CROATICA CHEMICA ACTA CCACAA **62** (2B) 377—390 (1989)

CCA-1866

YU ISSN 0011-1643
UDC 541.653
Original Scientific Paper

Calculations of Cotton Effects in the Vacuum UV Region for Chilar γ-Lactones. Correlation with the Absolute Stereochemistry

*Yoshihiro Nishida, Hiroshi Ohrui, and Hiroshi Meguro**

Department of Food Chemistry, Faculty of Agriculture, Tohoku University, Tsutsumidori-Amamiyamachi 1-1, Sendai 980, Japan

Toshio Konno

Faculty of Education, Niigata University, Igarashi, Niigata, Japan

Received October 27, 1988

A graphic method of Drude equations was applied to calculate the Cotton effects below 180 nm region for various types of α- and/or γ-substituted-γ-lactones *1—10*. The Cotton effects at *ca.* 170 nm were found to reflect the stereochemistry at C-2 (negative for β and positive for α) and C-4 (positive for β and negative for α) as well as the ring conformation (positive for E_3 and negative for ^3E) of which rotational contributions at 589 nm were suggested as the origin of Hudson's lactone rule.

There are many kinds of naturally occurring lactones, some of which are known as sugar lactones, steroid lactones and terpene lactones. Determination of their absolute stereochemistry is an important aspect of their biosynthetic or biological studies. Technically, molecular rotations ($[M]_D$), optical rotatory dispersion (ORD) and circular dichroism (CD) have been powerful tools providing several empirical or semi-empirical rules. Hudson[1,2] reported a molecular rotation rule to determine the configuration at C-4 position of chiral γ-lactones or at C-5 position of δ-lactones (Figure 1). On the other hand, a later technique of ORD and CD provided new rules based on the Cotton effect (due to the $n \rightarrow \pi^*$ transition of the carbonyl); a lactone sector rule was proposed by Snatzke *et al.*[3], and for aldono-γ-lactones independent rules to predict the configuration at C-2 and ring conformation were proposed by Okuda *et al.*[4] and Beecham[5]. We have also reported significant effects of the lone pair electrons of the substituent at C-2, like OH, NH_2 or X (halogens)[6], and the double bonds[7] at C-5 to determine the sign and intensity of the Cotton effects of chiral γ-lactones.

These rules also showed that the signs of the $[M]_D$ of chiral γ or δ-lactones were independent of the Cotton effect at *ca* 220 nm. This strongly suggests the presence of another Cotton effect below the 180 nm region not only to govern the sign of $[M]_D$ but also to reflect the absolute stereochemistry of

---

* To whom correspondence should be addressed.

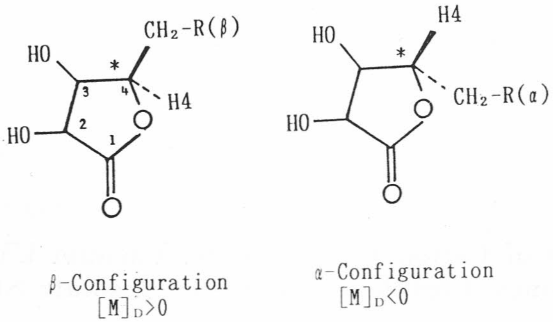


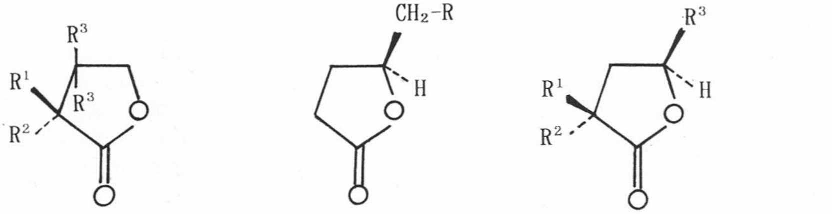
Figure 1. Hudson's lactone rule for aldono-γ-lactones[1,2]. Numbering of γ-lactone is in the conventional way for alkanoic acid lactone, where the carbonyl carbon is numbered as C-1.

γ-lactones which may be useful for the configurational or conformational studies of chiral lactones. Such a prospect prompted us to investigate the Cotton effect below the 180 nm region of a series of α- and/or γ-substituted γ-lactones.

