. Purdie and Irvine[6] concluded that this is a 1,4 ring, stating that "the fact that our tetramethyl gluconic acid [obtained by oxidation of tetramethyl glucose (+83)] forms a lactone shows that its unmethylated carbinol group is that in the γ-position." At the present time little weight can be given this evidence[8] because there are now known two tetramethyl galactonic, as well as mannonic, lactones, the structures of at least two of which must necessarily be other than γ-oxidic. The question of the position of the ring in the methyl glucosides must today be reëxamined.

The 1,2 ring has been excluded by Purdie and Irvine[6] because of the fact that a phenylosazone of tetramethyl glucose could not be produced. They state (p. 1027) that "although the substance reacted with phenylhydrazine, attempts to procure from it an osazone or crystallized hydrazone were not successful." Later Irvine and Scott[9] prepared from α-methyl glucoside by the methylation of its monobenzylidene derivative a dimethyl glucose (designated by them 2,3-dimethyl glucose) and stated that "the sugar formed no osazone, but a dimethoxyglucose phenylhydrazone was produced under conditions favorable to osazone formation. One methyl group must therefore be attached in Position 2." This excludes the possibility of a 1,2 ring in the methyl glucosides. Likewise Denham and Wood-

[3] Hirst and Purves, *J. Chem. Soc.*, **123**, 1352 (1923).
[4] Hirst and Robertson, *ibid.*, **127**, 358 (1925).
[5] Pryde, *ibid.*, **123**, 1808 (1923).
[6] Purdie and Irvine, *ibid.*, **83**, 1021 (1903).
[7] Irvine and Cameron, *ibid.*, **87**, 900 (1905).
[8] Irvine and Oldham [*ibid.*, **127**, 2729 (1925)] agree with this view.
[9] Irvine and Scott, *ibid.*, **103**, 575 (1913).

house[10] could obtain no osazone from a certain trimethyl glucose (designated by them 2,3,6-trimethyl glucose) which yielded the usual tetramethyl glucose (+83) on further methylation, a result which excludes ring (1,2). These agreeing data have made it reasonably certain, even though the evidence is of a negative character, that the 1,2 ring is not present in the methyl glucosides.

The 1,3 ring has been excluded by the proof of Freudenberg and Doser[11] that a certain monomethyl glucose[12] (prepared through the methylation of diacetone glucose) which yields the usual tetramethyl glucose (+83) on further methylation, has its one methoxy group attached to Carbon 3.

The 1,6 ring has been regarded as excluded because if it were present tetramethyl glucose (+83) should yield on oxidation with nitric acid a tetramethyl saccharic acid, but experiment has never yielded this product from it. The recent oxidation of methyl glucoside in alkaline solution to methyl glucuronic acid (obtained in the form of its brucine salt)[13] is an independent proof, by evidence of a positive nature, that the ring is not 1,6.[14] Irvine and Oldham's[8] recent work on the methylation of 6-bromomethyl glucoside also proves that the ring cannot be 1,6.

The eliminations that have now been reviewed leave only 1,4 and 1,5 rings as possibilities in the common structure of the methyl glucosides. Although a 1,4 ring is commonly assigned to them, such a conclusion does not appear ever to have been proved.[15] Proof that the ring cannot be 1,5 and must, therefore, be 1,4 will now be adduced from physicochemical considerations based upon the relations between rotatory power and structure in the sugar group.

It has recently been shown by the brilliant methylation researches of the St. Andrews school that methyl xyloside,[3] arabinoside,[4] and galactoside[5] possess 1,5 rings; hence the formulas for structurally analogous forms (α or β) of these substances are to be written as in I, II and III. Formula IV, then, represents the structure of the analogous hypothetical methyl glucoside of the 1,5 ring.

[10] Denham and Woodhouse, *J. Chem. Soc.*, **111**, 244 (1917).

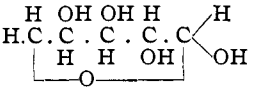
[11] Freudenberg and Doser, *Ber.*, **56**, 1243 (1923). See also Levene and Meyer, *J. Biol. Chem.*, **60**, 173 (1924).

[12] Ref. 9, p. 564.

