The authors wish to express their cordial gratitude to Prof. S. Kimoto for his kind guidance and unfailing encouragement. Thanks are also due to Prof. Emeritus E. Ochiai, University of Tokyo for his kind supply of the comparison samples, to the members of Analytical Center, University of Kyoto for elemental microanalyses and to Mr. J. Ōno and Miss S. Kataoka, for their technical assistance. A part of expenses of the present work was defrayed by a Grant-in-Aid for Scientific Research from the Ministry of Education, which is gratefully acknowledged.

Summary

Hydrogenation of isoquinolines, 2-methyl-1,2,3,4-tetrahydro-7-isoquinolinol (V), 7-isoquinolinol (VII), 2-methyl-7-methoxy-1,2,3,4-tetrahydroisoquinoline (IV), was carried out in three different ways. It was clarified that 2-methyl-2,3,4,4*a*,5,6,8,8*a*-octahydro-7(1*H*)-isoquinolone (IX) and a pair of corresponding 2-methyl-decahydro-7-isoquinolinols (VIa and VIb), thus obtained, possessed *cis* configuration at ring juncture. In addition, hydrolysis products of 7-methoxy-1,2,3,4,5,8-hexahydroisoquinoline (X) were discussed.

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98. Masuo Akagi, Setsuzo Tejima, and Masanobu Haga : On the Relative Rates of Displacement Reaction of Primary *p*-Tosyloxy Groups of Hexapyranose Derivatives with Sodium Iodide in Acetone Solution.

(*Faculty of Pharmaceutical Sciences, School of Medicine, Hokkaido University*[*1])

The tosylates (*p*-toluenesulfonates) of carbohydrates have been studied by many investigators due to peculiar characteristics which make them of great importance in carbohydrate chemistry.

Especially the displacement reaction of primary tosyloxy groups with sodium iodide in acetone was known as "Oldham and Rutherford rule"[1] and well studied for the preparation of sugar halohydrins and for the confirmation of primary hydroxyl structure.

On this subject, Tipson[2] described in his elaborate review on sugar sulfonates that it seems to be some configurational effects among sugars and anomers. That is, in hexose series, allose, altrose, mannose, and glucose derivatives react more easily with sodium iodide than galactose derivatives. Moreover, in the case of anomeric derivatives, Tipson also speculated that β-D-glucose and β-D-galactose derivatives are more reactive than the corresponding α-anomers from the reaction conditions and yields reported by different authors.

In a recent paper from this laboratory[3] the primary tosyloxy group of D-glucose derivatives was shown to replace easily by potassium thioacetate in acetone. However the authors observed the failure of this reaction for corresponding D-galactose derivatives.[4]

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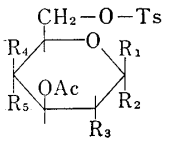
*1 Nishi-5-chome, Kita-12-jo, Sapporo, Hokkaido (赤木満洲雄, 手島節三, 羽賀正信).

1) J. W. H. Oldham, J. K. Rutherford : J. Am. Chem. Soc., **54**, 366 (1932).
2) R. S. Tipson : "Advances in Carbohydrate Chemistry" 8, 107 (1953). Academic Press Inc., New York.
3) M. Akagi, S. Tejima, M. Haga : This Bulletin, **10**, 562 (1962).
4) *Idem* : *Ibid.*, (1963) to be published.

It was now of interest to study the effect of configurational differences of pyranoid ring on the substitution rate at carbon 6. Thus, the present study was designed to confirm the Tipson's configurational effect in hexose series and to make clear the origin from which the effect is produced.

For this purpose, the anomeric 6-O-tosyl-1,2,3,4-tetra-O-acetyl-D-glucopyranoses (I and II), 6-O-tosyl-2-deoxy-2-acetamido-1,3,4-tri-O-acetyl-D-glucopyranoses (III and IV), and 6-O-tosyl-1,2,3,4-tetra-O-acetyl-D-galactopyranoses (V and VI) were chosen, since, in these compounds, it is not required to take an account of the effect of substituents



	R_1	R_2	R_3	R_4	R_5
I	H	OAc	OAc	H	OAc
II	OAc	H	OAc	H	OAc
III	H	OAc	NHAc	H	OAc
IV	OAc	H	NHAc	H	OAc
V	H	OAc	OAc	OAc	H
VI	OAc	H	OAc	OAc	H