MATERIALS AND METHODS

a) Model Compounds

Three α-substituted γ-lactones *1—3,* five γ-substituted-γ-lactones *4—8* and two α,γ-di-substituted γ-lactones *9* and *10* (Figure 2) were used as models to examine the effect of the substituents at C-2 and C-4 positions on the Cotton effect below the 180 nm region.



	R¹	R²	R³
1:	H	OH	Me
2:	NH_2	H	H
3:	NH_3Cl	H	H

	R
4:	OH
5:	Br
6:	I
7:	H
8:	$CH_2CH_2CH(CH_3)_2$

	R¹	R²	R³
9:	H	Me	CH_2OH
10:	Me	H	CH_2OH
11:	H	Me	$CH{=}CHC({=}CH_2)CH_3$
12:	Me	H	$CH{=}CHC({=}CH_2)CH_3$

Figure 2. Structures and absolute configurations of model γ-lactones *1—12*.

D-Pantolactone *1* was purchased from Wako Chemical Kogyo Co., LTD. in Tokyo, lactone *3* was prepared from L-homoserine by acid catalyzed lactonization[6] (refluxed with 2N HCl for 3 hrs and concentrated to dryness), and compound *2* was prepared by neutralizing *3* in methanol solution with methanolic 0.1 M KOH solution and used without isolation. Compounds *4—7* were prepared from L-glutamic acid according to the reported methods[8,9], lactones *8—10* were prepared in our previous report[10,11] and the details were cited therein.

b) ORD and CD Measurements

ORD and CD were measured, respectively, on Jasco J-20 and Mark-III-J spectrometer, at ca. 22 °C, at concentration ca. 1 mg/ml, and the solvents used were cited in Table I. The ORD curves were calibrated with 1% sucrose in aqueous solution ($[M]_D = +66.5°$) and CD maxima were calibrated with D-pantolactone solution in water ($[\Theta]_{max} = -17300$, $\lambda_{max} = 219$ nm)[12].

Table 1 Chiroptical Properties of α and γ-Substituted-γ-lactones.

Compounds	Solv.	λ_1/λ_2 (nm)	$[\theta_1]/[\theta_2]$[a)] x 10^{-3}	K_c x 10^{-8}	$[M_1]_D/[M_2]_D$[b)]	$[M]_D$
1	D_2O	219 160	-17.3 +14.8	-0.53 +0.36	-177 +112	-65
(R=OH)	MeOH	221 171	-13.1 +14.6	-0.46 +0.38	-155 +119	-36
	Dioxane	224 144	- 8.8 +14.1	-0.30 +0.31	-101 + 95	- 9
2 ($R=NH_2$)	MeOH	220 175	+ 4.8 - 8.9	+0.17 -0.24	+56 -75	-18
3 ($R=NH_3Cl$)	MeOH	216 175	+ 2.2 - 7.6	+0.075 -0.20	+25 -64	-39
4 (R=OH)	D_2O	208 170	-0.6 +7.7	-0.02 +0.20	-6 +63	+58
	MeOH	210 175	-0.7 +5.9	-0.02 +0.16	-7 +49	+42
	Dioxane	214 168	-0.9 +6.1	-0.03 +0.16	-10 +49	+40
5 (R=Br)	MeOH	214 165	-1.0 +9.0	-0.04 +0.22	-10 +66	+56
6 (R=I)	MeOH	214 140	-2.3 +11.0	-0.08 +0.24	-27 +65	+38
7 (R=H)	MeOH	210 165	-1.3 +6.1	-0.04 +0.17	-14 +51	+37
8 ($R=CH_2CH_2CH(CH_3)_2$)	MeOH	213 150	-0.7 +8.0	-0.03 +0.20	-9 +61	+52
9	MeOH	218 180	-2.2 +9.1	-0.07 +0.28	-23 +74	+51
10	MeOH	222 160	+0.2 +2.2	+0.01 +0.05	+ 2 +17	+22

a) $[\theta_2]$ values were calculated from the K2 values with Kronig-Krammer equation using an assumed Δ value = 13.5 nm.
b) Rotational contributions of each Cotton effect to the $[M]_D$ value.

c) Calculations of Cotton Effects below 180 nm

Recently[13-15] Cotton effects in the 160—180 nm region have been measured on vacuum CD-instruments. However, under the standard solution conditions with standard CD-instruments it is impossible to measure Cotton effects below the 180 nm region. In order to circumvent this problem, we applied a graphic method of Drude equations[16] in our preceding studies on carbohydrate molecules[17-19] and showed that the Cotton effects calculated in this manner well accorded with the real ones at ca. 190 nm measured by a computer accumulating method[18-19]. Here, we extended this theoretical calculation to chiral γ-lactones *1—10*.