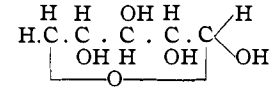
[13] Smolenski, *Roczniki Chemji*, **3**, 153 (1924); *C. A.*, **19**, 41 (1925).

[14] Since Bergmann and Wolff [*Ber.*, **56**, 1060 (1923)] have obtained pure crystalline α-menthyl glucuronic acid by oxidation in alkaline solution of α-menthyl glucoside the 1,6 ring would be excluded if experiment should show that the methylation of α-menthyl glucoside, followed by hydrolysis, yields the usual tetramethyl glucose (+83).

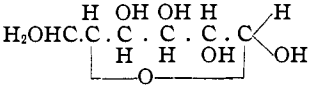
[15] Pringsheim states in his "Zuckerchemie" (p. 7) that "a strict proof of the 1,4-ring position for glucose [or, more exactly, for the methyl glucosides and tetramethyl glucose] does not appear ever to have been made; the best existing evidence seems to be the oxidation of tetramethyl glucose to tetramethyl gluconic lactone, which reacts like a γ-lactone." The insufficiency of this evidence has been mentioned.



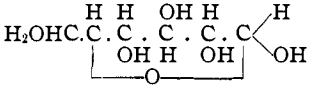
β-Methyl *l*-arabinoside (1,5) I[16]



α-Methyl *d*-xyloside (1,5) II



α-Methyl *d*-galactoside (1,5) III



α-Methyl *d*-glucoside (1,5) IV

The molecular rotations of these structures may be divided into two parts, namely, the rotation of asymmetric Carbon 4 (written $\pm r_4$) and that of the remainder of the structure (p or p'). It is assumed that r_4 has the same value in the pentoside and hexoside structures. Table I shows the formulation of the molecular rotations. The solution of Equations 1 to 4 gives the $[M]_D$ of α-methyl *d*-glucoside (1,5) as $X = 22{,}280$ and its $[\alpha]_D$ as $x = X/194 = +115$ in water. The $[\alpha]_D$ of the known α-methyl glucoside is far different from this, namely, +157.9; hence this substance cannot be the 1,5-ring form and must, therefore, in consideration of the evidence already adduced, have the 1,4-ring structure.

TABLE I

DERIVATION OF THE ROTATION OF α-METHYL *d*-GLUCOSIDE (1,5)

Substance	Mol. wt.	$[\alpha]_D$ in water	Molecular rotation	
β-Methyl *l*-arabinoside (1,5)	164	+245.5	$r_4 + p = 40{,}300$	(1)
α-Methyl *d*-xyloside (1,5)	164	+153.9	$-r_4 + p = 25{,}200$	(2)
α-Methyl *d*-galactoside (1,5)	194	+192.7	$r_4 + p' = 37{,}380$	(3)
α-Methyl *d*-glucoside (1,5)	194	x	$-r_4 + p' = X$	(4)

An independent comparison of the rotations of the acetates of these substances, the data referring now to chloroform solutions, leads clearly to the same conclusion that a 1,4-ring structure pertains to methyl glucoside. Consider the molecular rotations in chloroform of the fully acetylated derivatives of the four glucosides just discussed. Table II records the formulations of these rotations in the usual way and by solving Equations 5 to 8 the $[M]_D$ of α-methyl *d*-glucoside tetra-acetate (1,5) is found to be $Y = 30{,}000$ and its $[\alpha]_D = -y = Y/362 = +83$ in chloroform. This

TABLE II

DERIVATION OF THE ROTATION OF α-METHYL GLUCOSIDE (1,5) TETRA-ACETATE

Substance Fully acetylated derivative of	Mol. wt.	$[\alpha]_D$ in $CHCl_3$	Molecular rotation	
β-Methyl *l*-arabinoside (1,5)	290	+182.0	$R_4 + P = +52{,}800$	(5)
α-Methyl *d*-xyloside (1,5)	290	+119.6	$-R_4 + P = +34{,}700$	(6)
α-Methyl *d*-galactoside (1,5)	362	+133.0	$R_4 + P' = +48{,}100$	(7)
α-Methyl *d*-glucoside (1,5)	362	y	$-R_4 + P' = y$	(8)

[16] The naming of this structure a β-form whereas the others are designated α- is a matter of convention and is due to the fact that *l*-arabinose belongs in the *l*-series.

value is greatly different from that of the known tetra-acetate of α-methyl *d*-glucoside, which is +130.6 in chloroform and, therefore, the known substance cannot contain a 1,5 ring and must, accordingly, possess a 1,4 ring. This proof thus corroborates the previous one.

