

Stereochemistry of organic compounds(33) : On the optical contribution and solvent effects of nitrophenyl n-acetyl d-glucopyranosides

その他（別言語等）のタイトル	有機化合物の立体化学(33) : ニトロフェニルグルコサミニドの旋光寄与と溶媒効果
著者(英語)	Koko Satsumabayashi, Yoko Nishida, Kiyoshi Tanemura
journal or publication title	Bulletin of the Nippon Dental University. General education
volume	28
page range	51-60
year	1999-03-20
URL	http://doi.org/10.14983/00000500



Stereochemistry of Organic Compounds XXXIII¹⁾

On the Optical Contribution and Solvent Effects of Nitrophenyl N-Acetyl D-Glucopyranosides

Koko SATSUMABAYASHI, Yoko NISHIDA and Kiyoshi TANEMURA

The Nippon Dental University, School of Dentistry at Niigata,
Hamaura-cho, Niigata 951-8580, JAPAN

(Received November 27, 1998)

Optical contributions of various nitrophenyl glycosides have been reported^{2,3)}. As a result, the deacetylated glycosides having the C₁-nitrophenyl group showed the Cotton Effects in harmony with the configurations, but the acetylated glycosides showed atypical Cotton Effects, which affected the adjacent groups at C₂. Furthermore, glucosaminides introducing a sulfur atom at C₁ showed different optical contributions from those of an oxygen atom at C₁⁴⁾.

Now, this paper deals with glucosaminides having an acetyl group at C₂, as well as glucosaminides having sulfur atoms at C₁. For this purpose, the optical contributions were investigated by means of rotatory dispersion (RD), circular dichroism (CD), and ultraviolet absorption (UV) spectra, using five compounds and four solvents. In addition, the proton nuclear magnetic resonance (¹H-NMR) spectra were measured in dimethyl sulfoxide-*d*₆(DMSO-*d*₆).

The following five compounds were examined, as illustrated in **Figure 1** :

- o*-Nitrophenyl 2-Acetamido-2-deoxy- α -D-glucopyranoside (Compound **I**),
- p*-Nitrophenyl 2-Acetamido-2-deoxy- α -D-gulcopyranoside (Compound **II**),
- p*-Nitrophenyl 2-Acetamido-2-deoxy- β -D-gulcopyranoside (Compound **III**),
- p*-Nitrophenyl 2-Acetamido-2-deoxy 1-Thio- β -D-glucopyranoside (Compound **IV**),
- p*-Nitrophenyl 1-Thio- β -D-glucopyranoside (Compound **V**).