The method involves common procedure as follows. (1) Rotational contribution ($[M_1(\lambda)]$) from the Cotton effect at ca. 220 nm (the first band) was calculated by a modified *Kronig-Krammer* equation used by Moffit and Moscowitzs[20,21] as follows,

$$[M(\lambda)_1] = 2\,[\Theta_1]\,\Delta_1\lambda_1/\sqrt{\pi}\,(\lambda^2 - \lambda_1^2)$$

where

λ_1 = CD maximal wavelength (nm) of the first band

$[\Theta_1]$ = maximal molecular elipticity

Δ_1 = halfwidth (nm) of the CD peak

The molecular rotation ($[M(\lambda)]$) could be thus expressed by a generalized Drude equation with $[M(\lambda)]$ as follows,

$$[M(\lambda)] = [M(\lambda)_1] + \Sigma\, 2\,[\Theta_{1+i}]\,\Delta_{1+i}\,\lambda_{1+i}/\sqrt{\pi}\,(\lambda^2 - \lambda^2_{1+i}) \qquad (A)$$

or

$$[M(\lambda)] = K_1/(\lambda^2 - \lambda_1^2) + \Sigma\, K_{i+1}/(\lambda^2 - \lambda^2_{1+i}) \qquad (A')$$

where $K_i = 2\,[\Theta_i]\,\Delta_i\,\lambda_i/\sqrt{\pi}$

(2) The $[M(\lambda)]$ values at 600, 550, 500, 450, 400, 350, and 300 nm were read for the calculation from the ORD measurements.

(3) The calculation was performed first by a two term Drude equation based on equation *A* or *A'* to obtain the second band. When the two term equation did not match the calculations, a three term equation was next attempted to obtain the two bands (the second and third band).

RESULTS AND DISCUSSION

a) Existence of the Second Band at ca. *170 nm*

All compounds studied here gave ORD curves in the 300—600 nm region well accorded with the two-term Drude equation (Figure 3). This points to the existence of the second band in addition to the observable band at *ca.* 220 nm (the first band due to the $n \rightarrow \pi^*$ transition). The λ_{max} of the second band was in 140—175 nm, where the $\sigma \rightarrow \sigma^*$ or $n \rightarrow \sigma^*$ transition of the acyloxy bond (*C*—*O*—*C*=*O*) and the $n \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$ transition of a carbonyl double bond (—O—*C*=O) are involved. It seemed difficult to assign th second band to one of these possibilities because the UV data are not in our hands, and the signals may be associated with more than the two electron transition mechanisms in the same wavelength region. Thus, in this study our efforts were focussed on establishing their empirical relationship with the absolute stereochemistry of lactones rather than on determining their origins.