Objection may be made against both of these independent proofs on the ground that the final conclusion is made by a process of elimination. Can it not be that the known methyl glucoside possesses a 1,5 ring but has a rotation different from that here calculated due to a failure of optical superposition to apply in these comparisons or due to a difference in the value of r_4 (or R_4) for the pentoside and hexoside structures? What would apparently be a complete answer to this objection would be the preparation and isolation of a new methyl *d*-glucoside having the rotation here calculated for a 1,5-ring form, namely $[\alpha]_D = +115$, but this problem can now only be stated and its solution must be left to future experimental work. On the other hand, an answer which is almost as complete can be given at the present time from existing experimental data in the mannose and rhamnose series. It will now be shown that the provisional rings (1,B and 1,A) which were assigned to the structures of many known derivatives of mannose and rhamnose in the preceding article, are indeed 1,4 and 1,5 rings and that the calculated rotation of the hypothetical α-methyl *d*-glucoside (1,5) (+115) and that of the known α-methyl *d*-glucoside (1,4) (+157.9) fit accurately in the mannose-rhamnose classification as forms that are epimeric with classified forms of the mannose series. In other words, while the hypothetical α-methyl *d*-glucoside (1,5) (+115) is at present unknown, it can be shown that its epimer is a well known pure substance, namely, α-methyl *d*-mannoside (1,A) (+79). The proof of this conclusion will now be presented.

Correlation of Ring Structures in the Glucose Series with Those in the Mannose and Rhamnose Series. The "Epimeric Difference of Rotation"

Let the molecular rotation of α-methyl *d*-glucoside (1,4) (+157.9) be separated into the components r_2 (the rotation of asymmetric Carbon 2) and q (the rotation of the remainder of the structure); thus, $[M]_D = r_2 + q$. The rotation of its epimer, α-methyl mannoside (1,4), the identification of which with any known substance is not disclosed yet in the argument, then becomes $[M]_D = -r_2 + q$ and the "epimeric difference of molecular rotation" becomes, by subtraction of the two equations, $2r_2$. The rotations of the glucoside and mannoside of 1,5-ring structure may be similarly formulated (see Table III) and it is seen that their epimeric difference is likewise $2r_2$. Let it now be determined by trial whether there are two α-methyl mannosides, of different ring structures as shown by the allocations of the previous article, which differ in rotation from the two

α-methyl glucosides, of rings 1,4 and 1,5, respectively, by a constant quantity. The data of Table III show that such is the case and likewise show that the acetates of these four glycosides, the rotations of which refer to chloroform solutions, give an analogous constant difference of rotation.

TABLE III

CORRELATION OF STRUCTURALLY SIMILAR METHYL GLUCOSIDES AND MANNOSIDES BY THE PROOF OF A CONSTANT EPIMERIC DIFFERENCE OF ROTATION

Substance	Mol. wt.	$[\alpha]_D$ in water	Molecular rotation	Epimeric difference ($2r_2$ or $2R_2$)
α-Methyl *d*-glucoside (1,4)	194	+157.9	$+r_2 + q = 30{,}630$	6380 ($2r_2$)
α-Methyl *d*-mannoside (1,B)	194	+125[a]	$-r_2 + q = 24{,}250$	
α-Methyl *d*-glucoside (1,5)	194	+115[a]	$r_2 + q' = 22{,}280$	6950 ($2r_2$)
α-Methyl *d*-mannoside (1,A)	194	+ 79	$-r_2 + q' = 15{,}330$	
				Av. 6700
Tetra-acetates of		$[\alpha]_D$ in $CHCl_3$		
α-Methyl *d*-glucoside (1,4)	362	+130.6	$R_2 + Q = 47{,}300$	10,400 ($2R_2$)
α-Methyl *d*-mannoside (1,B)	362	+102[a]	$-R_2 + Q = 36{,}900$	
α-Methyl *d*-glucoside (1,5)	362	+ 83[a]	$R_2 + Q' = 30{,}000$	12,200 ($2R_2$)
α-Methyl *d*-mannoside (1,A)	362	+ 49.1	$-R_2 + Q' = 17{,}800$	
				Av. 11,300

[a] Calculated values as shown previously in this or the preceding article.