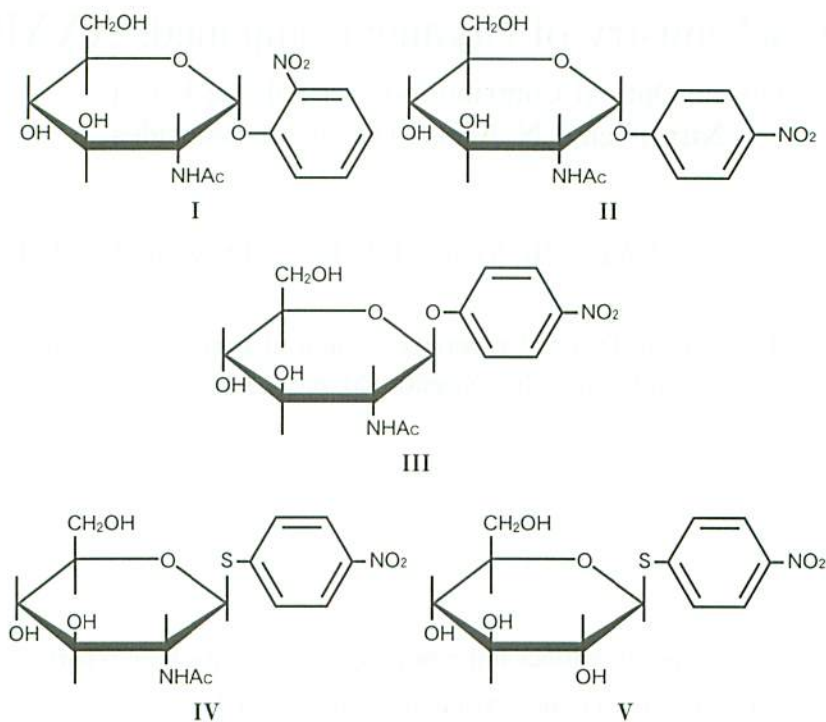


Figure 1. Compounds I ~ V examined.

Results and Discussion

The RD, CD and UV curves of Compounds I~V are shown in Figures 2~6 in THF, dioxane, ethanol and water respectively. The data of RD, CD and UV are summarized in Table 1.

As may be seen in Figures 2~6, all the α -anomers (Compounds I and II) show positive rotations over 350 nm, while all the β -anomers (Compounds III, IV and V) show negative rotations over 350 nm.

As is evident from the RD and CD curves in Fig. 2, Cotton Effects due to both $n \rightarrow \pi^*$ transition and benzenoid band of Compound I are strongly affected by the solvents. It is considered that the preferable rotamer will change from the interaction between the *ortho*-NO₂ introduced to the axial C₁-phenyl group and solvents.

Figure 3 illustrates the RD, CD and UV curves of Compound II, which has *para*-NO₂

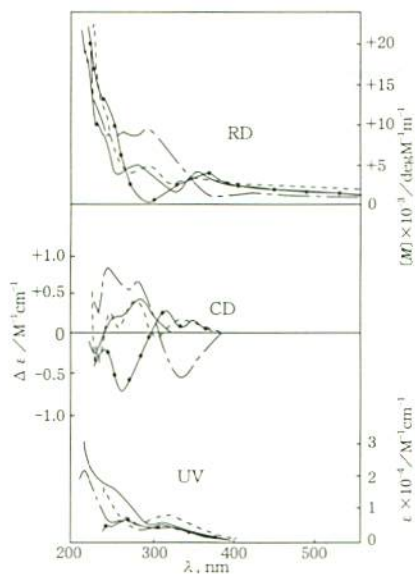


Figure 2. RD, CD and UV of I (— in THF, in dioxane, --- in ethanol, —●— in water).

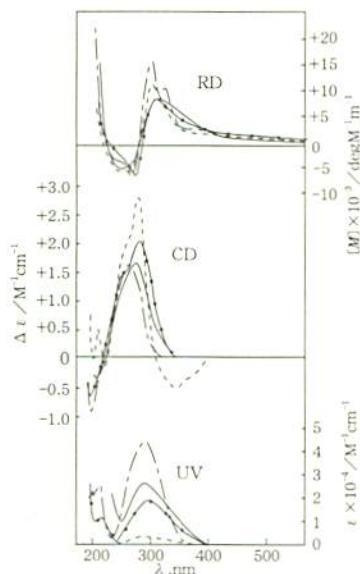


Figure 3. RD, CD and UV of II (— in THF, in dioxane, --- in ethanol, —●— in water).

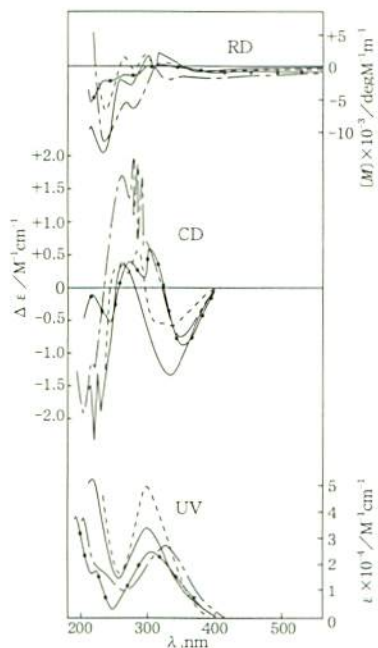


Figure 4. RD, CD and UV of III (— in THF, in dioxane, --- in ethanol, —●— in water).

