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199. Shigeharu Inouye*1 : Optical Rotatory Dispersion Curves of Some N-Salicylidene Amino-sugars.*2

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Optical rotatory dispersion and circular dichroism curves of sixteen members of N-salicylideneamino-sugars were meaured in methanol and, in part, in dioxane. It was found for the D-glucose derivatives that the positive Cotton effects near 405, 315 and 255 mμ were correlated with the D (S) configuration of the C-2 chromophore and that the negative sign with the L (R) configuration of the C-1 and C-3 chromophores. The Schiff bases showing strong absorption at 405 mμ exhibited strong Cotton effect near 405 mμ, which was qualitatively interpreted in terms of the intramolecular hydrogen bonding asymmetric solvation to the optically active azomethine. The optical rotatory dispersion curves of poly-N-salicylidene derivatives were determined not only by the rotatory power of the individual chromophores but by relative amounts of tautomers equilibrated in solution.

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The stereochemistry of carbohydrates which are transparent in the 210~700 mμ has been successfully investigated through anomalous optical rotatory dispersion (ORD) curves of the "chromophoric" derivatives, such as xanthates[1] and nitrates.[2] The chromophoric derivatives of amino-sugars, in which the chromophore is introduced on an amino group, represent another interesting field for the ORD studies, since a large number of amino-sugars are recently available in natural and synthetic products. The work presented in this paper was initiated originally with the purpose of determining the configuration of the amino group in amino-sugars through the sign of Cotton effect in the chromophoric derivatives. Among many of the "chromophores" proposed for the transparent amino group,[3] N-salicylidene Schiff base appeared as an attractive candidate by virture of the relative ease of preparation and the striking difference observed in the $[\alpha]_D$ values of the N-salicylidene derivatives of amino-sugars which otherwise showed very close $[\alpha]_D$.

Results

The N-salicylidene Schiff bases examined in this paper were listed in Table I, together with the molecular rotations at the sodium D-line ($[\phi]_D$), signs of the Coton effects in the ORD curves, maximum molecular ellipticities ($[\theta]$) in the circular dichroism (CD) curves and $[\phi]_D$ of the parent amino-sugars. Fig. 1 showed the electronic absorption spectra and the ORD curves of methyl N-salicylidene-3-amino-3-deoxy-α-D-mannopyranoside (XI) in methanol and in dioxane. As described in detail in a separate paper,[4] the electronic spectra of N-salicylidene amino-sugars were highly dependent upon the nature of solvents as well as sugar components. In methanol solution, four absorption bands were usually observed above 240 mμ, *i.e.*, at *ca.* 255, 280, 315 and 405 mμ, of which the 280 and 405 mμ bands decreased markedly in intensity in dioxane

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*2 Preliminary report, "Symposium Abstracts, 9th Symposium on the Chemistry of Natural Products," Osaka, October 13, 1965, p. 7.

1) Y. Tsuzuki, K. Tanabe, M. Akagi, S. Tejima : Bull. Chem. Soc. Japan, **37**, 162 (1964).
2) *a*) Y. Tsuzuki, K. Tanabe, K. Okamoto, N. Yamada : *Ibid.*, **39**, 1391 (1966). *b*) Y. Tsuzuki, K. Tanabe, K. Okamoto : *Ibid.*, **39**, 761 (1966).
3) C. Djerassi : Proc. Chem. Soc., 314 (1964).
4) S. Inouye : This Bulletin, **15**, 1540 (1967).

TABLE I. Molecular Rotations ($[\phi]$) at the Sodium D-Line, Signs of Cotton Effects and Maximum Molecular Ellipticities ($[\theta]$) in N-Salicylidene Amino-sugars in Methanol and Dioxane, and $[\phi]_D$ of Parent Amino-sugars in Water

No.	N-Salicylidene Derivative of	$[\phi]_D$ of Parent Amino-sugar H_2O	$[\phi]_D$ MeOH	$[\phi]_D$ Dioxane
1	β-D-Glucopyranosylamine (I)	+ 38°	0°	− 47°
2	β-D-Mannopyranosylamine (II)	− 23	+117	
3	Methyl 2-Amino-2-deoxy-α-D-glucopyranoside (III)	+291	+517	+440
4	Methyl 2-Amino-2-deoxy-β-D-glucopyranoside (IV)	− 55	+ 18	
5	2-Amino-2-deoxy-D-glucose (V)	+ 85	+292	+224[a]
6	2-Amino-2-deoxy-D-galactose (VI)		+182	
7	2-Amino-2-deoxy-D-mannose (VII)		+ 96	
8	2-Amino-2-deoxy-D-glucitol (VIII)	− 10	+291	+114
9	Methyl 3-Amino-3-deoxy-α-D-glucopyranoside (IX)	+300	+333	+324
10	Methyl 3-Amino-3-deoxy-β-L-glucopyranoside (X)	+ 66	+ 15	+ 21
11	Methyl 3-Amino-3-deoxy-α-D-mannopyranoside (XI)	+138	−160	+ 24
12	Methyl 6-Amino-6-deoxy-α-D-glucopyranoside (XII)	+317	+291	+339
13	5-Amino-5-deoxy-1,2-O-isopropylidene-α-D-xylofuranose (XIII)	− 23	− 21	− 38
14	Methyl 3,6-Diamino-3,6-dideoxy-α-D-glucopyranoside (XIV)	+290	+636	+576
15	Methyl 3,6-Diamino-3,6-dideoxy-α-D-mannopyranoside (XV)	+110	− 72	−128
16	Methyl 3,6-Diamino-3,6-dideoxy-α-D-altropyranoside (XVI)	+208	+208	+ 68