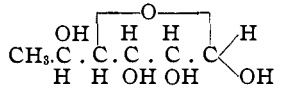
These results clearly show that the 1,A ring of the mannose and rhamnose series is a 1,5 ring and that 1,B is 1,4, the ring which has been shown to occur in the α- and β-forms of methyl glucoside.

Determination of the Structure of the 1,C Ring of the Mannose and Rhamnose Series

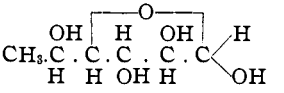
To complete the allocation of precise structures to the known rings of the mannose and rhamnose series there remains only the determination of the position for the 1,C ring. This can be made quite simply. A 1,6 ring is excluded in the case of rhamnose since its Carbon 6 grouping has the structure CH_3. Since 1,4 and 1,5 rings have been assigned to 1,B and 1,A, respectively, only Positions 1,2 and 1,3 remain as possible structures for 1,C. Fischer, Bergmann and Rabe have observed in the case of β-methyl *l*-rhamnoside (1,C) triacetate, and Dale in that of the analogous β-methyl *d*-mannoside (1,C) tetra-acetate that one acetyl group of the structures is not removed even by strong alkalies. It seems highly improbable that an acetyl group outside a ring could be so protected and hence the 1,2 ring, which could not contain an acetyl group within it, must be excluded and it follows by elimination that 1,C is 1,3. This is, indeed, the structure that Fischer, Bergmann and Rabe suggested when they discovered the unique behavior of their acetate.

The Ring Structure of β-Methyl *d*-Isorhamnoside

The determination of the epimeric difference, $2r_2$ or $2R_2$, supplies the data for a simple method of allocating ring forms to many substances of the sugar group. It is now possible to calculate the rotation of the epimers of various sugars, glycosides and acetates of known ring structure. An illustration of the use of the method will indicate its general applicability. The epimer of β-methyl *l*-rhamnoside [1,B = 1,4; $[M]_D$ = +16,900 (see preceding article)] of Structure V is β-methyl *l*-isorhamnoside (1.4) (Structure VI) of $[M]_D = +16{,}900 - 2r_2 = +10{,}200$ and $[\alpha]_D = 10{,}200/178 = +57$, and the *d*-form of this epimer, β-methyl *d*-isorhamnoside (1,4) is accordingly expected to show $[\alpha]_D = -57$ in water.



β-Methyl *l*-rhamnoside (1,4) V



β-Methyl *l*-isorhamnoside (1,4) VI

The well known β-methyl *d*-isorhamnoside of Fischer and Zach was found by them to show $[\alpha]_D = -55.2$ in water; hence it must be assigned the 1,4 ring. This proves the ring structure that Fischer and Zach assumed as probable.

Rotations of Various Substances of the *d*-Glucose Series

Attention is now directed to the use of the epimeric differences in the calculation of the rotations of the forms of *d*-glucose, methyl *d*-glucoside, etc., of various ring structures from the rotations of substances of the mannose series. The molecular epimeric difference, $2r_2$ = 6,700 in water, corresponds to 6,700/180 = 37° in the $[\alpha]_D$ of hexoses (mol. wt., 180) and 35° in that of methyl hexosides (mol. wt., 194). The molecular epimeric difference for the fully acetylated derivatives of hexoses (mol. wt., 390) and methyl hexosides (mol. wt., 362) corresponds similarly to $[\alpha]_D$ differences of 29 and 31, respectively, in chloroform, since $2r_2$ has the value 11,300 (see Table III). The rotations of the substances in the