Chart 1.

to each other. The behavior of these compounds was studied under the condition using equimolar sodium iodide in anhydrous acetone at 100° and the reaction was traced by a titration of residual inorganic iodide after the procedure described by Dostrovsky and Hughes.[5]

The reactions were found to be clean-cut second order in these reagents; moreover, it was shown[6] undoubtedly that some of tosyloxy groups of anhydropolyol, such as 2,5-di-O-tosyl-1,4; 3,6-di-anhydro-D-mannitol, were replaced in the mechanism of S_N2 type, so that indicated this reaction to be bimolecular (S_N2 type).

Making comparison between glucose and glucosamine derivatives, these substances are conceivable to be identical configurationally and conformationally in the situation of carbon 6. Therefore it would be expected that the rates of displacement reaction are equivalent between these derivatives. On the other hand, galactose corresponds to carbon 4 diastereoisomer of glucose and it would be also able to expect to be some differences between these derivatives if the configurational effect is true. Since, in galactose derivatives, the large neighbouring group (acetoxy group of carbon 4) bears reverse relation to glucose derivative about carbon 6.

As expected above, the reaction rates of glucose and glucosamine are approximately equivalent between the same anomeric derivatives and, in the case of galactose derivatives, the velocities are markedly slow as compared with the former two sugar derivatives.

In Table I are listed the average values of these compounds. (A complete list of all kinetic runs is contained in Table III in the Experimental).

Table I. Rate Coefficients

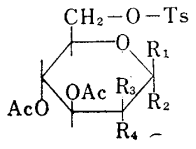
Tosylate	Glucose		Glucosamine		Galactose	
	α(I)	β(II)	α(III)	β(IV)	α(V)	β(VI)
$10^2 \times K$ L.•mole^{-1}•min^{-1}	67.9	32.0	68.9	31.9	5.41	1.73
Approximate relative rate	32	18	32	18	3	1
$[\alpha]_D^{18}$ in chloroform	+95.2	+22.5	+115.8	+14.8	+90.2	+10.2

However, it is of great interest that α-anomeric derivatives of these three sugars are more reactive than corresponding β-anomers in opposition to Tipson's observation. About the anomeric configuration of glucose and glucosamine derivatives, previously

5) I. Dostrovsky, E.D. Hughes: J. Chem. Soc., **1946**, 161.
6) S.J. Angyal, N.K. Matheson: *Ibid.*, **1952**, 1133; M. Jackson, L.D. Hayward: Can. J. Chem., **37**, 1048 (1959).

the authors proved that the more levorotatory anomeric derivatives (II and IV) (according to expression of Hudson's isorotation rule,[7] compound II and IV are depicted as β-anomers) have the *cis* relationship between acetoxy group of carbon 1 and carbon 6 by the action of alkaline reagent which makes them to form 1,6-anhydrides (*levo*-glycosan) respectively but from the corresponding anomers it fails to form 1,6-anhydride.[8,9]

Hence, also in galactose derivatives, it seems to be sure that the more levorotatory anomer (VI) is having the *cis* configuration between carbon 1 and carbon 6. For the further confirmation that the so-called *beta* configuration (*cis* relation between acetoxy group of carbon 1 and carbon 6) makes participation in the displacement reaction at carbon 6 theauthors have measured the reaction ratesfor the following methyl, ethyl, isopropyl, *tert*-butyl, and phenyl 6-O-tosyl-2,3,4-tri-O-acetyl-β-D-glucopyranosides (VIII to XII) and compared with the displacement rates of methyl 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-glucopyranoside (VII) and methyl 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-mannopyranoside (XIII) under the same conditions performed above.



	R_1	R_2	R_3	R_4
VII	H	-OMe	H	OAc
VIII	-OMe	H	H	OAc
IX	-OEt	H	H	OAc
X	-O-*iso*-Pro	H	H	OAc
XI	-O-*tert*-Bu	H	H	OAc
XII	-O-Ph	H	H	OAc
XIII	H	-OMe	OAc	H

Chart 2.

As listed in Table II, the tosyloxy group of methyl α-D-glucopyranoside derivative (VII) was displaced at the approximately equivalent rate being compared with α-derivatives (I and III). Notwithstanding, the displacement velocities of these β-D-glucopyranoside derivatives became slow in comparison with each of α-anomeric derivatives (I, III and VII) according to the bulkiness of *beta* substituent.