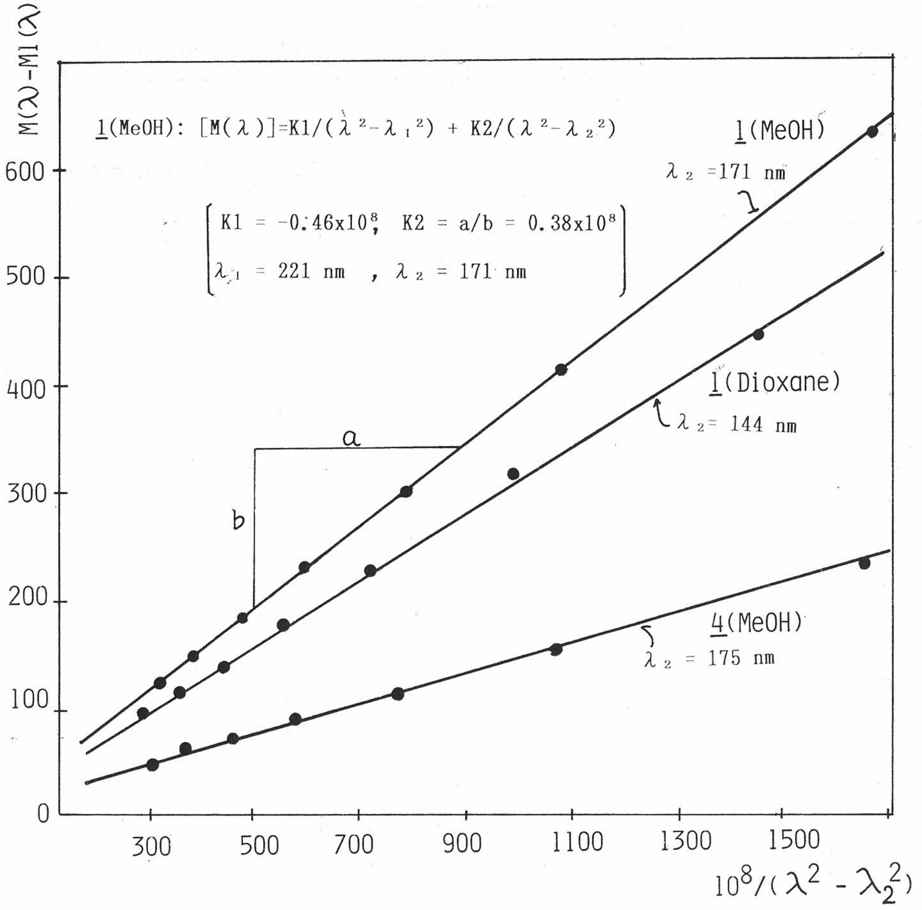


Figure 3. Graphic method of the two-term Drude equation for lactones *1* (in methanol and dioxane) and *4*.

For lactones *1—3*, the second band was as large as the first one, and its positive sign reflected the α-configuration at C-2. These results suggest that the second bands in *1—3* are prominently associated with the carbonyl chromophore. Molecular rotations ($[M]_D$) of *1—3* were small, irrespectively of their strong band at 220 nm, due to the counteractive contributions from the second band and the signs were dependent on the balance between these two bands. This also means that the rotational contributions from the asymmetrical α-position will be minor to the molecular rotations, which basically agrees with the theory of Hudson's rule.

For lactones *4—8* the second bands were in the same region as those of *1—3*. However, the first band was very small[7], while the second band is strong enough to cover the molecular rotations and its positive sign reflects the β-configuration at C-4. From these results as well as from the facts that the lactones have an asymmetric centre at C-4 in the vicinity of the ring oxygen, it was strongly expected that the second band of *4—8* would be associated with the transition of the ring oxygen (probably due to the $n \rightarrow \sigma^*$) rather than the carbonyl chromophore. The sign of the second band in lactones *4—8* accorded with Hudson's lactone rule, and this band was presumed to be an essential band for this rule.

Analogous results to those for *4—8* were obtained for lactones *9* and *10*; for both lactones the first band at *ca.* 220 nm was much smaller (though the sings reflected configuration at C-2), while the second band at *ca.* 170 nm determined their $[M]_D$ in accordance with the Hudson rule. However, the intensity of the second band was very different between *9* and *10*. This difference was understandable for the sum of the regional contributions at C-2 and C-4 predicted from the data of *3* and *4*, respectively; the smaller Kc in *10* could be ascribed to cancellation of the contribution at C-2 by a counter contribution at C-2 band.

The success of the Hudson rule of *10* seemed to be a result of the slight predominance of the C-4 contribution over the C-2 one.

b) Correction of the Kc Value of the Second Band

The previous results showed that two different bands may overlap in the close region around 170 nm; one band is associated with the transition of carbonyl (C=O) and the other with the transition of ring oxygen (—Or—). The data also showed that the chiroptical properties of *1—10* could be represented by these two bands and the first band of carbonyl $n \rightarrow \pi^*$ transition. In order to characterize each of the second bands more precisely, we attempted here to correlate the second bands of each lactone *1—10* with their absolute stereochemistry.