No.	Sign of Plain ORD (450∼600 mμ) MeOH	Sign of Cotton Effect ($[\theta]_{max}$ (mμ)) MeOH		
1	−		−(−1200(318))	−(−10000(261))
2	+	+(+ 81(405))	+(+2500(312))	+(+ 5400(252))
3	+	+	+	+
4	+		+(+2300(312))	+(+ 7900(260))
5	+	+(+1700(401))	+(+5200(313))	+(+11000(259))
6	+	+(+ 440(408))	+(+1200(312))	+
7				
8	+	+(+1500(405))	+(+2800(315))	+(+ 2500(257))
9	+		−(−1800(316))	−(− 2600(254))
10	+			
11	−	−(−2800(408))	−(−3500(315))	−(− 5700(255))
12	+	+	+	+
13	+		+(+ 740(317))	+
14	+	+(+ 900(405))	+(+2500(313))	+(+ 1700(257))
15	−	−(−2400(401))	−(−3400(310))	−(− 7900(253))
16	+	+(+2200(408))	+(+2700(320))	+(+23000(251))[b]

a) Contained 20% dimethylformamide.
b) Additional CD maximum in MeOH, −15000 (267). CD Maxima in dioxane, +6600 (316), +13000 (253), −94000 (271).

solution, with concomitant strengthening of the 255 and 315 mμ bands, as exemplified in Fig. 1. The ORD curve of XI in methanol displayed negative plain curve with negative $[\phi]_D$ value to about 450 mμ, beyond which three negative Cotton effects were successively observed, associated with three absorption bands near 405, 317 and 256 mμ. The ORD curve near 280mμ was obscured by the two strong Cotton effects located at longer and shorter wave-lengths (317 and 256 mμ), and no distinct Cotton effect could be observed. The intense absorption band near 215 mμ prevented further measurement of rotatory power beyond about 240 mμ. The three negative CD maxima shown in Fig. 2 confirmed negative signs in the three Cotton effects. Of most interest in XI was the fact that the $[\phi]$ and $[\theta]$ values

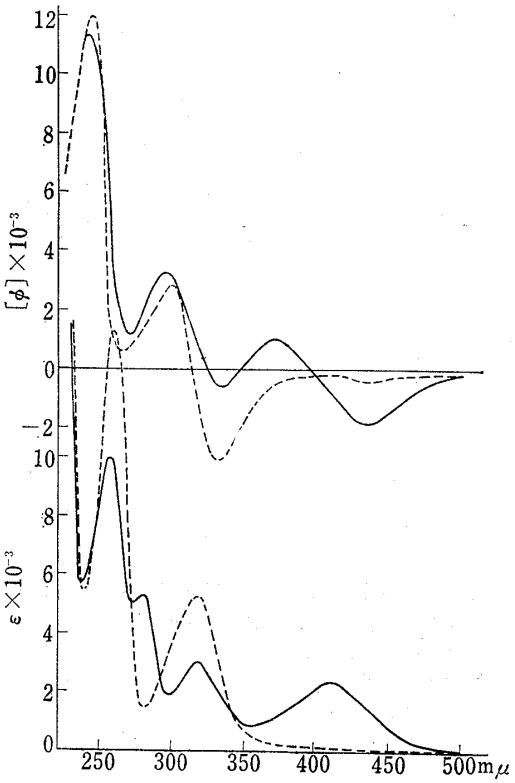

Fig. 1. ORD Curves and Electronic Absorption Spectra of Methyl N-Salicylidene-3-amino-3-deoxy-α-D-mannopyranoside (XI) in Methanol (——) and in Dioxane (- - -)

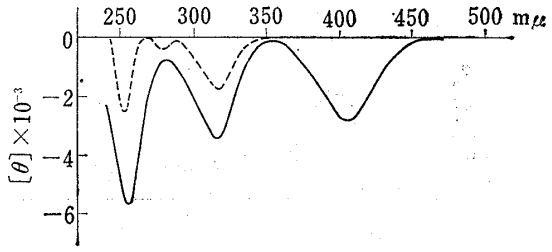

Fig. 2. CD Curves of N-Salicylidene Derivatives of Methyl 3-Amino-3-deoxy-α-D-mannopyranoside (XI) (——) and Methyl 3-Amino-3-deoxy-α-D-glucopyranoside (IX) (- - -) in Methanol

associated with the 405 mμ band were large enough to compare well with those associated with the 317 mμ band. Such large values near 405 mμ have not been observed in the N-salicylidene Schiff bases of acyclic alkylamines[5] and amino-steroids.[6] Undoubtedly, the negative dispersion in the visible region with negative $[\phi]_D$ value in XI was due to the large amplitude of the negative Cotton effect near 405 mμ, since the parent 3-amino-sugar exhibited positive background rotation in this spectral region. The Schiff base XI in dioxane displayed a weakly negative Cotton effect near 410 mμ, and two strong negative Cotton effects corresponding to a weak absorption band at 410 mμ and strong bands at 318 and 257 mμ in the electronic spectrum. Conversion of the negative $[\phi]_D$ to positive $[\phi]_D$ was due to the decreased contribution of the negative Cotton effect around 410 mμ.

