

Stereochemistry of Organic Compounds XXXV¹⁾

On the Optical Contribution and Solvent Effects of Nitrophenyl Xylo- and Fuco-pyranosides

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In our earlier studies²⁻⁵⁾, we reported the conformation of various nitrophenyl-glycosides. As a result, the deacetylated glycosides having the C₁-nitrophenyl group showed the Cotton effects in harmony with the configurations, but the acetylated glycosides having *o*-nitrophenyl group at C₁ showed an anomalous optical rotation. Furthermore, nitrophenyl *N*-acetylglucosaminide produced different Cotton effects due to the same transition of nitrophenyl chromophore, which affected the adjacent groups at C₂.

Now, this paper deals with xylopyranosides classified as a pentose and fucopyranosides classified as a 6-deoxyhexose, in order to investigate the optical contribution of C₄ and C₅ asymmetric carbon. For the purpose of discussing Cotton effects brought on by the C₁-nitrophenyl moiety, the following compounds (Compound I~VI) were employed:

- o*-Nitrophenyl β -D-xylopyranoside (Compound I),
- p*-Nitrophenyl β -D-xylopyranoside (Compound II),
- Triacetyl *o*-nitrophenyl β -D-xylopyranoside (Compound III),
- Triacetyl *p*-nitrophenyl β -D-xylopyranoside (Compound IV),
- o*-Nitrophenyl β -D-fucopyranoside (Compound V),
- p*-Nitrophenyl β -D-fucopyranoside (Compound VI),

Moreover, the following four compounds (Compound VII~X)^{3,4)}, will be employed

for comparison :

o-Nitrophenyl β -D-glucopyranoside (Compound VII),

p-Nitrophenyl β -D-glucopyranoside (Compound VIII),

o-Nitrophenyl β -D-galactopyranoside (Compound IX),

p-Nitrophenyl β -D-galactopyranoside (Compound X),

The structure of the compounds studied are illustrated in Figure 1.

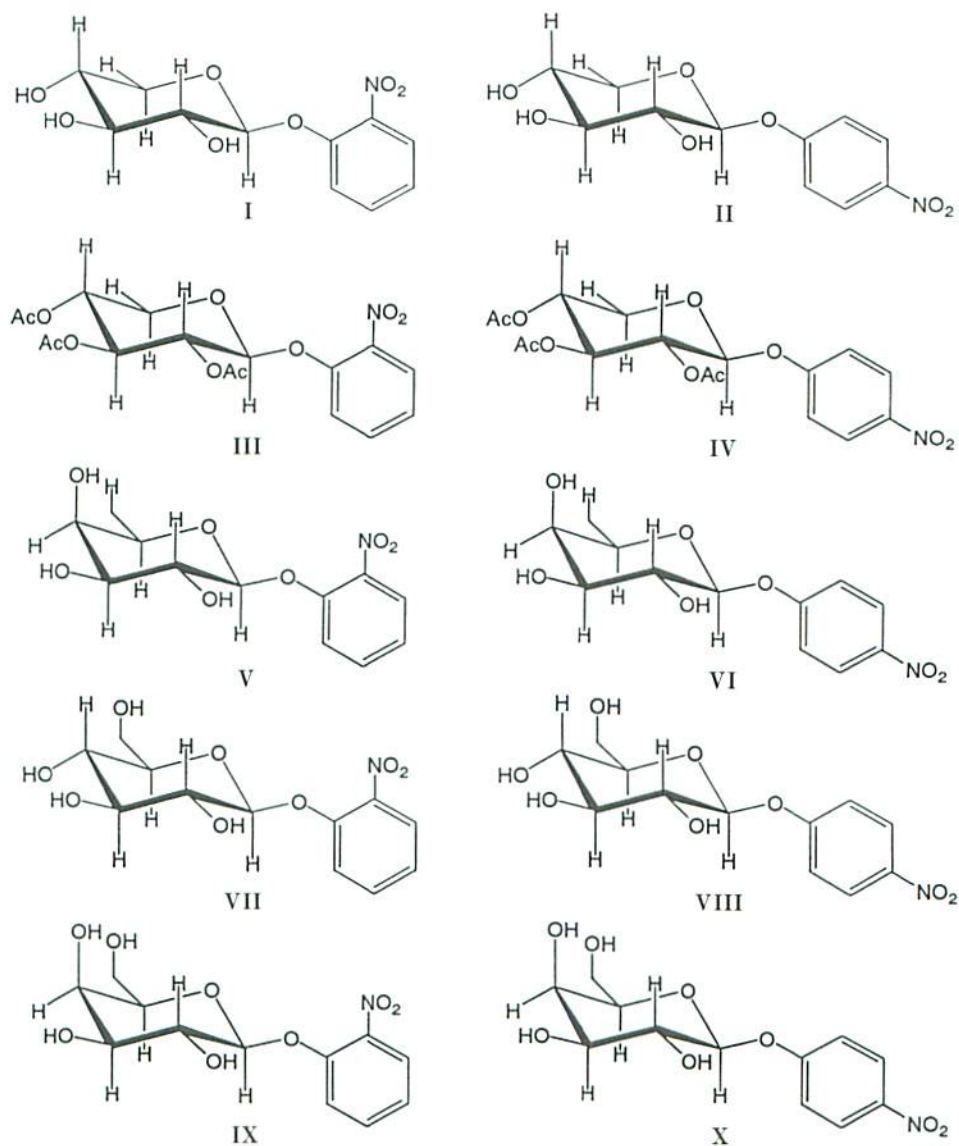


Figure 1. Compounds I ~ X examined.

For this purpose, the optical contributions were investigated by means of rotatory dispersion (RD), circular dichroism (CD), and ultraviolet absorption (UV) spectra, using acetonitrile (CH₃CN), ethanol (EtOH) and water (H₂O) as polar solvents and dioxane and tetrahydrofuran (THF) as non-polar solvents. In addition, the proton nuclear magnetic resonance (¹H-NMR) spectra were measured in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆).