First of all we assumed that the strength of the second band (K2) of lactones *1—10* can be expressed as the sum of the two contributions as follows

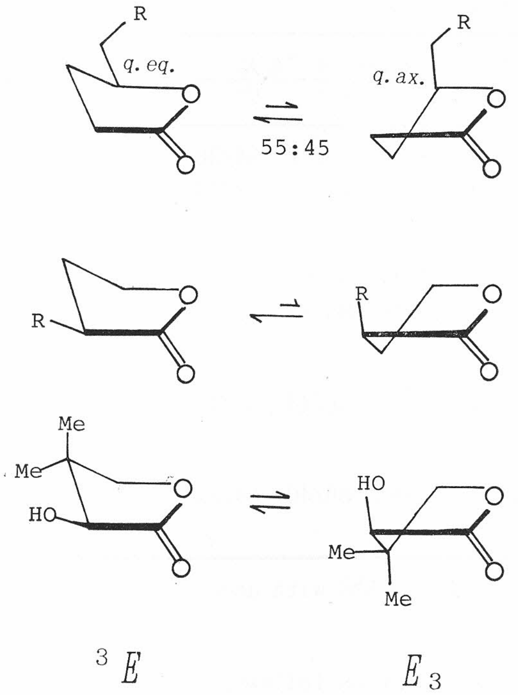
$$\mathrm{K2} = \mathrm{K2\,(C{=}O)} + \mathrm{K2\,(Or)} \tag{1}$$

where K2 (C=O) is the rotational strength due to electronic transition of a carbonyl (probably due to $n \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$), and K2 (Or) is the strength due to the ring oxygen (probably n—σ^*) transition.

Moreover, the data of lactones *1—3* showed that the decrease of the K1 value was accompanied by a decrease of K2. This is quite possible because the first [K1 (C=O)] and the second [K2 (C=O)] bands are both associated with a carbonyl group and are influenced by a C-2 group or the surrounding stereochemistry in the same manner as with each other. Thus, we have adopted the working hypothesis that K2 (C=O) could be expressed by the strength of the first band K1 (C=O) in the following equation.

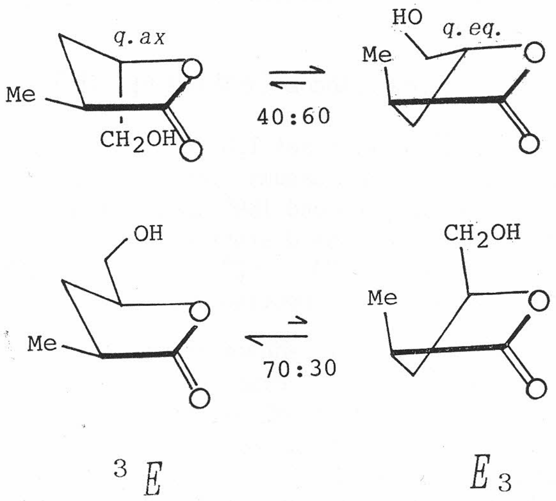
$$\mathrm{K2\,(C{=}O)} = a \times \mathrm{K1\,(C{=}O)} \tag{2}$$

Here, for convenience, a constant $a = -0.8$ was taken from the data of lactone *1* in MeOH. With equations (1) and (2), the K2(Or) values of lactones *1—10* could be calculated. The results were correlated with the ring conformation and the stereochemistry (conformations and configurations) at C-4, as illustrated in Figure 4a and 4b.



Compounds	K1(C=O)/K2(Or)
4 (MeOH)	-0.02/ 0.14
5	-0.04/ 0.19
6	-0.08/ 0.17
7	-0.04/ 0.14
8	-0.03/ 0.18
2	0.17/-0.10
3	0.08/-0.14
1 (H_2O)	0.53/ 0.06
(MeOH)	0.46/ 0.01
(Dioxane)	0.30/-0.07

Figure 4a. Conformations and corrections of the second bands of model compounds *1—8*. Lactone *1* is depicted as an enantiomer. K2(Or) was calculated by the equation; K2(Or) = K2 + 0.8 × K1(C=O).



Compounds	K1(C=O)/K2(Or)
9	0.07/-0.22
10	0.01/ 0.06

Figure 4b. Conformations and corrections of the second bands of model compounds *9* and *10*. Lactone *9* is depicted as one enantiomer.

Table 2 Conformational Properties of α- and γ-Alkylated-γ-Lactones.