In comparison, the ORD curve of methyl N-salicylidene-3-amino-3-deoxy-α-D-glucopyranoside (IX) (Fig. 3) showed, both in methanol and in dioxane, two negative Cotton effects with small amplitudes associated with the 316 and 255 mμ bands in the absorption spectrum. The weak Cotton effects in IX were substantiated by the low molecular ellipticities ($[\theta]$) of the negative CD maxima shown in Fig. 2. No anomaly in the ORD and CD curves was recognized to be associated with a weak absorption maximum at 405 mμ in methanol, even when the concentration of IX increased enough to compensate for the decrease in the absorbance in this spectral region. The positive dispersion in the visible region in IX was the reflection of the positive background rotation of the parent 3-amino-sugar, but not the rotatory power of the azomethine chromophore which should contribute to the negative dispersion. Methyl N-salicylidene-3-amino-3-deoxy-β-L-glucopyranoside X showed, in methanol, essentially the same absorption spectrum as the corresponding α-D-derivative (IX), but the Cotton effects in the ORD curve were too weak to determine their signs. Similarly, no maximum was recognized in the CD curve of X.

Methyl N-salicylidene-2-amino-2-deoxy-α-D-glucopyranoside (III) in methanol showed a higher dextrorotation than did the parent amino-sugar at the sodium D-line and its

5) H. E. Smith, R. Records: Tetrahedron, **22**, 813 (1966).
6) D. Bertin, M. Legrand: Compt. rend., **256**, 960 (1963).

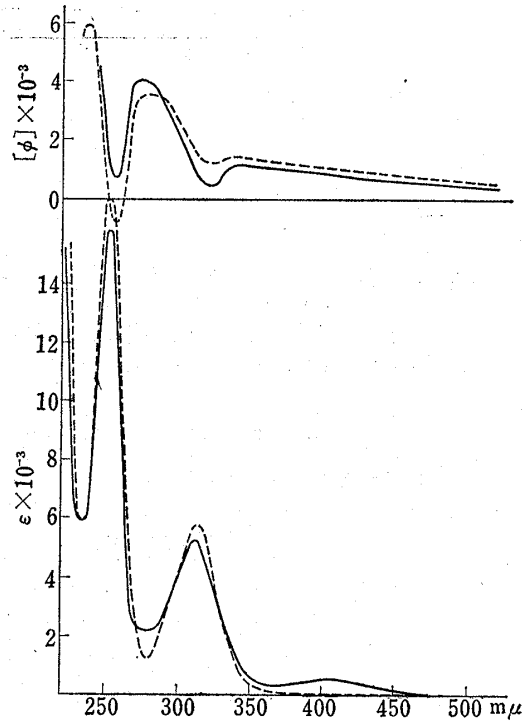

Fig. 3. ORD Curves and Electronic Absorption Spectra of Methyl N-Salicylidene-3-amino-3-deoxy-α-D-glucopyranoside (IX) in Methanol (——) and in Dioxane (- - -)

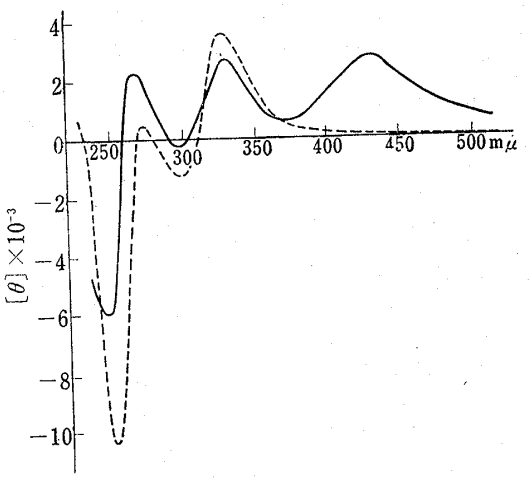

Fig. 4. ORD Curves of N-Salicylidene Derivatives of Methyl 2-Amino-2-deoxy-α-D-glucopyranoside (III) (——) and Methyl 2-Amino-2-deoxy-β-D-glucopyranoside (IV) (- - -) in Methanol

ORD curve illustrated in Fig. 4 displayed three positive Cotton effects centered near 405, 318 and 256 mμ. Again, the large amplitude associated with the large absorbance at 405 mμ was noted. In changing the solvent from methanol to dioxane, the Cotton effect near 405 mμ became weakened markedly, accompanied with the increase in amplitude of the Cotton effects near 318 and 256 mμ. The ORD curve of methyl N-salicylidene-2-amino-2-deoxy-β-D-glucopyranoside (IV) in methanol exhibited two positive Cotton effects around 315 and 255 mμ, but, in contrast with III, no anomalous ORD curve and no CD maximum were observed to be associated with the weak absorption maximum at 405 mμ, even in the concentrated solution. The Schiff base IV displayed positive dispersion with positive $[\phi]_D$ in the transparent region, irrespective of the laevorotatory background contribution of the β-D-glucoside type. This suggested that the effect of the C-2 chromophore which gave a positive contribution outweighed the effect of the C-1-β-methoxyl group whose contribution was negative in sign.[7]