Results and Discussion

The RD, CD and UV curves of Compounds I~VI are shown in Figures 2~7 in THF, dioxane, acetonitrile, ethanol and water respectively. The data of RD, CD and UV are summarized in Table 1.

In Figures 2~7, all RD curves show negative background rotation regardless of absorption bands, and the sign is constant with the C₁-configuration.

As may be seen in Figure 2, the RD curves of Compound I show negative peaks around 370-380 nm, and positive peaks around 260-340 nm in all solvents with the ethanol solvent showing a weak contribution at both peaks. The CD curves of Compound I exhibit negative peaks around 330-350 nm and positive peaks around 250-305 nm in all solvents with the ethanol solvent again showing a weak contribution.

The first negative CD bands are due to the $n \rightarrow \pi^*$ transition and the second positive CD bands are due to the $\pi \rightarrow \pi^*$ transition. In the first CD bands, the magnitude of the CD maximum decreases in the order of H₂O > CH₃CN > THF > dioxane > EtOH. In the UV curves of Compound I, the first bands appear around 305 nm, the second bands appear around 250-265 nm and the third bands appear around 210 nm. The first bands by $n \rightarrow \pi^*$ transition assigned to the nitro group are weakened by the sugar moiety of the nitro group in the neighborhood. Moreover, in the UV curves, both band 1 and band 2 in water are shifted 4-8 nm to the longer wavelength region compared with the other solvents, that is, the slight bathochromic shift is considered to be due to lower energy. The fact that the weakened transition contributes to the large CD maximum suggests that the favorable conformation may form due to the interaction between Compound I and the water solvent.

In Figure 3, both the RD and CD curves show the vibration caused by the unstable-

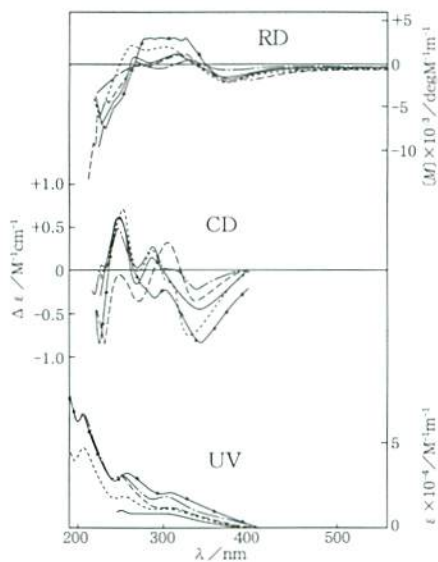


Figure 2. RD, CD and UV of I (— in THF, --- in dioxane, in acetonitrile, - - - in ethanol, \blacktriangle \blacktriangle in water).

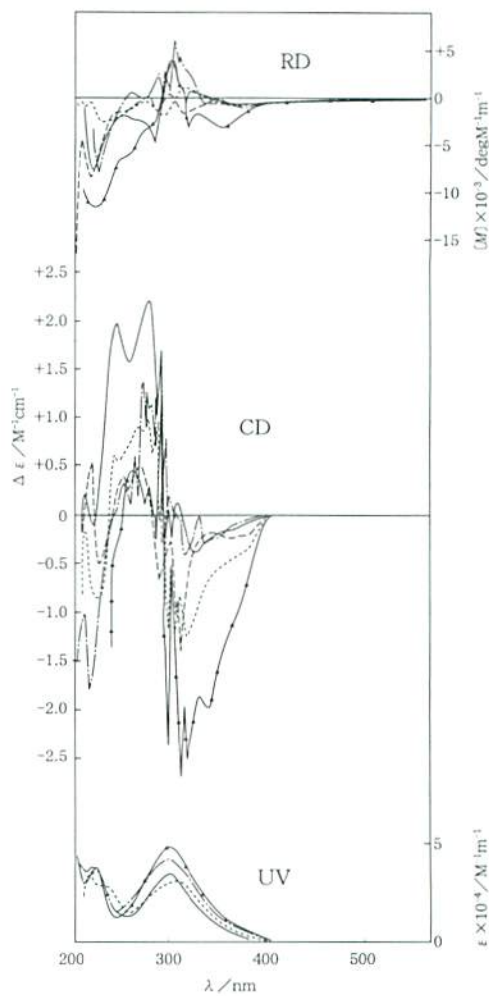


Figure 3. RD, CD and UV of II (— in THF, --- in dioxane, in acetonitrile, - - - in ethanol, \blacktriangle \blacktriangle in water).

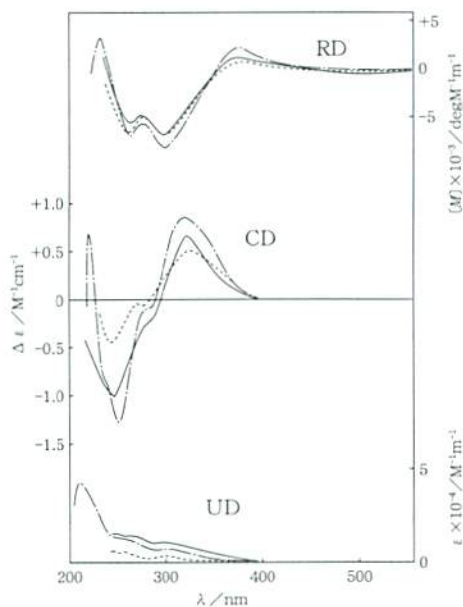


Figure 4. RD, CD and UV of III (— in THF, --- in dioxane, - - - in ethanol).