Table II. Rate Coefficients

Tosylate	VII	VIII	IX	X	XI	XII	XIII
$10\times K$ L.•mole^{-1}•min^{-1}	72.3	57.5	55.4	51.1	31.5	47.7	26.5

These glucosides (VIII to XII) were prepared by condensing of 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-glucopyranosyl bromide with respective hydroxylic compounds under the condition of Koenigs-Knorr reaction[10] which is well known as the preparation procedure of β-glucosides. On the anomeric configuration of methyl β-D-glucopyranoside, Wolfrom and Thompson,[11] in commenting on the formation of methyl β-D-glucopyranoside from 3,4,6-tri-O-acetyl-1,2-anhydro-α-D-glucopyranose and methanol,[12] suggested that the methoxy group bears a *trans* relation to the hydroxyl group of carbon 2 (namely, a *cis* relation to carbon 6). Consequently it seems to be sure that, in these glucosides (VIII to XII), the aglycon groups have a *cis* relation to carbon 6.

Besides the tosyloxy group in derivatives of methyl α-D-mannopyranoside (XIII) was displaced more slowly than corresponding tosyloxy groups of XII. XIII corresponds to

7) C.S. Hudson : J. Am. Chem. Soc., **31**, 66 (1909).
8) M. Akagi, S. Tejima, M. Haga : This Bulletin, **10**, 905 (1962).
9) *Idem* : *Ibid.*, **10**, 1035 (1962).
10) J. Conchie, G.A. Levvy, C.A. Marsh : Advances in Carbohydrate Chemistry, **12**, 157 (1957). Academic Press Inc., Publishers New York, N.Y.
11) M.L, Wolfrom, A. Thompson : "The Carbohydrate Chemistry, Biochemistry, Physiology" edited by W. Pigman. Academic Press Inc., Publishers New York, N.Y. p. 128 (1957).
12) P. Brigl : Z. physiol. Chem., **122**, 245 (1922).

C_2-diastereoisomer of XII and the acetoxy group of C_2 has a *cis* relation to carbon 6. From these results, it is evident that the anomeric substituent has some influences upon the reaction rate on carbon 6, moreover, it is most probable that the bulky substituents on pyranoid ring arranged in *cis* relation to hydroxymethyl group (carbon 6) have an effect to make slow the displacement rate on carbon 6.

On nucleophilic substitution reactions of the S_N2 type, it is well known that the reaction rates are more sensitive to steric interferences rather than electronic effects.[13]

As discussed above, it seems to be plausible that, in this displacement reaction, there are no substantial differences between derivatives such as I and V in steric and electronic effects.

The conformations of pyranoid rings have been discussed in detail by Reeves[14] and seemed to be in chair form. Namely in idealized model of six-membered ring, the interatomic distances between vicinal substituents are conceivable to be equivalent,[15] that is, the distances between carbon 6 and oxygen of carbon 4 are also assumable to be identical[16] as to glucose (I) and galactose (V). However, the differences of displacement rates between these derivatives (II and IV) are probably attributable to the steric hindrance, since, notwithstanding the equal ground state, it seems to be different in transition state.

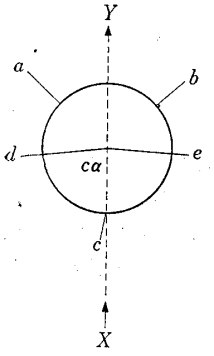
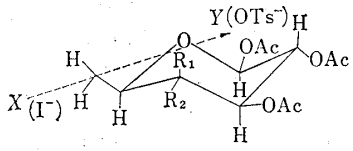


Fig. 1.

Dostrovsky, Hughes and Ingold[17] made exhaustive researches on the transition state of bimolecular substitution reaction and from the geometrical considerations deduced the following transition state: for example, the favorable transition state for the bimolecular displacement reaction on α-carbon of isobutane is shown in Fig. 1 represented by Newman's formula.

Here a and b represent methyl groups of β-carbon, c is β-hydrogen, d and e are α-hydrogens, and X and Y are the entering and departing nucleophilic groups.