The ORD curve of N-salicylidene-2-amino-2-deoxy-D-glucose (V), which was a mixture of α and β anomers, showed three positive Cotton effects and three positive CD maxima in methanol, similar to the curve III. N-Salicylidene-2-amino-2-deoxy-D-galactose (VI) in methanol, likewise, exhibited three positive Cotton effects, though the effects were reduced in strength. Unfortunately, no distinct conclusion was derived on the sign of the feeble Cotton effect in the ORD curve of N-salicylidene-2-amino-2-deoxy-D-mannose (VII). Noteworthy was the ORD and CD curves of N-salicylidene-2-amino-2-deoxy-D-glucitol (VIII). Although the parent acyclic amino-alcohol exhibited very low $[\phi]_D$ value, its Schiff base VIII in methanol displayed three positive Cotton effects with large amplitudes and three positive CD maxima with high molecular ellipticities near 405, 315 and 255 mμ.

7) I. Listowsky, G. Avigad, S. Englard: J. Am. Chem. Soc., 87, 1765 (1965).

As for the 1-salicylideneamino-sugars, the Schiff base of β-D-glucopyranosylamine (I) exhibited negative dispersion in the visible region and two negative Cotton effects in the ultraviolet region, whereas the Schiff base of β-D-mannopyranosylamine (II) showed positive dispersion and three positive Cotton effects in methanol. The respective CD curves of I and II confirmed the above assignments.

The ORD curves of methyl N-salicylidene-6-amino-6-deoxy-α-D-glucopyranoside (XII) and -5-amino-5-deoxy-1,2-O-isopropylidene-α-D-xylofuranose (XIII), where the chromophore was separated from the asymmetric center by one carbon atom, gave weak Cotton effects whose signs were all positive in methanol.

The ORD and CD measurements with methyl N-salicylidene-3,6-diamino-3,6-dideoxy-α-D-glucopyranoside (XIV) and -mannopyranoside (XV) were interesting, since the C-3 and C-6-salicylideneamino-sugars (IX, XI, XII) exhibited opposite signs in the Cotton effects and CD maxima.

Fig. 5 illustrated the CD curves of XIV and XV in methanol, which revealed the three positive maxima for XIV and three negative maxima for XV. The respective ORD curves resembled the curves of XII and XI. Thus, the positive sign in XIV coincided with the positive sign of the C-6 chromophore in XII, and the negative sign in XV with the negative sign of the C-3 chromophore in XI. Methyl N-salicylidene-3,6-diamino-3,6-dideoxy-α-D-altropyranoside (XVI) displayed both in methanol and in dioxane, three positive Cotton effects associated with the 404, 312 and 254 mμ bands. At wavelength near 270 mμ, XVI showed an additional negative Cotton effect, the presence of which was confirmed by the negative CD maximum. The origin of the last Cotton effect was not proved, but, it appeared more likely that it arised from the overlapping of the oppositely signed Cotton effects of similar amplitude[8] near 255 mμ, rather than the association with weak absorption shoulders near 280 and 260 mμ, because the similar extra CD maxima were frequently encountered in the poly-N-salicylideneamino-sugars.[9]

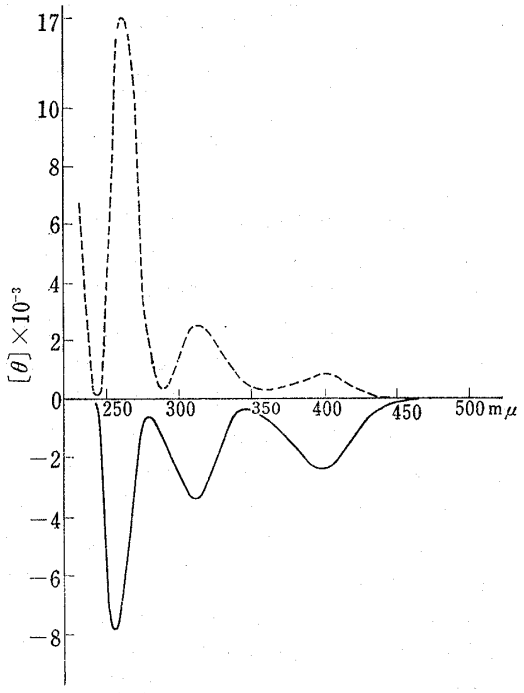

Fig. 5. CD Curves of N-Salicylidene Derivatives of Methyl 3,6-Diamino-3,6-dideoxy-α-D-glucopyranoside (XIV) (- - -) and Methyl 3,6-Diamino-3,6-dideoxy-α-D-mannopyranoside (XV) (——) in Methanol

Discussion

The sign of the Cotton effect in the chromophoric derivative was frequently succeeded to correlate with the absolute configuration of the nearest asymmetric center. Thus, Bertin and Legrand[6] reported that the α (S) configuration of the C-20 chromophore of 20-salicylideneamino-steroids could be correlated with the positive CD maximum at 315 mμ. Smith, *et al.*[5] mentioned that the positive sign in the Cotton effect associated with the 315 mμ band in N-salicylidene-aralkylamines was related with the S-configuration of the asymmetric carbon atom. Table II summarized the relationship between

8) K.M. Wellman, P.H.A. Laar, W.S. Briggs, A. Moscowitz, C. Djerassi: J. Am. Chem. Soc., **87**, 66 (1965).
9) S. Inouye: This Bulletin, **15**, 1612 (1967).