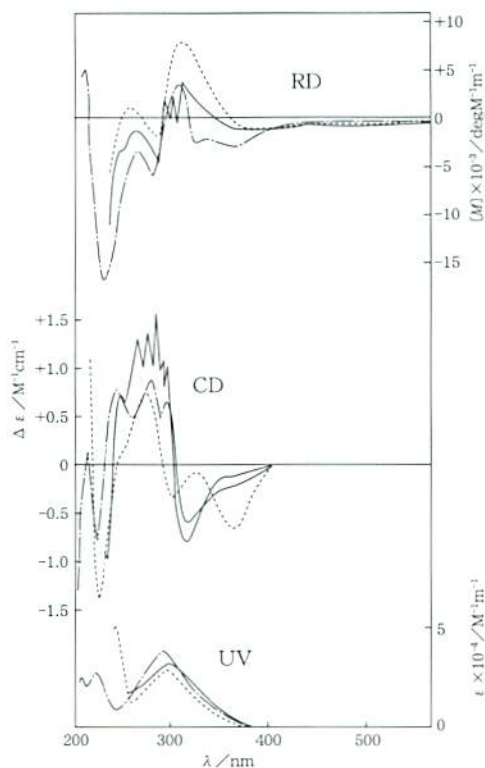


Figure 5. RD, CD and UV of IV (— in THF, ---- in dioxane, --- in ethanol).

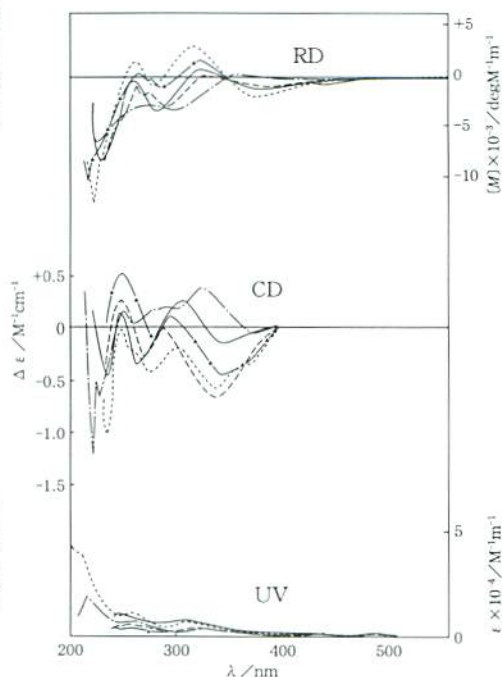


Figure 6. RD, CD and UV of V (— in THF, ---- in dioxane, in acetonitrile, --- in ethanol, —▲— in water).

ness of Compound II. However, negative and positive bands in CD curves are still clear in $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. In the UV spectra of Compound II, the first bands are larger than the bands of Compound I; it is because the sugar moiety far from the nitro group does not affect the $n \rightarrow \pi^*$ transition. On the other hand, the RD and CD of Compound I exhibit complex curves, since the Cotton effects in the RD and CD curves are attributed to the C_1 asymmetric carbon, which has the *p*-nitrophenyl group with the long conjugated system. In the CD curves, it is noted that the order of magnitude of the first Cotton effects becomes the reverse of the order of magnitude of the second Cotton effects.

Figure 4 illustrates the RD, CD and UV curves of Compound III, which is the acetylated derivative of Compound I. In the UV curves, the first bands around 300 nm

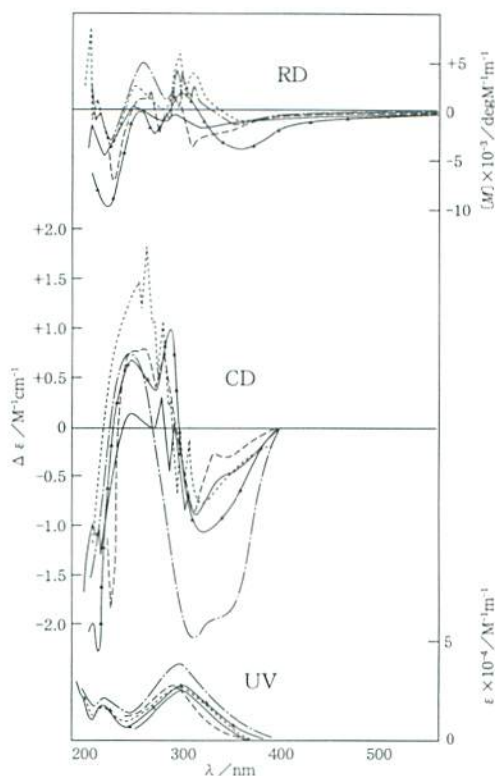


Figure 7. RD, CD and UV of VI(— in THF, --- in dioxane, in acetonitrile, —·— in ethanol, —▲— in water).

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	348 (-0.462), 286 (+0.148), 271 (-0.180), 250 (+0.630)
		dioxane	338 (-0.361), 305 (+0.340), 275 (-0.383), 252 (+0.0304), 232 (-0.880)
		CH ₃ CN	336 (-0.763), 290 (+0.238), 274 (-0.0349), 254 (+0.713), 232 (-0.133), 228 (+0.0614)
		EtOH	334 (-0.216), 289 (+0.294), 272 (+0.00343), 249 (-0.512), 228 (-0.0807)
		H ₂ O	346 (-0.838), 293 (-0.322), 252 (+0.634), 227 (-0.890)
	RD	THF	373 (-1830), 318 (+1200), 293 (+166), 266 (+905), 238 (-5080, I ¹), 229 (-7430)