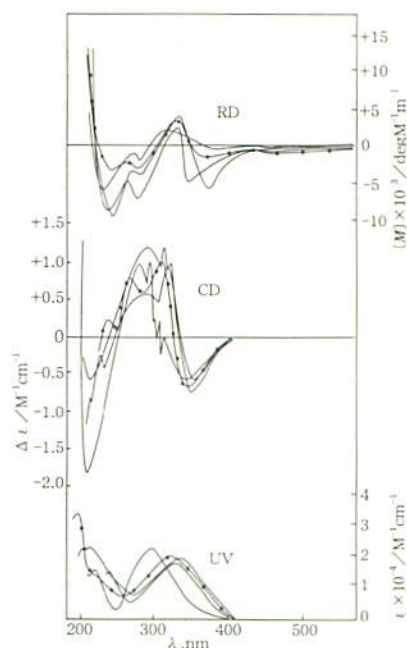


Figure 5. RD, CD and UV of IV (— in THF, in dioxane, --- in ethanol, —●— in water).

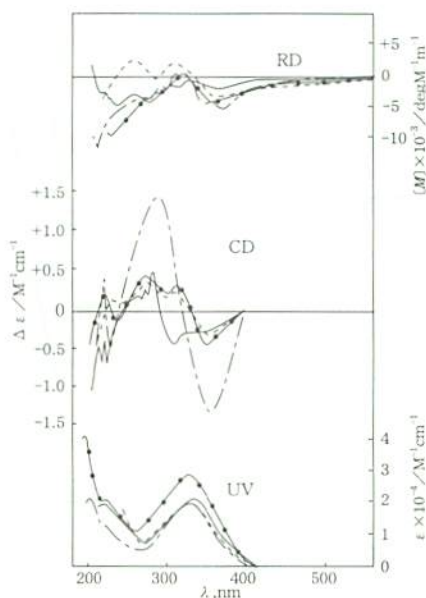


Figure 6. RD, CD and UV of V (— in THF, ---- in dioxane, -.- in ethanol, ●-● in water).

Table 1 Data of CD, RD and UV spectra

Compound spectrum	solvent	$\lambda_{\max}/\text{nm}(\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}; [\text{M}]/\text{deg M}^{-1}\text{m}^{-1}; \epsilon/\text{M}^{-1}\text{cm}^{-1})$		
I	CD	THF* ¹	284(+0.411), 256(+0.177), 229(-0.299)	
		dioxane	335(+0.174), 310(-0.0446), 282(+0.408), 258(-0.00304), 248(+0.249), 234(-0.461)	
		ethanol	334(-0.594), 280(+0.545), 244(+0.828), 232(+0.222)	
		water	348(+0.126), 318(+0.260), 266(-0.748)	
	RD	THF	357(+2090), 332(+1630), 284(+5200), 260(+4000), 238(+10400), 234(+9950)	
		dioxane	365(+3450), 334(+2690), 329(+2810), 323(+2690), 296(+5090), 275(+4100), 252(+9660, I* ²)	
		ethanol	427(+1400), 379(+935), 299(+9680), 283(+8690), 265(+9220), 253(+8480), 250(+9180), 247(+8640), 232(+12800)	
		water	365(+4070), 300(+347), 250(+12100, I)	
		UV	THF	312(4930), 280-255(5230-11000, shoulder), 215(29400)
			dioxane	312(5260), 278-256(4620-7070, shoulder), 239(16800)
ethanol	315(4110), 260(6400), 212(21700)			
water	320(3880), 264(6350), 246-235(4690-3290, shoulder)			
II	CD	THF	280(+1.61), 217(-0.386)	
		dioxane	349(-0.505), 323(-0.300), 283(+2.75), 228(-0.243), 218(+0.468), 210(-0.0386)	