The case of carbohydrate derivatives also requires the same reference to Fig. 1, that is, where a is lactalic oxygen and $c\alpha$ and b correspond to carbon 6 and 4 respectively. Accordingly it would be able to conclude that the departing group crosses over pyranoid ring, and the transition state would be representable as depicted in Chart 3.



β-D-glucopyranose derivatives (II) R_1=H, R_2=OAc
β-D-galactopyranose derivatives (V) R_1=OAc, R_2=H

Chart 3. Transition State of β-Glucopyranose Derivatives

Obviously galactose derivatives (V and VI) have a bulky substituent (acetoxy group of carbon 4) close to the passage of departing group in transition state. Consequently it would be more reasonable that the decreased reactivities of galactose derivatives (V and VI) compared with glucose and glucosamine derivatives (I, II, III, and IV) attribute to the

13) J. Hine: "Physical Organic Chemistry" p. 93 (1956). McGraw-Hill Book Company, Inc., New York.
14) R.E. Reeves: "Advances in Carbohydrate Chemistry," **6**, 108 (1951). Academic Press Inc., Publishers. New York, N.Y.
15) W. Klyne: Progress in Stereochemistry, **1**, 36 (1954). Butterworths Scientific Publications, London.
16) 2.88 Å calculated by using the distance: C-C, 1.54; C-O, 1.42 Å, and assuming tetrahedral angles. See ref. 15).
17) I. Dostrovsky, E.D. Hughes, C.K. Ingold: J. Chem. Soc., **1946**, 173.

steric interference of acetoxy group of carbon 4 in transition state. In addition, the retarding effects of β-configuration of these derivatives and acetoxy group of carbon 2 in mannose derivatives (XIII) also would be able to refer to the steric effect of this kind. In another words, it would be conceivable that these results indicate the validity and indispensability of the transition state discussed by Dostrovsky, Hughes and Ingold.[17]

Experimental

Materials——1) Anomeric 6-O-tosyl-1,2,3,4-tetra-O-acetyl-D-glucopyranoses were prepared as crystals by a modification of the procedure reported by Hardegger and Montavon.[18]

Twenty grams of anhydrous D-glucose was dissolved in 300 cc. of anhydrous pyridine, and to this solution 22.0 g. of tosyl chloride was added in one portion and the reaction mixture was shaken vigorously until a solution became clear.

After standing overnight at room temperature (22°), 85 g. of acetic anhydride was added to this mixture and the solution was immediately, evaporated under reduced pressure to a thick syrup (water pump, at 50°).

The colored syrup was then dissolved in 200 cc. of abs. EtOH, left at room temperature until crystallization had practically ceased, and finally in the refrigerator overnight. The crude material (II) was then filtered off and washed with 50 cc. of cold EtOH. It ammounted to 24 g. (ca. 44%), melted at 193～194°.

Several recrystallizations from acetone fromed pure β-anomer, m.p. 196～198°; $[\alpha]_D^{18}$ +22.5° (c=1.0, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{26}O_{12}S$: C, 50.19; H, 5.21; S, 6.47. Found: C, 50.21; H, 5.27; S, 6.24.

The alcoholic solution was evaporated under reduced pressure to a thick syrup. The dark colored product (35 g.) was dissolved in $CHCl_3$ and the organic layer was washed with dilute sulfuric acid, sodium bicarbonate solution, and H_2O successively. The solution was then treated with charcoal and concentrated under reduced pressure. The slightly colored syrup was further extracted with hot water to remove pentaacetate, dissolved in 70 cc. of EtOH and allowed to stand at room temperature. 28 g. of crude α-anomer (I) melting at 114～115° was obtained as colorless crystals. Recrystallizations from absolute MeOH gave pure I, m.p. 118～120°; $[\alpha]_D^{18}$ +95.2° (c=0.96, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{26}O_{12}S$: C, 50.19; H, 5.21; S, 6.47. Found: C, 50.19; H, 4.92; S, 6.34.

2) The preparation of anomeric 6-O-tosyl-2-deoxy-2-acetamido-1,3,4-tri-O-acetyl-D-glucopyranoses (III and IV) was reported previously.[10]

α-Anomer (III), m.p. 152～153°; $[\alpha]_D^{18}$ +115.8° (c=2.0, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{27}O_{11}NS$: C, 50.29; H, 5.43; N, 2.79; S, 6.38. Found: C, 49.95; H, 5.54; N, 2,82; S, 6.36.