Compounds	JH3, H4 (Hz)	JH3', H4 (Hz)	Ratio of $^3E/E_3$ A$^{a)}$	B$^{a)}$	C$^{a)}$
9 (2,4-*trans*)	7.5	3.5	58/42	60/40	64/36
10 (-*cis*)	8.8	5.1	72/28	73/27	77/23
11 (-*trans*)	7.6	4.1	59/41	61/39	65/35
12 (-*cis*)	10.1	5.4	85/15	85/15	90/10
4, 5, 6	~7$^{a)}$	~5$^{a)}$	53/47	56/44	60/40
7	7.5	4.2	58/42	60/40	64/36

a) First Order Analysis on 99.5 MHz ^{1}H-NMR with accuracy $J_{H,H}$ ± 0.4 (Hz).
b) Accuracy $J_{H,H}$ ± 1 (Hz).
c) Calculated with equation A, B and C as follows,
A: ^3E=100x(JH3, H4-1.9)/9.6, E_3=100-^3E
B: ^3E=100x(JH3, H4-1.1)/10.6, E_3=100-^3E
C: ^3E=100x(JH3, H4-0.86)/10.3, E_3=100-^3E

The equations A - C are based a Karplus equation of Haasnoot et al. (ref. 24) as below;

$$JH,H = 13.22\cos^2\phi - 0.99\cos\phi + \Sigma\Delta\chi i[(0.87-2.46\cos^2(\xi\phi+19.9|\Delta\chi i|)],$$

where factors of electronegativity ($\Delta\chi i$) were set 1.3 (ring oxygen), 0.4 (C-3 and C-5) for A - C. The equation A assums perfect staggered conformations of ^3E and E_3 with ± 60 and 180° angles between the C3-H3 and C4-H4 bonds, while B and C assum distorted conformations of ^3E (the angles between the C3-H3β and C4-H4 = 190° for B and = 200° for C) and E_3 (-70° and -80° for B and C, respectively).

In Figure 4a and 4b, compounds *1* and *9* are shown as one enantiomer for convenince. The position of equilibrium of ring conformations between ^3E and E_3[22,23] is indicated by the length of arrow based on the ^{1}H-NMR data in Table II and a hypothesis that the *quasi-equatorial (q. eq)* conformation is more favored than the *quasi-axial (q. ax)* one when only one substituent at C-2 or at C-4 is present. For lactones *4—10*, the vicinal coupling constants between H-4 and H-3β were used to calculate the time averaged populations of the two possible ring conformers ^3E and E_3[22,23] (Table 2.). For the calculation, three types of equations *A*, *B* and *C* based on a Karplus equation of Haasnoot *et al.*[24] were used assuming possible distortions of the ring conformations from the perfect ^3E and E_3 into the flattered ones. Here, distinction between H-3α and H-3β signals was based on the assumption that lactones *4*—*10* would favor a ring conformation with a bulky substituent at C-4 in a *quasi-equatorial* direction. The data in Table 2. show that lactones *4*—*6* took conformational equilibrium between ^3E and E_3 in an approximate ratio of *ca.* 55/45 and *7* and *9* of *ca.* 60/40 and *10* of 70/30. The high ^3E population in lactone 10 seemed to be due to the unfavorable 1,3-diaxial interaction between the C-2 and the C-4 substituents in the E_3 conformation, and a similar result was obtained in marmelo lactones *11* and *12* with analogous structures[7]. These conformational properties as described for *4*—*12* are in good accordance with our previous ^{13}C-NMR studies on α,γ-dialkylated γ-lactones[11].

The K2(Or) value of each of the lactones *1*—*10* was then correlated with their absolute stereochemistry as follows.

1) Compounds *2* and *3* gave K2(Or) of —0.10 and —0.14, respectively, which suggested that ^3E conformation had negative contribution, and the enantiomeric E_3 had positive ones on the 170 nm bands. The larger K2(Or) in *3* suggested more abundant ^3E in *3* than that in *2*.

Table 3 ORD Data of Lactones 1-10.

Compounds	Solvent	[M](λ) 600	550	500	450	400	350	300
1	MeOH	-35	-46	-58	-81	-128	-226	-510
	Dioxane	-9	-12	-17	-25	-48	-101	-315
2	MeOH	-17	-19	-23	-28	-32	-33	+2
3	MeOH	-41	-51	-61	-74	-102	-142	-205
4	H_2O	+58	+69	+83	+104	+133	+189	+287
	MeOH	+37	+47	+53	+70	+87	+120	+183
	Dioxane	+42	+51	+61	+75	+99	+133	+194
5	MeOH	+55	+66	+80	+103	+136	+191	+289
6	MeOH	+34	+41	+50	+63	+81	+96	+91
7	MeOH	+37	+43	+51	+61	+86	+123	+178
8	MeOH	+53	+58	+71	+91	+118	+153	+235
9	MeOH	+51	+57	+72	+90	+120	+162	+264
10	MeOH	+22	+24	+28	+36	+48	+66	+102

2) Compounds *10* and *4—9* gave K2(Or) of +0.06 and +0.14 ~ +0.22 as the sum of two effects of (a) the ring conformation (—0.10 ~ —0.14) and (b) the configuration at C-4. Subtraction showed that the latter should be +0.16 ~ +0.36 indicating that the β-configuration at C-4 had positive contributions, and the enantiomeric α-configuration had negative contribution.