TABLE IV

CALCULATED ROTATIONS OF SUBSTANCES OF THE *d*-GLUCOSE SERIES

Substance	Mol wt.	Specific rotation: 1,5 Ring Calcd.	1,5 Ring Obs.	1,4 Ring Calcd.	1,4 Ring Obs.	1,3 Ring Calcd.	1,3 Ring Obs.
α-*d*-Glucose	180	+ 66	...	+114	+113	...	...
β-*d*-Glucose	180	− 28	...	+ 20	+ 19	...	...
α-Methyl *d*-glucoside	194	+114	...	+158	+158	...	...
β-Methyl *d*-glucoside	194	− 77	...	− 33	− 32	...	...
α-Methyl *d*-glucoside tetra-acetate	362	+ 80	...	+133	+131	+153	...
β-Methyl *d*-glucoside tetra-acetate	362	− 68	...	− 16	− 18	+ 4	...
α-*d*-Glucose penta-acetate	390	+ 55	...	+104	+102	+122	...
β-*d*-Glucose penta-acetate	390	− 43	...	+ 6	+ 4	+ 24	...
α-Chloro-acetyl *d*-glucose	367	+115	...	+167	+166	+187	...

d-glucose series have been obtained from those of their epimers of the mannose series, which are recorded in Table III of the preceding article, by adding the epimeric differences of specific rotations. The rotations of the chloro-acetyl glucose forms are obtained by similar calculation, the epimeric difference of $[\alpha]_D$ being in this case 31. The results appear in Table IV.

In 1909 the writer showed that the rotation of the chain of the α- and β-forms of glucose has the same value as that of the analogous methyl glucosides. The present results (see Table IV) prove that the four substances possess a common ring, namely, 1,4. Likewise, the two glucose penta-acetates, which Behrend correlated some years past with the two forms of glucose, are now shown by the new evidence to possess the 1,4 ring. Regarding α-chloro-acetyl glucose it may be thought that its ring is not yet shown since it may be considered that the substance falls in the 1,4-ring column because in obtaining the coefficient A_{Cl} necessary for the calculation of the rotation of α-chloro-acetyl mannose (1,4) the ring of α-chloro-acetyl glucose was assumed to be the same as that of the glucose penta-acetates. However, the independent determination of A_{Cl} from the rotations of the α- and β-forms of chloro-acetyl fructose,[17] which gave a normal value, shows that α-chloro-acetyl glucose possesses indeed the 1,4 ring. The isolation in pure form of derivatives of glucose possessing the 1,3 or 1,5 rings, the calculated rotations of some of which are shown in Table IV, will doubtless be only a matter of time in view of the rapid advances that are being made in many countries today in the study of the carbohydrates. Doubtless the so-called γ-methyl glucoside of Fischer and the methylated products which Irvine obtained from it are mixtures that contain substances of such ring types.

Looking backward over the gradual development of the quantitative relations between rotatory power and structure in the sugar group, it is seen now to have been a fortunate circumstance that the α- and β-forms of glucose and the other substances of the glucose series possess a common ring. They were assumed from the start to be such a series because the assumption gave a quantitative explanation, in terms of the Van't Hoff hypothesis of optical superposition, of various numerical relations among the rotatory powers of substances of the glucose and several other sugar series. The various coefficients obtained from such rotations were accordingly considered normal values. The exceptional rotations of the mannose, rhamnose and lyxose series, which were for many years so difficult to understand, have now been reconciled with the rotations of the glucose series and the results have opened the way, in combination with the methylation data of Irvine's school, to a general solution of the problem of the ring structures of the sugars. If the glucose series had been repre-

[17] Hudson, THIS JOURNAL, **46**, 477 (1924).

sented by substances as varied in ring structure as those of the mannose or rhamnose series the problem might conceivably have been much more complicated and difficult of solution. It now remains to extend these ring classifications step by step in obvious directions. Much emphasis must be placed upon the necessity of carefully purifying such substances as may be included in the consideration of rotatory relations. Many of the substances of the sugar group in particular are difficult to separate as pure individuals that are free from isomeric forms. The writer believes that the values of the rotations of the substances that have furnished the foundations for the present classification of ring forms are substantially correct, since they have been accurately measured and the substances have been carefully purified. The extension of the classifications will be greatly aided if research workers who discover new substances of the sugar group will use all necessary care to purify them fully to constant rotation and will measure the rotations either in water or in chloroform, whenever possible.