β-Anomer (IV), m.p. 174～175°; $[\alpha]_D^{18}$ +14.8° (c=1.2, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{27}O_{11}NS$: C, 50.29; H, 5.43; N, 2.79; S, 6.38. Found: C, 50.22; H, 5.49; N, 3.06; S, 6.34.

3) The anomeric 6-O-tosyl-1,2,3,4-tetra-O-acetyl-D-galactopyranoses (V and VI) were prepared after the method reported by Ohle and Thiel.[19]

α-Anomer (V), m.p. 114～115°; $[\alpha]_D^{18}$ +90.2° (c=0.89, $CHCl_3$), reported[19] m.p. 117°; $[\alpha]_D$ +89.1°. *Anal.* Calcd. for $C_{21}H_{26}O_{12}S$: C, 50.19; H, 5.21; S, 6.47, Found: C, 50.24; H, 5.32; S, 6.34.

β-Anomer (VI), m.p. 123～124°; $[\alpha]_D^{18}$ +10.2° (c=1.2, $CHCl_3$) reported[19] m.p. 126～127°; $[\alpha]_D$ +9.31°. *Anal.* Calcd. for $C_{21}H_{26}O_{12}S$: C, 50.19; H, 5.21; S, 6.34. Found: C, 50.08; H, 5.34; S, 6.54.

The pyranose structure of these compound was proved by Haworth, *et al.*[20]

4) Anomeric methyl 6-O-tosyl-2,3,4-tri-O-acetyl-D-glucopyranosides. α-Anomer (XII) was prepared according to the method of Helferich, *et al.*,[20] m.p. 74～75°; $[\alpha]_D^{18}$ +118.4° (c=2.4, $CHCl_3$), reported,[21] m.p. 77～78.5°; $[\alpha]_D$ +126.3°. *Anal.* Calcd. for $C_{20}H_{26}O_{11}S$: C, 50.26; H, 5.52; S, 6.71. Found: C, 50.48; H, 5.76; S, 6.92.

β-Anomer (VII) were prepared from 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-glucopyranosyl bromide and methanol in the presence of silver carbonate after the procedure reported by Compton,[22] m.p. 170～171°; $[\alpha]_D^{18}$ +8.8° (c=1.0, $CHCl_3$), reported[22] m.p. 170～171°; $[\alpha]_D$ +7.2. *Anal.* Calcd. for $C_{20}H_{26}O_{11}S$: C, 50.62; H, 5.52; S, 6.71. Found: C, 50.54; H, 5.64; S, 6.64.

5) Ethyl 6-O-tosyl-2,3,4-tri-O-acetyl-β-D-glucopyranoside was prepared as follows: Ten grams of 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-glucopyranosyl bromide[22] was stirred vigorously with 15 g. of silver carbonate in 100 cc. of abs. EtOH (25°) for 6 hr. in dark. The precipitates were removed by filtration

18) E. Hardegger, R. Montavon: Helv. Chim. Acta., **29**, 1199 (1946).
19) H. Ohle, H. Thiel: Ber., **66**, 525 (1933).
20) W.H. Haworth, J. Jackson, F. Smith: J. Chem. Soc., **1940**, 620.
21) B. Helferich, E. Himmen: Ber., **61**, 1825 (1928).
22) J. Compton: J. Am. Chem. Soc., **60**, 395 (1938).

and washed three times with 50 cc. of $CHCl_3$. The filtrate and washings were combined and evaporated under reduced pressure to dryness.

The resulted crystals were recrystallized from EtOH to pure Ⅷ, m.p. 144～145°; $[\alpha]_D^{18}$ −7.1°(c=1.4, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{28}O_{11}S$: C, 51.62; H, 5.84; S, 6.56. Found: C, 51.54; H, 5.63; S, 6.59.

6) Isopropyl 6-O-tosyl-2,3,4-tri-O-acetyl-β-D-glucopyranoside (Ⅸ) was prepared from 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-glucopyranosyl bromide and isopropanol similar to Ⅷ, m.p. 127～128°; $[\alpha]_D^{18}$ −11.6° (c=1.2, $CHCl_3$). *Anal.* Calcd. for $C_{22}H_{30}O_{11}S$: C, 52.57; H, 6.01; S, 6.38. Found; C, 52.52; H, 5.85; S, 6.38.