3) In compounds *9* and *10,* the larger K2(Or) of *9* (+0.24) suggested a higher contribution from the *quasi-axial* configuration (*ca.* ±0.4 ~ 0.5) of the C-4 substituent that the *q. eq.* configuration (*ca.* ±0 ~ 0.1).

4) The small and solvent dependent signs of K2(Or) of compound *1* suggested a higher ${}^3E$ abundance in H_2O and lower ${}^3E$ in dioxane at equilibrium.

CONCLUSION

We have found new bands at *ca.* 170 nm region calculated by a graphic method of Drude equation. The assignments of the electronic transitions of these bands were difficult baceuse the UV data are missing and several transitions are possible in this region. However, the comparison of the data of α-substituted lactones *1—3* and γ-substituted lactones *4—8* was useful for correlating the signs and intensities of the second bands with the absolute stereochemistry of the chiral γ-lactones and lead to the conclusion that the 170 nm bands could be divided into two types: one band is asscoiated with

Rule 1 Effects of the C-2 Configurations on the Bands due to the Carbonyl Transitions.

	C-2β(q.eq)		C-2β(q.ax)
K1(C=O) 220 nm	+	<	+
K2(C=O) 170 nm	—	>	—
[M]$_D$	positive	<	positive

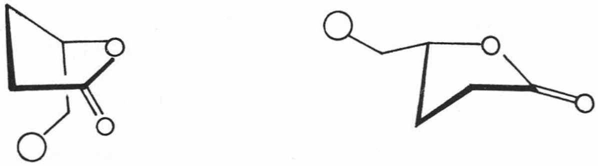
	C-2α(q.ax)		C-2α(q.eq)
K1(C=O) 220 nm	—	<	—
K2(C=O) 170 nm	+	>	+
[M]$_D$	negative	<	negative.

Figure 5.

Rule 2

Effects of the Ring Conformation, C-4 Configuration and Conformation on the Second Bands at 170 nm due to the Ring Oxygen.

	^3E,	C-4β(q.eq)	E_3	C-4β(q.ax)
K2(Or) 170 nm	−	+	+	++
$[M]_D$	small		large positive	



	^3E,	C-4α(q.ax)	E_3	C-4α(q.eq)
K2(Or) 170 nm	−	−−	+	−
$[M]_D$	large negative		small	

Figure 6.

the carbonyl transition as the counter peak of the $n \rightarrow \pi^*$ band and the other is associated with the ring oxygen transition. The signs of each 170 nm band reflected the stereochemistry at C-2 and C-4 and ring conformations, as summarized in *Rule 1* and *Rule 2*.

Rule 1 shows that the C-2 β-configuration has a negative and C-2 α-configuration has positive effect on the 170 nm band due to the carbonyl. *Rule 2* shows that the ^3E ring conformation has negative and E_3 has positive effects on the 170 nm band due to the ring oxygen, and C-4 β-substituent has positive and C-4 α-one has negative effects on this band. We observed in compounds *9* and *10* that these bands were additive.

We have found also that the signs of the 170 nm band due to the ring oxygen accorded with the sign of Hudson's lactone rule. Its intensity, however, was not so large (K2(Or) = ±0 ~ 0.5 × 10^8) to cancel all the other possible contributions from the C-2 and ring. Therefore, for sugar lactones and the related lactones with asymmetric centre both at C-2 and C-4, the success of Hudson's rule would depend on the sum of the rotational contributions associated with their absolute stereochemistry.