	dioxane	445 (-616, I), 375 (-1090), 321 (+1050), 280 (-318), 267 (+372), 237 (-4960), 234 (-4100), 226 (-6810), 224 (-5960), 220 (-9330)	
	CH ₃ CN	371 (-2250), 308 (-1910), 279 (-1560), 263 (+2070), 225 (-5720)	
	EtOH	371 (-789), 325 (+491), 302 (-548), 265 (-113)	
	H ₂ O	365 (-1600), 326 (+3120), 320 (+2750), 313 (+3070), 307 (+2850), 294 (+3140), 287 (+3060), 277 (+3200), 234 (-7950), 231 (-7350)	
UV	THF	310 (7590), 254 (9620)	
	dioxane	312 (12700)	
	CH ₃ CN	311 (11500), 258 (18200), 211 (46700)	
	EtOH	309 (17100), 257 (28900), 211 (66600)	
	H ₂ O	316 (19800), 264 (32000), 209 (64700), 193 (78400)	
II	CD	THF	325 (-0.394), 306 (+0.172), 303 (-0.328), 299 (+0.174), 296 (-0.167), 290 (+1.81), 278 (+2.26), 244 (+2.03), 222 (-0.223), 213 (+0.236), 206 (-2.47)
	dioxane	365 (-0.234), 312 (-1.41), 306 (-1.06), 290 (-0.665), 270 (+0.578), 253 (+0.418), 230 (-0.529), 220 (-0.567)	
	CH ₃ CN	318 (-1.30), 305 (-1.18), 296 (-1.15), 292 (+0.463), 291 (-0.271), 287 (+1.05), 275 (+1.11), 268 (+0.990), 244 (+0.617), 226 (-0.863), 204 (-1.51)	
	EtOH	336 (-0.282), 332 (+0.026), 316 (-0.415), 305 (+0.0416), 300 (+0.415), 296 (+0.871), 290 (+1.38), 286 (+1.58), 281 (+1.87), 277 (+1.32), 273 (+1.43), 264 (+0.643), 253 (+0.355), 218 (-1.82)	
	H ₂ O	340 (-2.15), 317 (-2.58), 311 (-2.79), 299 (-2.39), 291 (+0.813), 286 (-0.280), 278 (+0.335), 260 (+0.499), 221 (-5.51)	
RD	THF	360 (-766), 319 (+761), 312 (-590), 299 (+3640), 281 (-4940), 270 (-2190, I), 248 (-1630), 220 (-8140)	
	dioxane	435 (-356), 428 (-352), 335 (-447), 328 (-442), 313 (-1450), 297 (+667), 287 (-1370), 278 (+406), 240 (-1470, I), 216 (-8400), 209 (-3630)	
	CH ₃ CN	367 (-679), 310 (+1100), 291 (-1890), 271 (-376), 230 (-2600), 215 (-272), 210 (-646), 205 (+84.1)	
	EtOH	510 (-202, I), 430 (-390, I), 342 (-245), 333 (-654), 307 (+4530), 306 (+3260), 302 (+6390), 295 (+391), 293 (+3300), 289 (+573), 286 (+2760), 284 (-472), 258 (+846), 224 (-8520), 216 (-2700), 214 (-5930)	
	H ₂ O	456 (-176, I), 349 (-3280), 326 (-1600), 319 (-3300), 311 (+1600), 308 (-1280), 301 (+4520), 275 (-3600, I), 254 (-6350, I), 222 (-11900)	
UV	THF	299 (24600)	
	dioxane	296 (34400)	
	CH ₃ CN	305 (30500), 229 (30000), 215 (34700)	
	EtOH	296 (43300), 221 (37300)	

III	CD	H ₂ O	299 (48000), 221 (3650)	
		THF	325 (+0.658), 247 (-1.23)	
		dioxane	323 (+0.532), 283 (-0.0649), 242 (-0.480)	
	RD	EtOH	319 (+0.847), 252 (-1.33), 221 (+0.684)	
		THF	514 (-284), 375 (+1370), 302 (-7240), 278 (-4910), 262 (-5950)	
		dioxane	484 (-274), 375 (+580), 302 (-7170), 280 (-4820), 263 (-6630)	
	UV	EtOH	375 (+2190), 302 (-8540), 278 (-5610), 263 (-7300), 233 (+3510)	
		THF	298 (10400), 276-262 (11500-14400, shoulder), 246 (15700)	
		dioxane	300 (3950), 254 (6150)	
IV	CD	EtOH	301 (7910), 255 (13700), 209 (43500)	
		THF	315 (-0.814), 292 (+1.07), 290 (+1.17), 283 (+1.60), 275 (+1.44), 265 (+1.34), 247 (+0.734), 232 (-0.983)	
		dioxane	363 (-0.783), 300 (-0.348), 271 (+0.798), 224 (-1.37)	
	RD	EtOH	314 (-0.614), 292 (+0.667), 277 (+0.941), 241 (+0.808), 222 (-0.811), 211 (+0.145)	
		THF	456 (-522), 433 (-501), 376 (-831), 306 (+3960), 300 (-868), 297 (+2850), 294 (-242), 289 (+2240), 283 (-4320), 257 (-1330), 248 (-3560), 243 (-3300)	
		dioxane	368 (-905), 302 (+7800), 282 (-2050), 253 (+1130)	
	UV	EtOH	504 (-382, I), 446 (-433, I), 439 (-430, I), 364 (-747), 328 (-2070), 317 (-2910), 305 (+3620), 279 (-6230), 260 (-3200), 227 (-16800), 205 (+2880)	
		THF	296 (34000)	
		dioxane	295 (29500), 241 (52900)	
	V	CD	EtOH	291 (40000), 220 (29400), 204 (26900)
			THF	344 (-0.193), 307 (+0.245), 265 (-0.388), 248 (+0.124), 234 (-0.443)
			dioxane	338 (-0.635), 275 (-0.466), 233 (-1.05)
RD		CH ₃ CN	340 (-0.681), 275 (-0.299), 249 (+0.344), 226 (-0.779)	
		EtOH	375 (-0.0537), 327 (+0.381), 289 (+0.181), 280 (+0.178), 251 (+0.177), 237 (-0.512), 228 (-0.732), 221 (-1.31)	
		H ₂ O	343 (-0.476), 292 (+0.101), 279 (-0.111), 249 (+0.514)	
		THF	443 (-534), 438 (-526), 384 (-954), 322 (+720), 286 (-3560), 260 (-361), 231 (-8430)	
		dioxane	382 (-860), 326 (+48.1), 295 (-2790), 273 (-1540), 270 (-1750), 263 (-785), 250 (-4180), 249 (-4120)	
		CH ₃ CN	378 (-1950), 317 (+3160), 282 (-1090), 261 (+1640), 230 (-8300), 228 (-8250), 221 (-12600)	
UV		EtOH	511 (-250), 357 (+313), 302 (-3220), 263 (-2700), 227 (-6550)	
		H ₂ O	450 (-485, I), 382 (-1300), 324 (-1710), 287 (-1060), 278 (-437), 275 (-557), 267 (+319), 217 (-10400)	
		THF	311 (8530), 254 (10700)	
		dioxane	308 (3920), 254 (5370)	