7) *tert*-Butyl 6-O-tosyl-2,3,4-tri-O-acetyl-β-D-glucopyranoside (Ⅹ) was prepared from 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-glucopyranosyl bromide and *tert*-butanol (initially at 30°) by the same method as described above. m.p. 156～157°; $[\alpha]_D^{18}$ +11.6°(c=1.2, $CHCl_3$). *Anal.* Calcd. for $C_{23}H_{32}O_{11}S$: C, 53.47; H, 6.24; S, 6.21. Found: C, 53.46; H, 6.12; S, 6.01.

8) Phenyl 6-O-tosyl-2,3,4-tri-O-acetyl-β-D-glucopyranoside (Ⅺ) was prepared from 6-tosylacetobromoglucose and phenol after the procedure reported by Glaser and Wulwek,[23] m.p. 153～154°; $[\alpha]_D^{18}$ −22.8°(c=1.0, $CHCl_3$). *Anal.* Calcd. for $C_{25}H_{32}O_{11}S$: C, 55.96; H, 5.26; S, 6.98. Found: C, 55.64; H, 5.24; S, 6.68.

9) Methyl 6-O-tosyl-2,3,4-tri-O-acetyl-α-D-mannopyranoside (Ⅻ) was prepared by unimolar tosylation and successive acetylation of methyl α-D-mannopyranoside. To a solution of 10 g. of methyl α-D-mannopyranoside (192～193°) in 150 ml. of anhyd. pyridine was added 10 g. of tosyl chloride in one portion under vigorous stirring. After standing for 24 hr. at room temperature, 40 g. of acetic anhydride was added portionwise and the mixture was allowed to stand at room temperature for 6 hr. The mixture was poured into 1 L. of ice-water and the resulted syrup was taken up in $CHCl_3$, washed with dilute sulfuric acid, sodium bicarbonate, and H_2O successively, and treated with charcoal. The $CHCl_3$ extract was concentrated to syrup. 5 g. of this material was diluted to 50 cc. with MeOH and chromatographed on 400 g. of Celite-charcoal (1:1).

The material was then eluted with MeOH, and in the second 200 cc. portion of effluent 4.6 g. of syrupy material was obtained.

All attempts to crystallize this syrup Ⅻ were failed. $[\alpha]_D^{18}$ +64.2°(c=0.82, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{26}O_{11}S$: C, 50.62; H, 5.52; S, 6.71. Found: C, 50.38; H, 5.54; S, 7.02.

Kinetic Measurements——Acetone was purified by the method of Conant and Kirner.[24] Sodium iodide was dried in a vacuum at 120° in an Abderhalden apparatus.

Each aliquot (2 cc.) of Me_2CO solution of sodium iodide and tosylate (0.05M, respectively) was pipetted into pressure tube (OS-type, 40 cc.), stoppered, and placed in thermostat at 100°. At appropriate time intervals, the tubes were taken up and cooled by ice-water. The reaction mixture was immediately added to dist. water (100 cc.), and titrated the residual with KI.[5]

Since all the reactions were of second order, the rate coefficient were calculated from the formula $k=\frac{1}{t}\left(\frac{1}{Mt}-\frac{1}{Mo}\right)$ where Mt and Mo are the concentration of iodide, taken at time t and initial. The results are listed in Table Ⅲ.

Table Ⅲ. Rate Coefficients ($10^2 \times K$ L.·mole^{-1}·min^{-1})

Time (min.) / Compound	10	20	30	40	60	80	120	180	mean
I	66.7	67.8	67.7	67.9	68.7	68.6	67.9	68.1	67.9
II	30.5	32.6	32.3	32.0	32.9	31.6	32.6	31.6	32.0
III	70.1	69.5	69.8	69.8	66.1	67.7	68.1	68.5	68.6
IV	29.6	32.0	31.1	33.0	32.0	31.3	32.5	33.3	31.9
VII	74.3	72.9	71.6	71.2	70.9	72.2	72.7	71.2	72.3
VIII	59.6	58.2	58.6	55.1	57.1	57.3	58.6	56.3	57.5
IX	59.1	55.1	56.7	55.1	53.4	55.7	55.5	54.6	55.4
X	50.5	48.3	52.6	51.1	52.0	51.8	51.3	51.3	51.1
XI	32.7	31.1	31.5	31.5	32.5	31.1	29.8	31.5	31.5
XII	47.8	46.4	46.8	47.8	48.4	47.8	47.6	48.9	47.7
XIII	28.2	29.2	25.7	26.6	26.1	25.7	24.5	25.7	26.5
Time (min.) / Compound	90	120	240	480	720	960	1440	1920	mean
V	5.46	5.89	5.32	5.32	5.38	5.22	5.30	5.42	5.41
VI	1.82	1.79	1.70	1.68	1.71	1.79	1.69	1.71	1.73