Table II. Absolute Configuration and Sign of Cotton Effect in Some Salicylideneamino- and O-Nitro-D-glucoses

Configuration at C-1	Position of Chromophore	Aboslute Configuration of Chromophore	ORD Sign	
			Salicylideneamino (MeOH)	Nitrate ($CHCl_3$)
β	C-1	L(R)	−	−[a]
α	C-2	D(S)	+	−[b]
β	C-2	D(S)	+	−[c]
α	C-3	L(R)	−	+[d]
β	C-3	L(R)	?*	?*,[e]
α	C-6	L(R)[f]	+	+[g]

a) 2,3,4,6-Tetra-O-acetyl-1-O-nitro-β-D-glucopyranose
b) 1,3,4,6-Tetra-O-acetyl-2-O-nitro-α-D-glucopyranose
c) 1,3,4,6-Tetra-O-actyl-2-O-nitro-β-D-glucopyranose
d) Methyl 4,6-O-benzylidene-3-O-nitro-α-D-glucopyranoside
e) Methyl 4,6-O-benzylidene-3-O-nitro-β-D-glucopyranoside
f) Absolute configuration at C-5
g) Methyl 2,3,4-tri-O-acetyl-6-O-nitro-α-D-glucopyranoside
* The Cotton effect was too weak to determine the sign.

the absolute configuration*[3] and the sign of the Cotton effect found for the glucose derivatives. It has seen from Table II that the C-1 and C-3 salicylideneamino-derivatives having the L (R) configuration showed negative sign, whereas the C-2 salicylideneamino-derivatives having the D (S) configuration exhibited positive sign, in accord with the regularity observed for the other classes of compounds. In this connection, it was interesting to note that the rotatory contribution of the salicylideneamino-chromophores in D-glucose coincided in sign with those of the nitrate substituents reported by Tsuzuki, *et al.*,[2] with the exception of the C-2 and C-3 substituted α-anomers (Table II). In the exceptional case, inversion of the sign was observed in the nitrate derivatives.

Extension of the regularity observed for the salicylideneamino-glucoses to the mannose derivatives was not always successful. Thus, the compound II exhibited positive Cotton effect in spite of the L (R) configuration at the C-1 atom. Similarly, two 3,6-disalicylideneamino-sugars (XIV and XV) showed opposite signs in the ORD and CD curves, though both had the same absolute configurations with regards to the C-3 and C-6 chromophores. 3-Salicylideneamino-mannose derivative (XI), on the other hand, showed negative Cotton effects in agreement with the glucose counterpart (IX). These results suggested that the sign of the Cotton effect in N-salicylideneamino-sugars was not determined by the absolute configuration alone.

Another complicated phenomenon in the ORD curves of N-salicylideneamino-sugars was a large variation of amplitudes of the Cotton effects associated with the 405 mμ band. Of particular significance was the unusually large amplitude in III, V, VII and XI corresponding with the large absorbance in the electronic spectra. A qualitative interpretation on the ORD difference near 405 mμ could be derived from the structure of the salicylideneaminochromophore discussed in the separate paper.[4] Of the four absorption bands, the 255 and 315 mμ bands were assigned to the π-π^* transitions of the phenolimine species, whereas the 280 and 405 mμ bands were assigned to the π-π^* transitions of the ketoamine species. In aprotic solvents such as dioxane, the tautomeric equilibrium was predominantly shifted to the phenolimine side, but in protic solvents such as methanol,

*3 The assignment of R or S to the "chromophoric" sugars was made on the basis of the relative bulkness of the exo- and cyclic-substituents determined according to Bose, *et al.* (A.K. Bose, B.G. Chafferiece: J. Org. Chem., **23**, 1425 (1958)).

the ketoamine species increased owing to the stabilization by solvation or intramolecular hydrogen bonding involving the alcoholic hydroxyl group (Fig. 6).

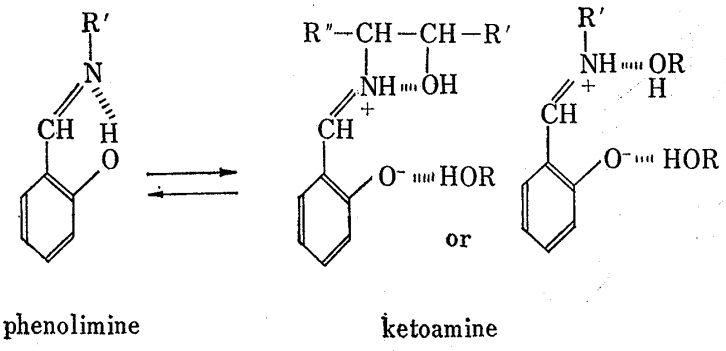

Fig. 6. Schematic Representation of Structures of the Phenolimine and Ketoamine Species in Hydroxylic Solvents