VI	CD	CH ₃ CN	311 (8100), 256 (12000), 233–224 (14400–19300, shoulder), 206 (42800)	
		EtOH	486–463 (10.2–19.8, shoulder), 448–416 (28.8–44.6, shoulder), 313 (5490), 256 (8290), 216 (20500)	
		H ₂ O	308 (3930), 254 (5380), 241 (5370)	
		THF	318 (–0.948), 306 (–0.890), 297 (+0.275), 293 (–0.473), 281 (+0.312), 275 (–0.0331), 249 (+0.153), 222 (–1.29)	
		dioxane	357 (–0.291), 314 (–0.936), 283 (+0.680), 266 (+0.788), 250 (+0.793), 232 (–1.90)	
		CH ₃ CN	323 (–0.801), 305 (–0.602), 297 (–0.644), 294 (+0.400), 282 (+1.14), 274 (+1.11), 268 (+1.88), 260 (+1.49), 206 (–2.94)	
		EtOH	316 (–2.21), 255 (+0.780), 218 (–1.13)	
		H ₂ O	323 (–1.08), 292 (+0.924), 251 (+0.694), 219 (–2.36), 204 (–4.20)	
		RD	THF	320 (–1840), 296 (–255), 290 (–1410), 250 (+320), 224 (–5000), 210 (–1610)
			dioxane	450 (–611, I), 313 (–3900), 301 (+1360), 298 (+106), 294 (+2200), 289 (–851), 285 (+80.2), 281 (–1710), 270 (+2050), 266 (+1030), 260 (+1380), 233 (–7410)
			CH ₃ CN	365 (–1100), 312 (+3620), 306 (+915), 298 (+5730), 286 (–103), 252 (+2480), 230 (–4280), 214 (+1330), 211 (–1240), 208 (+8430)
			EtOH	358 (–1410), 314 (+3050), 310 (+948), 308 (+1790), 303 (–1100), 296 (+4530), 294 (+1080), 290 (+2160), 286 (+897), 262 (+5040), 227 (–3360), 219 (–3.02), 216 (–842)
			H ₂ O	363 (–3930), 300 (+1990), 274 (–2480), 258 (+53.9), 226 (–10300)
		UV	THF	300 (27000)
			dioxane	296 (29400)
CH ₃ CN	298 (26700), 221 (16500)			
EtOH	297 (38000), 222 (22400), 202 (27400)			
H ₂ O	301 (27800), 222 (18300)			

*¹Inflection point

are weakened in a similar manner to Compound **I**. It was stated^{3–5} that the so-called “optical anomaly of *ortho*-nitro” was observed in acetylated glycosides with nitro group at *ortho*-position of the phenyl group. The RD and CD spectra of Compound **III** show the optical anomaly of *ortho*-NO₂; that is, the first Cotton effects attributed to the $n \rightarrow \pi^*$ transition show positive regardless of the C₁-configuration. It turned out that the “optical anomaly of *ortho*-nitro” took place in the case of acetylated pentose, therefore, the C₅-substituent of pyranoside was not involved in causing the anomaly.

As evident in the RD and CD curves, the solvent dependency is the largest in ethanol.

The RD, CD and UV curves of Compound **IV** are given in **Figure 5**. Compound **IV**, which is the acetylated derivative of Compound **II**, shows the first negative Cotton effect attributed to the $n \rightarrow \pi^*$ transition and the second positive Cotton effect attributed to the $n \rightarrow \pi^*$ transition bands around 300 nm. The shape of the UV curve of Compound **IV** is similar to that of Compound **II** due to the same reason. As is evident from the RD and CD curves in **Figure 5**, Cotton effects due to both the $n \rightarrow \pi^*$ transition and the benzenoid band of Compound **IV** are strongly affected by the solvents. Especially, in the first Cotton effect of RD and CD, the solvent dioxane has an effect on the attribution to the positive rotation and the red shift. However, since Compound **IV** lacks any free hydroxyl groups, the RD and CD spectra show stable curves compared with those of Compound **II**.

Figure 6 illustrates the RD, CD and UV curves of Compound **V**, which is the *o*-nitrophenyl derivative of 6-deoxygalactose having axial-OH at C₄. In the UV curves, the first bands around 310 nm are weakened in a similar manner as those of Compound **I**. Moreover, since only in the ethanol were two weak shoulders measured at around 416–486 nm, it suggests an appreciable interaction between Compound **V** and the solvent. This is supported by the fact that the strength of the optical contribution of RD was weakened and the first Cotton effect of CD was shifted about 40 nm to the longer wavelength region in ethanol.

For Compound **VI** which is the *p*-nitrophenyl isomer of Compound **V**, the RD, CD and UV curves were shown in **Figure 7**. Those spectra are similar to the spectra of Compound **II** showing a strong contribution in ethanol, and the assignment to absorptions and to Cotton effects are also the same as in Compound **II**.

The RD and CD curves of Compounds **I**, **V**, **VII** and **IX** are given in **Figures 8~12** in THF, dioxane, acetonitrile, ethanol and water respectively. These Compounds are different in sugar moiety but have the same *o*-nitrophenyl as an aglycon. By comparing Compounds **I**, **V**, **VII** and **IX** in RD and CD, small differences in their tendencies are recognized in all solvents except in ethanol.

The RD and CD curves Compounds **II**, **VI**, **VIII** and **X** are given in **Figures 13~17** in THF, dioxane, acetonitrile, ethanol and water respectively. These Compounds are different in sugar moiety but have the same *p*-nitrophenyl as an aglycon. By compar-

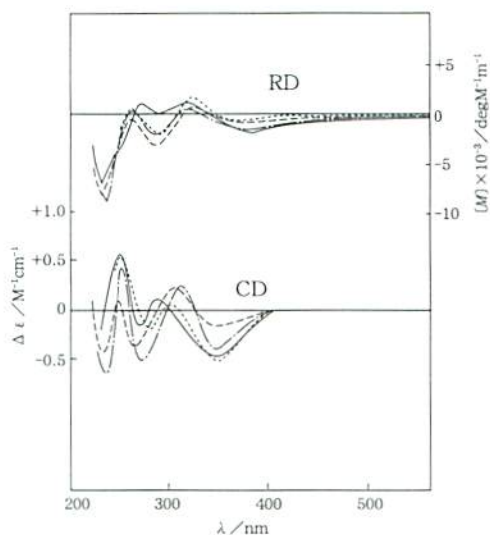


Figure 8. RD and CD of I, V, VII and IX in THF(—I, ---- V, - - - VII, IX).