23) E. Glaser, W. Wulwek: Biochem. Z., **145**, 514 (1924).
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Products of Reaction——The reaction of 3 g. of tosylate with 3 g. of NaI in Me_2CO (15cc.) at 100° was allowed to proceed for 4 hr. (20 cc.). The mixture was poured into 100 cc. of H_2O and the resulted precipitates were filtered off and recrystallized from EtOH. Especially galactose derivatives (V and VI) were heated at 120° for 12 hr. The results are given in Table IV.

Table IV. Reaction Products

Compound	m.p. (°C)	$[\alpha]_D^{18}$ in $CHCl_3$	Yield (%)	Analysis (%) Calcd. C	Calcd. H	Calcd. I	Found C	Found H	Found I	Ref.
6-Deoxy-6-iodo-tetraacetyl-α-D-glucopyranose	148~149	+102 (c=0.9)	Theoretical	36.69	4.18	27.69	36.52	4.26	27.64	18)
6-Deoxy-6-iodo-tetraacetyl-β-D-glucopyranose	180~181	+10.0 (c=1.2)	〃		4.18		36.78	4.33	27.94	〃
6-Deoxy-6-iodo-tetraacetyl-α-D-glucopyranosamine	196~197	+92.2 (c=1.2)	〃	36.78	4.41	27.75	36.78	4.51	27.98	10)
6-Deoxy-6-iodo-tetraacetyl-β-D-glucopyranosamine	192~193	+8.8 (c=1.0)	〃				36.50	4.63	27.64	〃
6-Deoxy-6-iodo-tetraacetyl-α-D-galactopyranose	107~103	+70.2 (c=0.94)	58	36.69	4.18	27.69	36.44	4.02	27.78	
6-Deoxy-6-iodo-tetraacetyl-β-D-galactopyranose	113~114	+10.4 (c=0.96)	46				36.82	4.32	27.62	
Methyl-6-deoxy-6-iodo-triacetyl-α-D-glucopyranoside	150~151	+116.1 (c=1.0)	Theoretical	36.29	4.45	29.50	36.38	4.47	29.42	
Methyl-6-deoxy-6-iodo-triacetyl-β-D-glucopyranoside	114~115	+2.4 (c=1.2)	〃	36.29	4.45	29.50	36.54	4.62	29.78	21), 22)
Ethyl-6-deoxy-6-iodo-triacetyl-β-D-glucopyranoside	146~147	−1.7 (c=1.2)	〃	37.84	4.76	28.57	38.02	4.68	28.29	
Isopropyl-6-deoxy-6-iodo-triacetyl-β-D-glucopyranoside	162~163	+4.4 (c=1.15)	〃	39.32	5.06	27.69	39.47	4.92	27.69	
tert-Butyl-6-deoxy-6-iodo-triacetyl-β-D-glucopyranoside	141~142	−3.9 (c=1.03)	〃	40.89	5.33	26.87	40.95	5.20	26.87	
Phenyl-6-deoxy-6-iodo-triacetyl-β-D-glucopyranoside	133~134	−36.2 (c=1.88)	〃	43.92	4.30	25.78	44.13	4.26	25.60	
Methyl-6-deoxy-6-iodo-triacetyl-α-D-mannopyranoside	68~69	+44.6 (c=2.33)	〃	36.29	4.45	29.50	36.19	4.57	29.38	

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Summary

Rates of displacement of primary tosyloxy groups of acetylated carbohydrate derivatives with iodide ion have been measured. The products of the reaction have been isolated in all instances. The displacement reaction is second order and the differences in rate coefficients are discussed by the geometry of transition state.

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