		ethanol	271(+1.62), 206(-0.926)
		water	286(+1.99), 206(-0.701)
	RD	THF	309(+8100), 252(-3990)
		dioxane	305(+10600), 268(-4730), 260(-4460), 251(-4480)
		ethanol	325(+9330), 318(+8860), 308(+14400), 269(-5030), 258(-2710, I), 206(+64900)
	UV	water	309(+8050), 279(-5390), 260(-2480, I)
		THF	296(26600), 217(42200)
		dioxane	294(4290)
		ethanol	295(44200), 221(25900), 206(22700)
		water	303(19300), 223(12100)
III	CD	THF	390(-0.214), 330(-1.34), 257(+0.425), 228(-1.82), 218(-2.37)
		dioxane	330(-0.589), 281(+0.611), 259(+0.475), 248(+0.373)
		ethanol	347(-0.741), 292(+0.700), 286(+1.69), 279(+1.74), 272(+1.95), 257(+1.91), 219(-1.24), 205(-1.95)
		water	352(-0.893), 298(+0.610), 271(+0.444), 239(-0.536), 206(-2.03)
	RD	THF	374(-581), 312(+2140), 307(-412), 299(+1970), 271(-2910), 254(-1700), 232(-13500)
		dioxane	370(-1670), 348(-1660), 324(-2010), 293(+1710), 278(-864), 260(+1340), 235(-7070)
		ethanol	468(-269), 442(-260), 379(-586), 315(+741), 277(-6460), 265(-5590), 235(-11700)
		water	446(-518, I), 384(-752), 312(+208), 305(-615), 298(+9.46), 276(-1890), 260(-1270), 235(-2260), 231(-2230), 212(-5580)
	UV	THF	296(34800), 214(52100)
		dioxane	296(49800)
		ethanol	326(27600), 250-224(12400-19600, shoulder), 202(37800)
		water	301(25100), 220(17000), 191(37900)
IV	CD	THF	350(-0.592), 312(+0.875), 281(+0.617), 232(-0.472), 215(-0.879)
		dioxane	348(-0.752), 326(+0.494), 319(+1.04), 309(+1.21), 289(+1.23), 213(-0.603)
		ethanol	337(-0.598), 311(+0.0125), 307(-0.289), 303(+0.171), 301(-0.046), 299(+0.247), 291(+1.04), 276(+0.990), 208(-1.84)
		water	342(-0.685), 307(+1.01), 265(+0.813), 236(+0.256)
	RD	THF	440(-756, I), 370(-6140), 329(+3890), 280(-4380), 268(-3560), 243(-9340)
		dioxane	436(-934, I), 344(-5100), 328(+2380), 279(-7570), 262(-4690), 239(-9090)
		ethanol	444(-205), 436(-199), 377(-950), 309(+2100), 282(-2250), 270(-1260), 248(-3240, I), 230(-6430)
		water	450(-1020), 433(-910), 382(-1880), 328(+3380), 278(-3290), 262(-2300), 241(-3760)

V	UV	THF	333(21400), 214(26000)	
		dioxane	327(19600), 240(15500)	
		ethanol	295(24900), 220(17800), 203(24700)	
	CD	water	322(21600), 246-218(9730-16100, shoulder), 196(37500)	
		THF	349(-0.271), 307(-0.432), 284(+0.484), 274(+0.259), 263(+0.176), 227(-0.689), 221(-0.681)	
		dioxane	353(-0.324), 307(+0.237), 275(+0.378), 228(+0.149), 213(-0.603)	
		ethanol	357(-1.29), 290(+1.44), 228(-0.418), 223(+0.458), 202(-4.14)	
		water	351(-0.451), 311(+0.352), 274(+0.423), 235(-0.0874), 222(+0.236)	
		RD	THF	376(-1390), 324(-280), 317(-1390), 311(-946), 281(-3240), 262(-1910), 237(-3610), 230(-2430), 228(-2500), 223(-1840), 218(-2280)
			dioxane	362(-2500), 309(+1610), 288(-8.11), 259(+2330)
			ethanol	372(-4280), 354(-3390), 350(-3510), 323(+839), 318(-62.7), 312(+57.9), 301(-1880), 297(-1000), 277(-3130), 270(-2580), 216(-9690)
		UV	water	460(-828, D), 355(-3200), 321(+193), 293(-2330), 283(-1670), 233(-7590)
THF	329(21600), 216(19700)			
dioxane	325(19700)			
	ethanol	326(20000), 219(13000), 202(20300)		
	water	325(28100), 211(21200), 196(41000)		