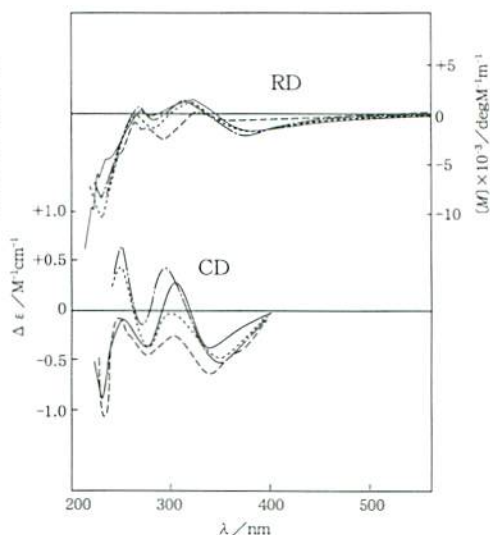


Figure 9. RD and CD of I, V, VII and IX in dioxane(—I, ---- V, - - - VII, IX).

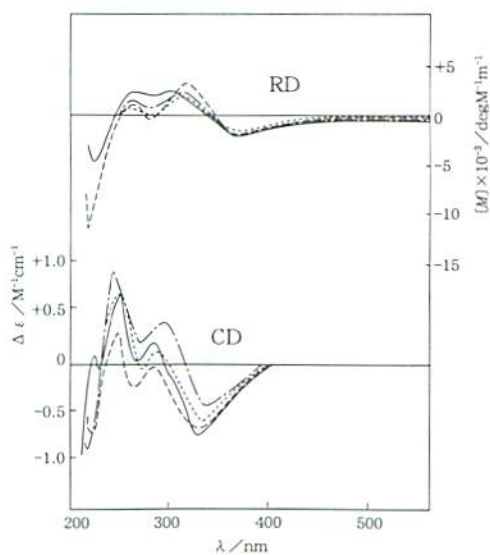


Figure10. RD and CD of I, V, VII and IX in acetonitrile(—I, ---- V, - - - VII, IX).

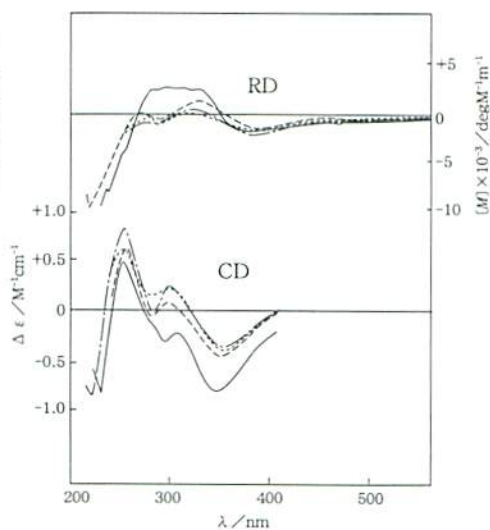


Figure11. RD and CD of I, V, VII and IX in ethanol(—I, ---- V, - - - VII, IX).

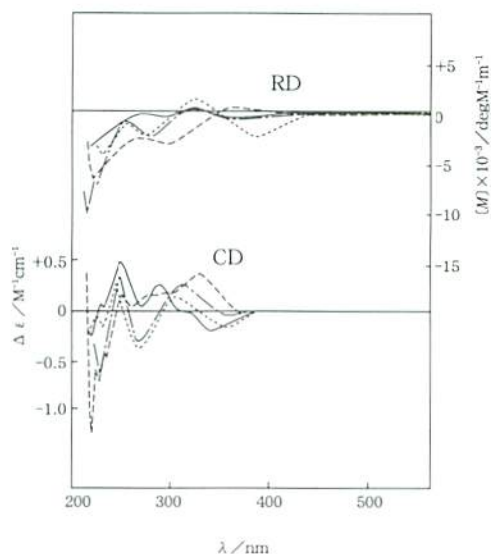


Figure 12. RD and CD of I, V, VII and IX in water (— I, ---- V, - - - VII, ····· IX).

ing Compounds II, VI, VIII and X in RD and CD, the signs of the first and second Cotton effects are consistent but the optical contributions are different in amplitude or magnitude.

In order to investigate the conformation of Compounds I~IV, geometry optimizations were carried out using MM2 calculations. Figure 18 shows the molecular structures created by the calculations using minimized energy. It is possible that all structures in Figure 18 propose the preferable conformation.

The six-membered ring in the xylose has a chair form that is the equilibrium shown (in Figure 19). Usually, the C1-form, which has four equatorial hydroxyl groups, is more stable and predominates in the equilibrium mixture.

However, as for Compound III, geometry optimization by MM2 calculation showed that the preferable conformation is the 1C type conformation as given in Figure 18. This explains the reason for the optical anomaly of *ortho*-nitrophenyl group at β -C₁ of 2,3,4-triacetylxylopyranoside. The contribution to the anomeric effect of the preferable conformation in the 1C-form is small in the solvent and changes to the polarity of the solvent.