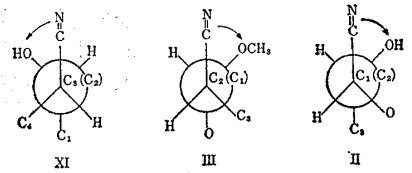

Fig. 7. Newman Projection of N-Salicylidene Derivatives of Methyl 3-Amino-3-deoxy-α-D-mannopyranoside (XI), Methyl 2-Amino-2-deoxy-α-D-glucopyranoside (III) and β-D-Mannopyranosylamine (II)

It may be readily seen from the structure of the ketoamine that the direction of solvation or intramolecular hydrogen bonding played a vital role in determining the sign and strength of the Cotton effect, since the solvent and hydroxyl group interacted directly with the π electron system of the conjugated chromophores and since they locked the chromophore in space. Let us consider, for example, the ketoamine structures of III and XI, where the intramolecular hydrogen bonding was suggested between the equatorial azomethine group and the *cis*-axial substituents.[4] When the two compounds were projected along the C-2 (3) to C-1 (2) according to Newman (Fig. 7), it was immediately seen that the *cis*-substituents internally bonded in III and XI were located oppositely against the C=N chromophore, *i.e.*, left in III and right in XI. The Newman projection of the β-D-mannosylamine derivative (II) shown in Fig. 7 indicated that the spacial relationship between the C-2-*cis*-axial hydroxyl group and C-1-equatorial chromophore was the same as that of III. Accordingly, if we assumed that the relative configuration as seen in II and III contributed to the positive Cotton effect, and that the configuration in XI contributed to the negative Cotton effect, outweighing the effect of the absolute configuration of the nearest asymmetric carbon, apparent discrepancy between the mannose and glucose derivatives became disappeared. Obviously, further experiment was required to test the validity of this assumption. The absence or very weakness of the Cotten effect near 405 mμ in the cases of IV, IX and X may be ascribed to the local symmetry of the vicinal substituents and solvation against the azomethine chromophore. That the weakness in these compounds was not due to the decreased concentration of the ketoamine species was demonstrated by the fact that no strong Cotten effect was observed even in the concentrated solution to compensate for the decrease in the absorbance.

Stereochemical correlation of the sign of the Cotton effect in the poly-N-salicylideneamino-sugars was much complicated, since various tautomeric species could be present in solution. In the methanol solution of methyl N-salicylidene-3,6-diamino-3,6-dideoxy-α-D-mannopyranoside (XV), for example, four tautomers (a, b, c, d) existed (Fig. 8). Then, the measured or macroscopic equilibrium constant (K_T) was represented by the following equation,

$$K_T=\frac{[\text{ketoamine}]}{[\text{phenolimine}]}=\frac{2[d]+[b]+[c]}{2[a]+[b]+[c]}.$$

If the microscopic equilibrium constants (k_t) were defined by $k_{t1}=[b]/[a]$, $k_{t2}=[c]/[a]$, $k_{t3}=[d]/[b]$ and $k_{t4}=[d]/[c]$,