*¹Tetrahydrofuran, *²Inflection point

introduced to the equatorial C₁-phenyl group. As may be seen in **Fig. 3**, the optical contributions are larger than those in Compound **I**, because of the long conjugated system by the *para*-NO₂. It is notable that the CD and UV curves in dioxane change in different solvents (THF, ethanol and water). In all solvents, the CD curves show the positive Cotton Effects around 290 nm, which are attributed to the $n \rightarrow \pi^*$ transition of the *para*-NO₂ group.

As may be seen in **Fig. 4**, the first Cotton Effect of Compound **III** is negative in all solvents, whereas its α -anomer (Compound **II**) shows positive Cotton Effects except in dioxane. The second complex Cotton Effects around 260 nm are positive, and as to these Cotton Effects in the CD curves as well as RD curves, the optical contribution in ethanol is strongly affected in comparison with in the other solvents.

The RD, CD and UV curves of Compound **IV** are given in **Fig. 5**. Compound **IV**, which has a sulfur atom at C₁ instead of the oxygen atom of Compound **III**. As is

evident in Figs. 4 and 5, Compounds **III** and **IV** indicate the same contribution to the CD and RD, however, Compound **IV** was less affected than Compound **III** by solvents.

Figure 6 illustrates the RD, CD and UV curves of Compound **V**, which has a free OH at C₂. By comparing Compounds **V** and **IV** in RD and UV, only small differences in their tendencies are observed in all solvents. While in the case of **V**, the contribution to the CD is smaller than **IV** in THF in dioxane and water, because of the absence of NHAc moiety at C₂, but, larger in ethanol.

The CD curves of Compounds **I** and **II** in Fig. 7 will be discussed by comparing them with the *ortho*-nitrophenyl and *para*-nitrophenyl at axial C₁. It is clear that in the case of Compound **II**, there are strong positive Cotton Effects around 280 nm due to the $n \rightarrow \pi^*$ transition of nitro group, but the other Cotton Effects show irregularity. In the previous study²⁾, in the cases of Tetraacetyl *o*-nitrophenyl α -D-glucopyranoside and Tetraacetyl *p*-nitrophenyl α -D-glucopyranoside, the signs of Cotton Effects were not affected by the solvent polarity. Therefore, it is considered that C₂-NHCOCH₃ interacts between the solvent and C₁-nitrophenyl group.

The CD curves of Compounds **II** and **III** in Fig. 8 will be discussed by comparing them with the axial- and equatorial-nitrophenyl at C₁. Based on a comparison of the first Cotton Effects, the sign of the Cotton Effect of Compound **III** is negative in all