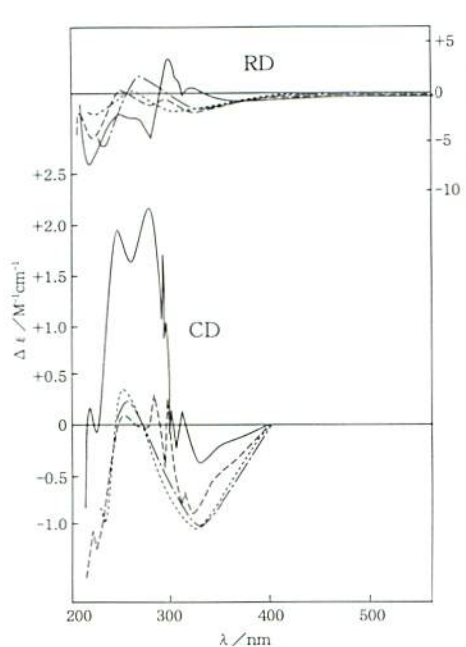


Figure 13. RD and CD of II, VI, VIII and X in THF (— II, --- VI, ---- VIII, X).

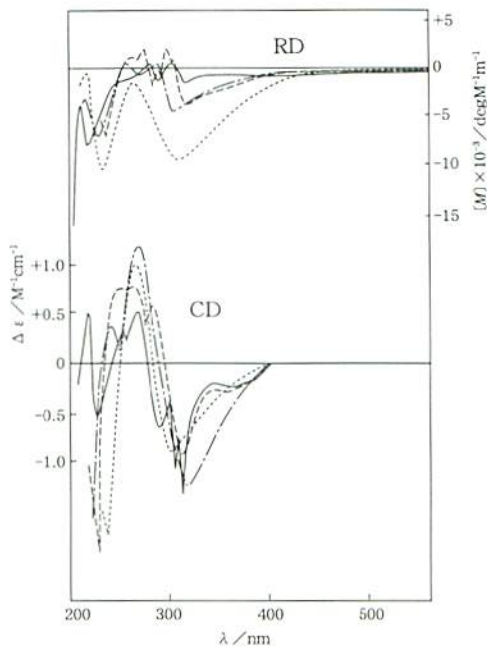


Figure 14. RD and CD of II, VI, VIII and X in dioxane (— II, --- VI, ---- VIII, X).

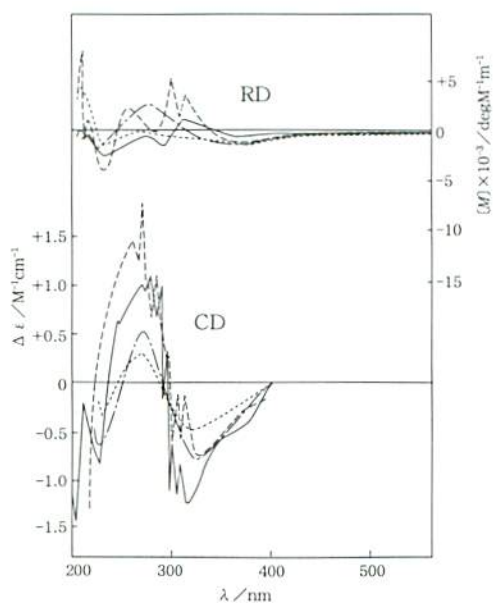


Figure 15. RD and CD of II, VI, VIII and X in acetonitrile (— II, --- VI, ---- VIII, X).

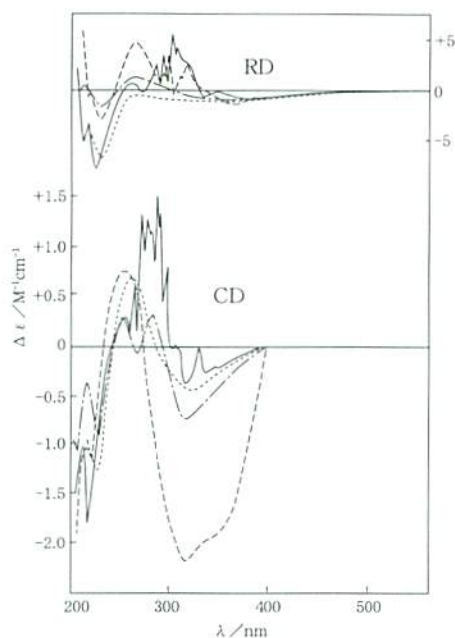


Figure 16. RD and CD of II, VI, VIII and X in ethanol (— II, ---- VI, ——— VIII, X).

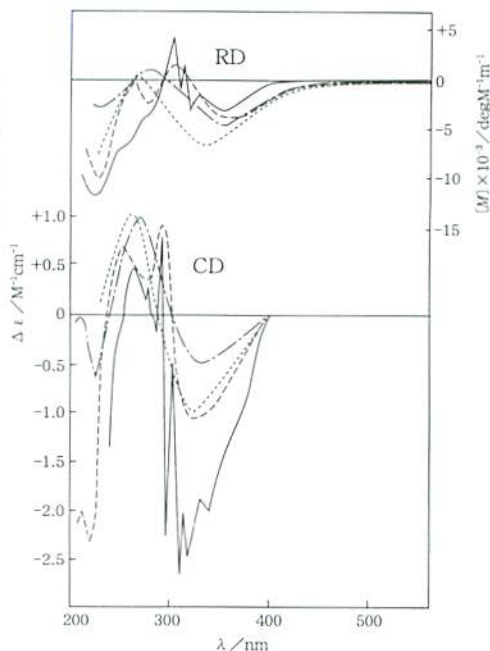


Figure 17. RD and CD of II, VI, VIII and X in water (— II, ---- VI, ——— VIII, X).

The position of the equilibrium could not be decided by the results of RD and CD, but due to the structures (in Figure 18) proposed by the minimized steric energy method the following conclusions could be reached:

1. The **CI**-form is predominant in Compounds **I** and **II**.
2. The pyranose rings for *para*-nitrophenyl derivatives **II** and **IV** are almost the same, despite whether hydroxy groups of $C_2 \sim C_4$ are acetylated or not acetylated.
3. The **IC**-form is predominant in the triacetyl *ortho*-nitrophenyl derivative **III**.
4. The anomeric effect in the pyranose ring results from not only the property of aglycon but also the result of the interaction among the $C_2 \sim C_4$ substituents.