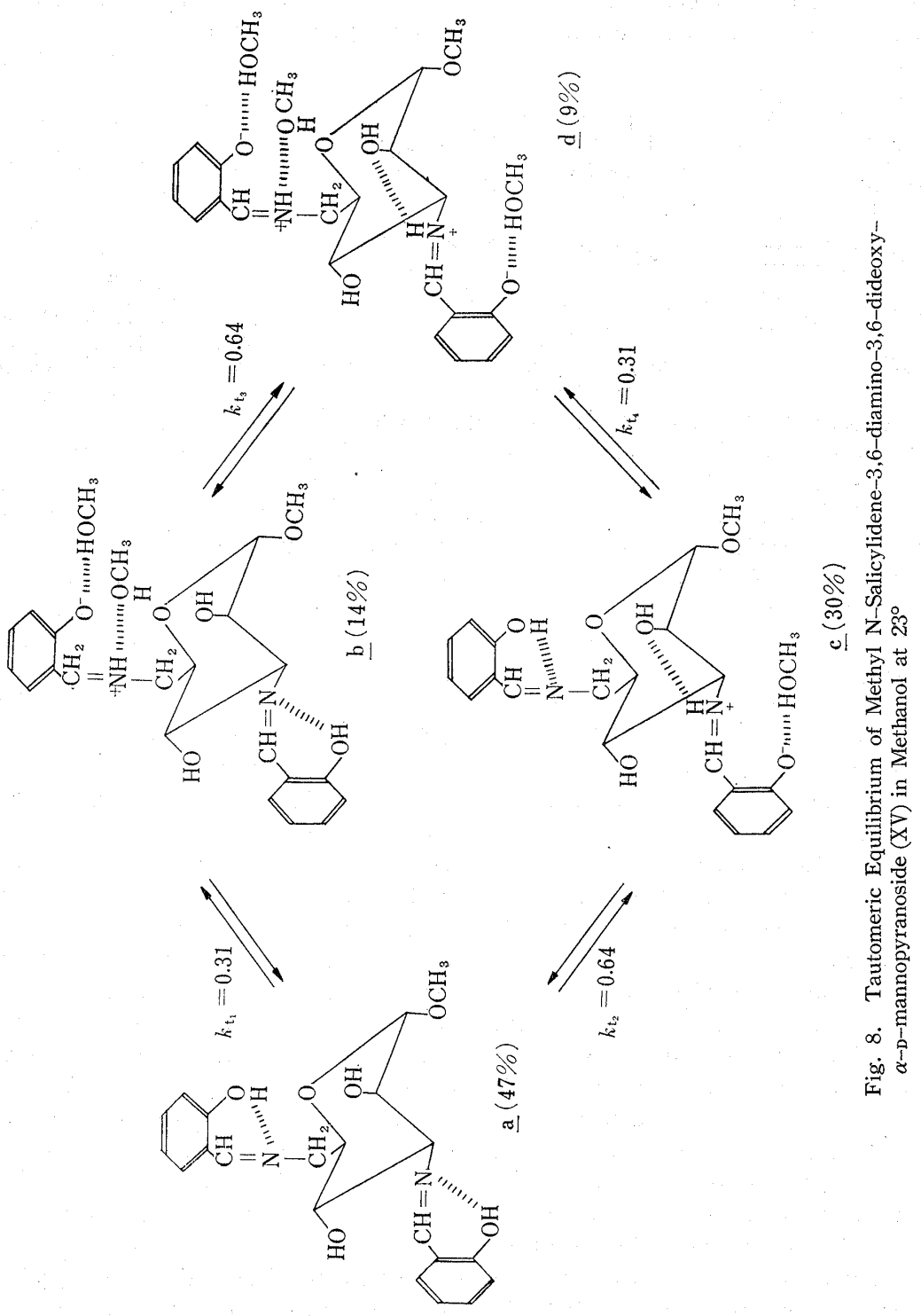

Fig. 8. Tautomeric Equilibrium of Methyl N-Salicylidene-3,6-diamino-3,6-dideoxy-α-D-mannopyranoside (XV) in Methanol at 23°

the macroscopic $K_T=\frac{k_{t1}+k_{t2}+2k_{t1}\cdot k_{t3}}{k_{t1}+k_{t2}+2}=\frac{k_{t1}+k_{t2}+2k_{t2}\cdot k_{t4}}{k_{t1}+k_{t2}+2}$.

The microscopic k_t values, which were difficult to determine experimentally, were estimated from the K_T values of the compounds XI (0.64) and XII (0.31) Calculatson of the K_T of XV using the assumed k_t values gave very close value (0.46) to the ovserved one (0.43), indicating the validity of the k_t assumed. From the microscopic k_t, it was possible to calculate the relative amounts of tautomers in methanol, which were shown in Fig. 8. If the above calculation was correct, the C-3 ketoamine chromophore of c was

a dominant contributor to the 405 mμ band and probably to the negative Cotton effect near 405 mμ, while the negative sign near 315 mμ was attributable to the two phenolimine chromophores on C-3 and C-6 of d species. Here, the C-3 chromophore probably predominated over the C-6 chromophore in the rotatory contribution, considering from the larger amplitude of the C-3 chromophore in XI.

Similar calculation on methyl N-salicylidene-3,6-diamino-3,6-dideoxy-α-D-glucopyranoside (XIV) assuming $k_{t1}=k_{t3}=0.31$ (K_T value of XII) and $k_{t2}=k_{t4}=0.07$ (K_T value of IX) gave the macroscopic $K_T=0.17$, very close to that found (0.16) and the respective percentages of four tautomers (a=72% (C-3 and C-6 phenolimine), b=22% (C-6 ketoamine, C-3 phenolimine), c=5% (C-3 ketoamine, C-6 phenolimine) and d=1% (both ketoamine). Then, the main ketoamine species responsible for the 405 mμ band and the positive sign near 405 mμ seemed to be b, in which the C-6 chromophore took the ketoamine form. These results suggested that the signs of the Cotton effects near 405 and 315 mμ may be not always the same, as indeed found for some tetra- and penta-N-salicylideneamino-sugars.[9]

Experimental

The preparation of the salicylidene Schiff bases employed in this work were reported in the separate paper.[4] The ORD and CD measurements were performed on a JASCO Model ORD/UV-5 instrument (Japan Spectroscopic Co., Ltd.) using a quartz cell of 1.0 cm. thickness at 20~25°. Unless otherwise stated, the concentrations used were 0.4~0.2% in the 600~450 mμ region, 0.2~0.02% in the 450~350 mμ region, 0.02~0.01% in the 350~280 mμ region and 0.005~0.003% in the 280~230 mμ region. The ORD data were summarized in Table III. Values of $[\phi]$ and $[\theta]$ were generally reproducible to within 10% when a ratio of the amplitude or $[\theta]_{max}$ to the ε value (molar absorption coefficient) was above 1. When a ratio was below 0.5, these values were much less reliable. Optical rotatory power at the sodium D-line was measured with a visible polarimeter using 1.0% solution and 10 cm. cell tube at 20~25°. The electronic absorption data of salicylidene Schiff bases recorded with a Hitachi EPS-2U spectrometer were assembled in Table IV.