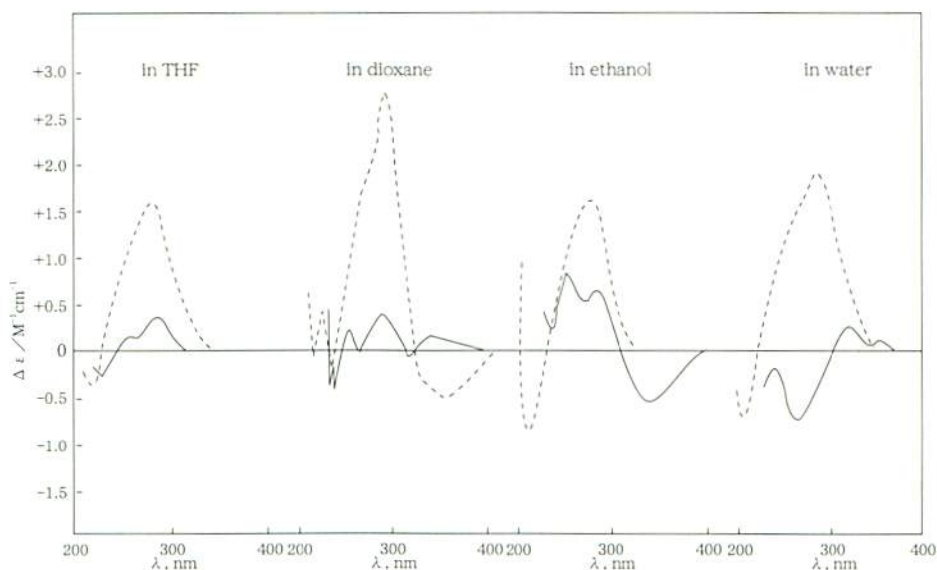


Figure 7. CD of **I** and **II** in THF, dioxane, ethanol, and water(—**I**, - - - **II**).

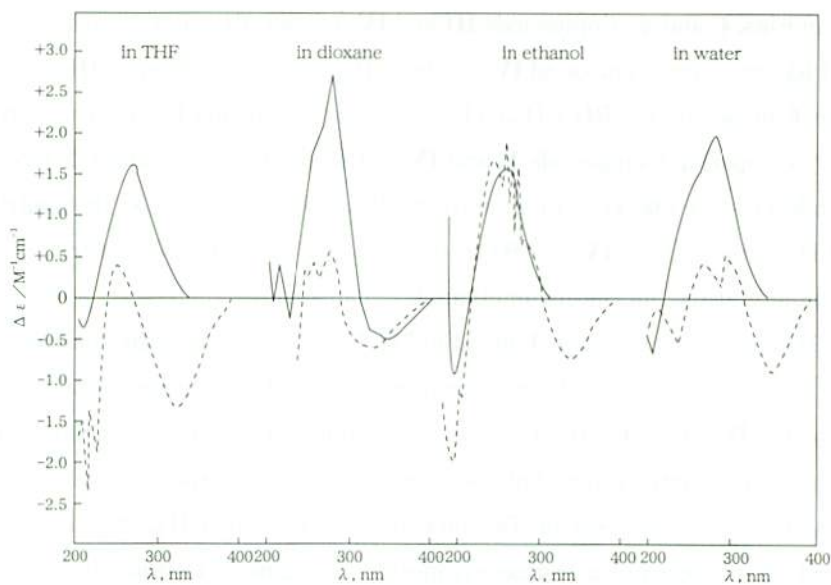


Figure 8 . CD of II and III in THF, dioxane, ethanol, and water(— II, III).