And also the following conclusions could be made about solvent effects:

1. Compounds **I** and **II** show large values of RD, CD and UV in the solvent water.
2. In Compounds **III**, **IV** and **VI**, the values and patterns of RD and CD concerning Cotton effects are highly affected in the solvent ethanol. In the case of

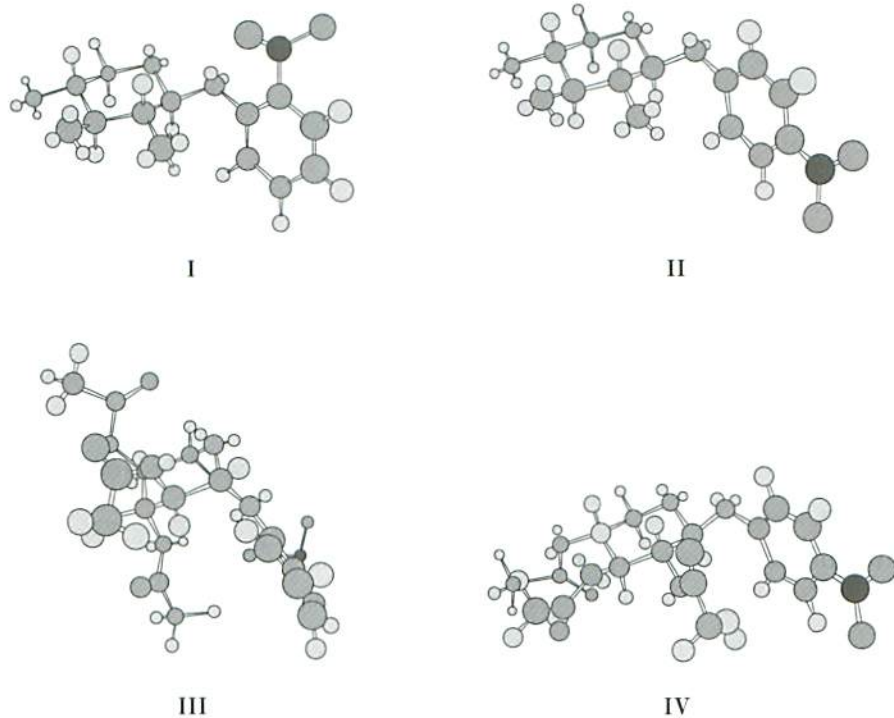
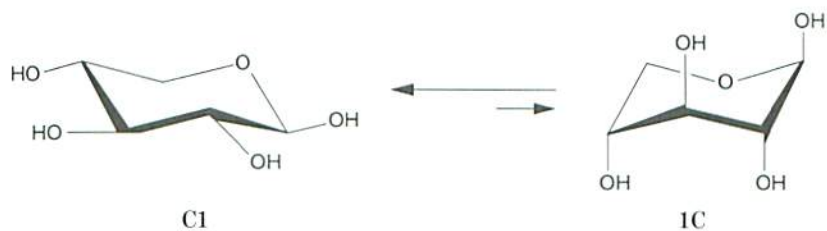


Figure 18. Energy minimized molecular mode of I ~ IV.

Figure 19. Chair form of β -D-Xylose.

Compound V, there is also an appreciable difference of the RD and CD curves in the solvent ethanol.

Experimental

Measurements. The RD and CD were measured in tetrahydrofuran, dioxane, acetonitrile, ethanol and water at 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 ¹H-NMR spectra were measured on a Hitachi Model R-24B at room temperature in DMSO-*d*₆ as a solvent. Chemical shifts are in ppm (δ) from SiMe₄ as the internal standard and *J*-values are given in Hz.

Materials. Nitrophenyl xylopyranosides (Compounds I and II) and nitrophenyl fucopyranosides (Compounds V and VI) were obtained from commercial suppliers and were used without further purification. Triacetylxylopyranosides (Compounds III and IV) were prepared according to the methods described in the literature⁶.

o-Nitrophenyl β -D-xylopyranoside (Compound I). mp 166-167°C; ¹H-NMR δ = 2.99-4.12 (6H, m), 4.83-5.56 (3H, m) and 6.98-8.03 (4H, m).

p-Nitrophenyl β -D-xylopyranoside (Compound II). mp 153-154°C; ¹H-NMR δ = 2.96-4.10 (6H, m), 4.88-5.66 (3H, m), 7.19 (2H, d, *J* = 9.6Hz) and 8.18 (2H, d, *J* = 9.2Hz).

Triacetyl *o*-nitrophenyl β -D-xylopyranoside (Compound III). mp 111-112°C; ¹H-NMR δ = 2.02 (9H, s), 3.46-4.34 (3H, m), 4.74-5.43 (2H, m), 5.66 (1H, d, *J* = 4.8Hz) and 7.08-8.01 (4H, m).

Triacetyl *p*-nitrophenyl β -D-xylopyranoside (Compound IV). mp 137-138°C; ¹H-NMR δ = 2.01 (9H, s), 3.70-4.29 (2H, m), 4.76-5.50 (3H, m), 5.74 (1H, d, *J* = 6.5Hz), 7.18 (2H, d, *J* = 9.2Hz) and 8.22 (2H, d, *J* = 9.2Hz).

o-Nitrophenyl β -D-fucopyranoside (Compound V). mp 175-176°C; ¹H-NMR δ = 1.16 (3H, s), 3.28-4.00 (5H, m), 4.57 (1H, d, *J* = 5.2Hz), 4.77 (1H, d, *J* = 5.2 Hz), 4.90-5.24 (1H, m) and 6.98-8.02 (4H, m).

p-Nitrophenyl β -D-fucopyranoside (Compound VI). mp 184-185°C; ¹H-NMR δ = 1.15 (3H, d, *J* = 6.2Hz), 3.28-4.08 (4H, m), 4.06 (1H, d, *J* = 5.2Hz), 4.82 (1H, d, *J* =

5.6Hz), 5.06 (1H, d, $J=6.4\text{Hz}$), 5.21 (1H, d, $J=4.4\text{Hz}$), 7.19 (2H, d, $J=9.2\text{Hz}$) and 8.18 (2H, d, $J=8.8\text{Hz}$).

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