Postscript

After the present article and the preceding one were prepared there has appeared a paper by Hirst and Macbeth[18] in which it is shown that methyl *l*-rhamnoside (1,A)(—62.5) possesses a 1,5 ring. The evidence consists in their preparation from this substance of a trimethyl rhamnose which on oxidation by nitric acid yielded *l*-arabotrimethoxy-glutaric acid, identical with the acid previously obtained by Hirst and Robertson[4] from the oxidation of trimethyl *l*-arabinose (1,5). These results can be used to allocate precise positions to the 1,A and 1,B rings of the mannose and rhamnose series because the assignment of Structure 1,5 in the rhamnose series to ring 1,A, followed by the allocation of 1,3 to the 1,C ring from the evidence of Fischer, Bergmann and Rabe and of Dale, leaves 1,4 as the only probable structure for the 1,B ring since the 1,2 structure may be excluded on the ground of instability. Two independent proofs leading to the same conclusion have thus been adduced for the allocation of the rings in the mannose and rhamnose series.

In a recent article Charlton, Haworth and Peat[19] have presented experimental evidence concerning the relative rates of mutarotation of various methylated lactones of the sugar group, from which they conclude that α- and β-methyl glucoside possess 1,5 rings. The present results are obviously in disagreement with this conclusion. It may be remarked in this connection that since it has been shown in the present article that β-methyl isorhamnoside possesses the same ring as the α- and β-methyl glucosides the methylation method that Hirst and Macbeth have used to prove the 1,5-ring structure of methyl rhamnoside appears applicable for deciding

[18] Hirst and Macbeth, *J. Chem. Soc.*, January, **1926**, p. 22.

[19] Charlton, Haworth and Peat, *ibid.*, January, **1926**, p. 89.

whether the ring of methyl isorhamnoside, and therefore, that of the methyl glucosides, have the 1,5 structure.

Summary

A summary of the evidence from the methylation studies of Purdie, Irvine and their students shows that the position of the ring in the α- and β-methyl glucosides is limited to 1,4 and 1,5. The recent proof from the methylation studies of the St. Andrews school that methyl xyloside, arabinoside and galactoside possess 1,5 rings leads to a proof from rotatory relations, which is now presented, that the α- and β-methyl glucosides and β-methyl isorhamnoside possess a 1,4 ring and that the rings of the mannose and rhamnose series, which were provisionally designated 1,A, 1,B and 1,C in the preceding article are, respectively, 1,5, 1,4 and 1,3. In the postscript it is shown that Hirst and Macbeth's recent proof of the 1,5-ring structure of methyl rhamnoside (1,A) supplies the basis for an independent corroborative proof of the present classifications in the mannose and rhamnose series. The proof of the 1,4-ring structure of the methyl glucosides is in disagreement with Charlton, Haworth and Peat's recent conclusion, from a different type of evidence, that they possess a 1,5 ring.

WASHINGTON, D. C.

NEW BOOKS

Fundamentals of Physical Chemistry, for Students of Chemistry and Related Sciences. By DR. ARNOLD EUCKEN, Professor of Physical Chemistry in the Technischen Hochschule, Breslau, Germany. Translated and adapted from the second German edition by ERIC R. JETTE, Ph.D., Instructor in Chemistry, and VICTOR K. LAMER, Ph.D., Assistant Professor of Chemistry, Columbia University. International Chemical Series, H. P. TALBOT, Ph.D., Sc.D., Consulting Editor. McGraw-Hill Book Co., Inc., 370 Seventh Avenue, New York, 1925. xxiii + 699 pp. 99 figs. 21 × 14 cm. Price $5.50.

The subject matter of this treatise is presented in four sections, as follows: Mathematical-Physical Introduction; Physical Thermodynamics; Chemical Thermodynamics, including Electrochemistry; The Structure of Matter.

The first of these sections appears to reflect the feeling that it is necessary to defend the use of mathematics in physical chemistry. The material it contains is well chosen and well presented, but it is not likely to assist those who are deficient or interest those who are not. One wonders whether it might not be possible to make use of mathematics wherever it is advantageous to do so, without apology or explanation.

"Thermodynamics," in the titles of the second and third sections, is evidently intended in a more inclusive sense than is usual. Actually, the kinetic theory and the quantum theory are used extensively in the interpretation of phenomena relating to ideal solids, liquids and perfect