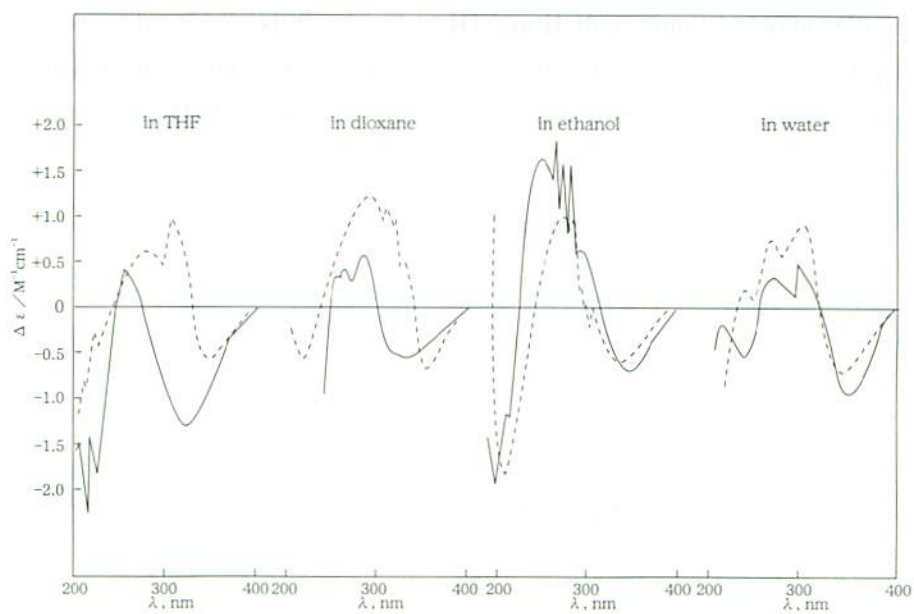


Figure 9 . CD of III and IV in THF, dioxane, ethanol, and water(— III, IV).

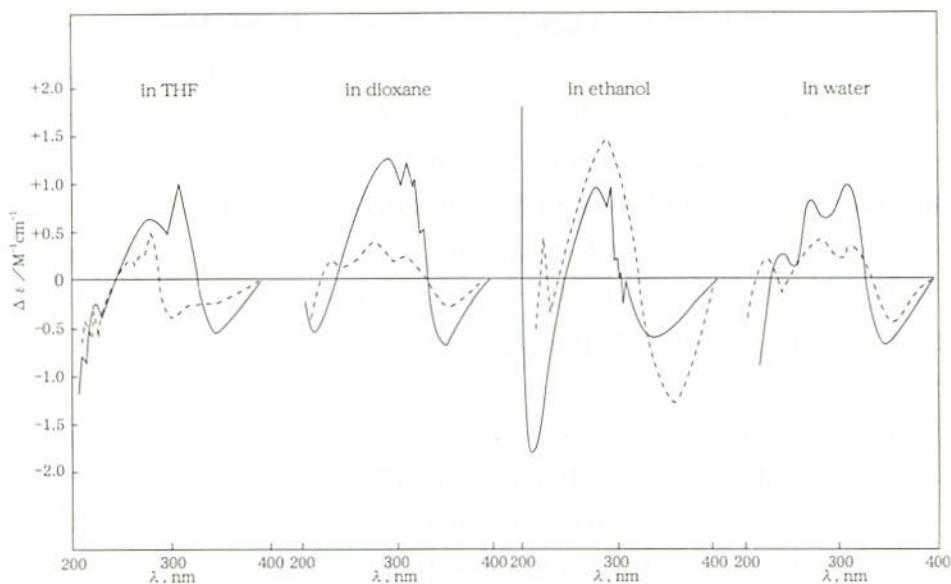


Figure 10. CD of IV and V in THF, dioxane, ethanol, and water (— IV, - - - V).

solvents, and that of Compound **II** is positive except in dioxane.

Figure 9 shows the CD curves of Compounds **III** and **IV** in order to get information on hetero atoms between oxygen and sulfur. Compared to the CD curves of **III** and **IV**, the Compound **IV** with a sulfur atom contributes to the red shift of the first and second maximum.

Figure 10 shows the CD curves of Compounds **IV** and **V**, when the compounds are affected by different C_2 -substituents. The C_2 -NHAc substituent had a greater effect on the CD curves of Compounds **IV** and **V** except in ethanol.

In conclusion, the compounds containing a sulfur atom showed a red-shift. The compound which contained the *ortho*-NO₂ that is close to C_2 -NHAc, was easily affected by solvents.

Experimental

Measurements. The RD and CD were measured in tetrahydrofuran, dioxane, ethanol and water at 22–25°C, in the wavelength region from 200 to 600 nm with JASCO/UV-5 type optical rotatory dispersion recorder. The UV spectra were measured with the

same conditions as the RD and CD measurements by Hitachi Model 320 Spectrophotometer. The $^1\text{H-NMR}$ spectra were measured on a Hitachi Model R-24B at room temperature in $\text{DMSO-}d_6$ as a solvent. Chemical shifts are in ppm (δ) from SiMe_4 as the internal standard and J -values are given in Hz.