REFERENCES

1. C. S. Hudson, *J. Am. Chem. Soc.* **32** (1910) 338.
2. C. S. Hudson, *J. Am. Chem. Soc.* **61** (1939) 1525.
3. a) G. Snatzke, H. Ripperger, C. Horstmann, and K. Schreiber, *Tetrahedron* **22** (1966) 3103.
   b) P. Welzel H. Bulian, A. Maulshagen, D. Muller, and G. Snatzke, *Tetrahedron* **40** (1984) 3657.
4. T. Okuda, S. Harigaya, and A. Kiyomoto, *Chem. Pharm. Bull., Jpn.* **12** (1964) 504.
5. A. F. Beecham, *Tetrahedron Lett.* (1968) 2355.
6. a) H. Meguro, T. Konno, and K. Tuzimura, *Tetrahedron Lett.* (1975) 1305.
   b) H. Meguro, T. Konno, and K. Tuzimura, *Tetrahedron Lett.* (1975) 1309.
7. a) Y. Nishida, T. Konno, H. Ohrui, and H. Meguro, *Agric. Biol. Chem.* **47** (1983) 2683.
   b) Y. Nishida, H. Ohrui, H. Meguro, and K. Mori, *Agric. Biol. Chem.* **50** (1986) 813.
8. M. Taniguchi, K. Koga, S. Yamada, *Tetrahedron* **30** (1974) 3549.
9. K. Mori, *Tetrahedron* **31** (1975) 3012.
10. Y. Nishida, H. Ohrui, and H. Meguro, *Agric. Biol. Chem.* **48** (1984) 1211.
11. Y. Nishida, M. Konno, Y. Fukushima, H. Ohrui, and H. Meguro, *Agric. Biol. Chem.* **50** (1986) 191.
12. T. Konno, H. Meguro, and K. Tuzimura, *Anal. Biochem.* **67** (1975) 226.
13. C. Bertucci, P. Salvadori, G. Zullino, D. Pini, W. C. Johnson, *Carbohydrate Res.* **149** (1986) 299.
14. E. R. Morris, E. S. Stevens, S. A. Frangou, and D. A. Rees, *Biopolymers* **25** (1986) 959.
15. A. Gedanken, H. D. Lagier, J. Schiller, A. Klein, and J. Homes, *J. Am. Chem. Soc.* **108** (1986) 5342.
16. E. Iizuka and J. T. Yang, *Biochemistry* **3** (1964) 1519.
17. a) H. Meguro, E. Ohtaki, and K. Tuzimura, *Tetrahedron Lett.* (1977) 4335.
    b) E. Ohtaki, H. Meguro, and K. Tuzimura, *Tetrahedron Lett.* (1977) 4339.
18. a) K. Kohata, T. Konno, and H. Meguro, *Tetrahedron Lett.* (1980) 3771.
    b) K. Kohata and H. Meguro, *Agric. Biol. Chem.* **46** (1982) 927.
19. K. Kohata, E. Ohtaki, C. Suzuki, and H. Meguro, *Bull. Chem. Soc., Jpn.* (1982) 1609.
20. C. Djerassi, *Optical Rotatory Dispersion-Application to Organic Chemistry*, McGraw Hill, 1961.
21. W. Moffit and A. Moscowitz, *J. Chem. Phys.* **30** (1959) 648.
22. S. Bystricky, T. Sticzay, S. Kucar, and C. Pecial, *Collect. Czech. Chem. Commun.* **41** (1976) 2749.
23. D. Horton and Z. Walaszek, *Carbohydrate Res.* **105** (1982) 111.
24. C. A. G. Haasnoot, F. A. A. Leeuw, and C. Altona, *Tetrahedron* **36** (1980) 2783.

SAŽETAK

Računanje Cottonovih efekata u vakuumskom UV-području za kiralne γ-laktone i korelacija s apsolutnom stereokemijom

Yoshihiro Nishida, Hiroshi Ohrui, Hiroshi Meguro i Toshio Konno

Grafička metoda Drudeove jednadžbe korištena je za računanje Cottonovih efekata u području ispod 180 nm za različite tipove α i/ili γ-supstituiranih γ-laktona *1—10*. Nađeno je da Cottonov efekt kod *cca.* 170 nm odražava stereokemiju na C-2 (negativan za β, pozitivan za α) i na C-4 (pozitivan za β, negativan za α), kao i konformaciju prstena (pozitivan za E_3, negativan za ^3E). Pretpostavlja se da su rotacijski doprinosi tog efekta vrpci kod 589 nm izvor Hudsonova laktonskog pravila.