Table IV. Electronic Absorption Data of N-Salicylidene Derivatives in Methanol and Dioxane at 23°C

Compound	Solvent	λ_{max} mμ ($\varepsilon \times 10^{-4}$)			
I	MeOH	257 (1.44)		319 (0.44)	405 (0.01)
II	MeOH	256 (1.30)		317 (0.43)	405 (0.02)
III	MeOH	256 (1.20)	280 (sh)	318 (0.31)	405 (0.16)
III	Dioxane	257 (1.23)		318 (0.44)	
IV	MeOH	256 (1.35)		317 (0.40)	405 (0.02)
V	MeOH	256 (1.33)	280 (sh)	317 (0.39)	405 (0.10)
VI	MeOH	257 (1.02)	280 (sh)	316 (0.35)	403 (0.12)
VII	MeOH	256 (1.02)	280 (sh)	316 (0.37)	403 (0.10)
VIII	MeOH	254 (0.99)	277 (0.47)	316 (0.29)	403 (0.20)
IX	MeOH	255 (1.33)		316 (0.42)	405 (0.04)
IX	Dioxane	256 (1.39)		317 (0.47)	
X	MeOH	255 (1.42)		316 (0.43)	405 (0.04)
XI	MeOH	256 (1.03)	277 (0.58)	317 (0.30)	405 (0.26)
XI	Dioxane	257 (1.29)		318 (0.46)	
XII	MeOH	254 (1.07)	280 (sh)	316 (0.34)	405 (0.14)
XII	Dioxane	257 (1.32)		318 (0.45)	
XIII	MeOH	255 (1.30)	280 (sh)	316 (0.41)	405 (0.14)
XIV	MeOH	255 (2.62)	280 (sh)	316 (0.78)	404 (0.16)
XV	MeOH	256 (2.36)	280 (sh)	316 (0.70)	405 (0.38)
XVI	MeOH	254 (2.04)	280 (sh)	312 (0.78)	404 (0.17)
XVI	Dioxane	256 (2.60)		316 (0.88)	

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TABLE III. ORD Data of N-Salicylidene Derivatives in Methanol and Dioxane (22~25°C)

Compound[a]	Solvent	$[\phi]_{589}$	$[\phi]_{450}$	$[\phi]$ (mμ) at Peak and Trough in ORD Curve						
I	MeOH	− 9°	− 110°	−2000°(340)	+ 820°(314)	−4700°(284)	+21000°(260)	− 2400°(243)	+ 3600°(232)	
II	MeOH	+110	+ 280	+ 380(408)	+ 360(400)	+2300(332)	− 2100(290)	+ 4500(262)	− 2300(238)	
III	MeOH	+490	+2300	+2800(432)	+ 600(362)	+2900(332)	− 280(298)	+ 2400(266)	− 6600(246)	
III	Dioxane	+440	+1000	+3800(334)	0(295)	+4400(263)				
IV	MeOH	+ 25	+ 100	+3500(328)	−1300(302)	+ 500(273)	−10000(250)			
V	MeOH	+280	+1700	+2400(432)	+ 200(380)	+3800(332)	− 4000(300)	− 250(273)	−12000(250)	
VI	MeOH	+140	+1000	+1700(430)	0(380)	+1500(340)	− 1500(302)	+ 2000(280)		
VII	MeOH	+120	+ 640							
VIII	MeOH	+300	+1200	+2200(422)	− 900(370)	+1700(330)	− 2500(296)	+ 2300(269)	− 3400(257)	+ 2900(240)
IX	MeOH	+320	+ 650	+1200(340)	+ 460(324)	+4000(276)	+ 700(259)			
IX	Dioxane	+380	+ 780	+1400(340)	+1200(322)	+3600(280)	− 900(260)	+ 6000(238)		
X	MeOH	+ 15	+ 60							
XI	MeOH	−170	−1400	−1800(432)	+1000(370)	− 600(333)	+ 3300(294)	+ 1200(270)	+11000(240)	
XI	Dioxane	+ 30	− 230	− 290(433)	− 180(400)	−3200(331)	+ 2900(298)	+ 600(264)	+12000(243)	
XII	MeOH	+260	+ 900	+1000(430)	+ 900(390)	+2300(334)	− 900(295)	+ 800(264)	− 2400(250)	
XII	Dioxane	+290	+ 520	+2100(336)	−1400(310)	+ 600(272)	+ 4000(260)	+ 1500(246)		
XIII	MeOH	− 13	+ 66	+ 210(410)	+1600(322)	− 870(305)				
XIV	MeOH	+700	+1800	+2300(428)	+1300(388)	+3900(335)	+ 1000(310)	+ 8000(281)	+ 7100(276)	+12000(266) +11000(253)
XV	MeOH	− 72	−1100	−1700(430)	+2400(370)	+1600(347)	+ 4400(292)	− 2200(274)	−33000(260)	+ 9600(240)
XVI	MeOH	+200	+1800	+2300(434)	−1500(380)	+ 800(344)	− 7600(308)	− 6800(300)	− 8400(286)	
XVI	Dioxane	+ 56	+ 300	+4800(338)	−7000(310)	−5900(296)	− 6400(290)	+22000(263)	− 8000(258)	

a) For numbering of compounds, see Table I.