Materials. All Compounds I~V were of commercial origin by Sigma Chem. Co..

o-Nitrophenyl 2-Acetamido-2-deoxy- α -D-glucopyranoside (Compound I). mp 202°C; $^1\text{H-NMR}\delta = 1.86(3\text{H, s}), 2.98-4.16(7\text{H, m}), 4.30-4.78(1\text{H, dd, } J = 4.4 \text{ and } 2.4 \text{ Hz}), 4.82-5.03(1\text{H, d, } J = 3.2 \text{ Hz}), 5.08-5.36(1\text{H, d, } J = 4.8 \text{ Hz}), 5.66-5.90(1\text{H, d, } J = 1.6 \text{ Hz})$ and 7.04-8.02(5H, m).

p-Nitrophenyl 2-Acetamido-2-deoxy- α -D-glucopyranoside (Compound II). mp 260°C; $^1\text{H-NMR}\delta = 1.88(3\text{H, s}), 3.10-4.28(7\text{H, m}), 4.38-4.76(1\text{H, m}), 4.88-5.34(2\text{H, dd, } J = 4.2 \text{ and } 4.4 \text{ Hz}), 5.52-5.86(1\text{H, d, } J = 2.2 \text{ Hz}), 7.10-7.61(2\text{H, d, } J = 2.2 \text{ Hz}), 7.10-7.61(2\text{H, d, } J = 9.6 \text{ Hz}), 7.83-8.12(1\text{H, d, } J = 7.2 \text{ Hz})$ and 8.14-8.49(5H, d, $J = 9.0\text{Hz}$).

p-Nitrophenyl 2-Acetamido-2-deoxy- β -D-glucopyranoside (Compound III). mp 211°C; $^1\text{H-NMR}\delta = 1.81(3\text{H, s}), 2.88-4.06(7\text{H, m}), 4.42-5.46(4\text{H, m}), 7.00-7.48(2\text{H, d, } J = 8.8 \text{ Hz}), 7.64-7.79(1\text{H, d, } J = 8.4 \text{ Hz})$ and 8.03-8.40(2H, d, $J = 8.8\text{Hz}$).

p-Nitrophenyl 2-Acetamido-2-deoxy 1-Thio- β -D-glucopyranoside (Compound IV). mp 226°C; $^1\text{H-NMR}\delta = 1.83(3\text{H, s}), 2.98-4.12(7\text{H, m}), 4.38-5.36(4\text{H, m}), 7.39-7.74(2\text{H, d, } J = 9.2 \text{ Hz}), 7.76-7.99(1\text{H, d, } J = 8.2 \text{ Hz})$ and 8.00-8.38(2H, d, $J = 7.8\text{Hz}$).

p-Nitrophenyl 1-Thio- β -D-glucopyranoside (Compound V). mp 159°C; $^1\text{H-NMR}\delta = 2.88-4.02(7\text{H, m}), 4.36-5.34(3\text{H, m}), 5.38-5.66(1\text{H, d, } J = 4.8 \text{ Hz}), 7.48-7.91(2\text{H, d, } J = 8.4 \text{ Hz})$ and 8.02-8.36(2H, d, $J = 6.4\text{Hz}$).

References

- 1) K. Satsumabayashi, Y. Nishida and K. Tanemura, This Bulletin, **27**, 55 (1998).
- 2) K. Satsumabayashi, Y. Nishida and K. Tanemura, *ibid.*, **25**, 43 (1996).
- 3) K. Satsumabayashi, Y. Nishida and K. Tanemura, *ibid.*, **24**, 95 (1995); **23**, 59 (1994).
- 4) K. Satsumabayashi and Y. Nishida, *ibid.*, **16**, 89 (1987).