OPTICAL ACTIVITY OF LACTONES AND LACTAMS—I

CONFORMATIONAL DEPENDENCE OF THE CIRCULAR DICHROISM OF 1,3-DIOXOLAN-4-ONES

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Abstract—Several optically active 1,3-dioxolan-4-ones were synthesized from corresponding α-hydroxy acids. The Cotton effect sign of these compounds can be explained by Weigang's sector rules. The existence of an equilibrium between envelope and planar conformations of the 5-membered ring was established on the basis of substituent and solvent influence on the CD. It was found that hindered rotation of phenyl group affects the CD of 5-phenyl substituted 1,3-dioxolan-4-ones.

Considerable attention has been paid to the CD and ORD studies of lactones and lactams in recent years.[1,2] Many efforts have been made to relate the Cotton effect (CE) sign associated with the lowest energy $n{\rightarrow}\pi^*$ electronic transition to the stereochemical features of these compounds. Several sector rules have been proposed for this correlation and attempts have been made to differentiate between contributions to observed CE from inherent chirality within the lactone or lactam ring and contributions arising from vicinal effects due to asymmetric substitution.[1]

Aiming to extend these CD studies 1,3-dioxolan-4-ones and 4-oxazolidinones, the heterocyclic analogues of γ-lactones and γ-lactams, were selected as models. It is noteworthy, that these simple compounds with unequivocal absolute configuration are easy to obtain from the corresponding α-hydroxy acids.

The present paper reports the results of the investigations on 1,3-dioxolan-4-ones aiming to establish the conformation of the five-membered ring. The knowledge of preferred conformations may serve as a basis for testing the sector rules governing the CE sign for $n{\rightarrow}\pi^*$ transition of lactones.
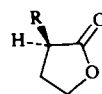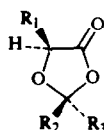
Synthesis and absolute configuration

The synthesis of 1,3-dioxolan-4-ones is based on acid catalysed reaction of α-hydroxy acids with aldehydes and ketones.[3–5] Several optically active 5-, 2,5-, and 2,2, 5-substituted 1,3-dioxolan-4-ones 1–5 with unequivocal configuration have been obtained from (S)-α-hydroxy acids and corresponding carbonyl compounds. The same reaction with aldehydes as substrates give mixtures of diastereoisomers 6–9, which have been separated by fractional crystallization and by column chromatography.

Attempts to establish the configuration of these compounds have been made by analysis of their NMR spectra (Table 1). The assignment of cis- and trans-diastereoisomers is easy for compounds with 5-phenyl substituent 8a, b and 9a, b; for example liquid isomer 8a is assigned as cis and solid 8b as trans. Support for this appointment comes from appearance of the aromatic signals; 8a shows a complex multiplet centered at δ 7.27

and the signal from 8b is almost singlet at δ 7.33. This is a result of hindered rotation of phenyl group interacting with a nearby t-butyl group, which causes a marked difference in the local magnetic environment for each of aromatic protons. In a similar way, diastereoisomers 9a and 9b were assigned as cis and trans stereochemistry respectively. The protons at C–5 and C–2 of 8b show signals at higher field than those of 8a which can be explained on the basis of shielding effects of substituents at C–2 and C–5 on the protons on the same side of the ring.[6] Compounds 6a and 7a, whose protons at C–2 and C–5 show signals at lower field, should be cis and 6b and 7b with these signals at higher field should be trans. Since the shielding effects of C–C bonds of t-butyl and isopropyl groups are rather low, the difference between chemical shifts of diastereoisomer protons studied are also low and the stereochemical assignments are hazardous and should be supported by other methods.†

The NMR spectra of 1,3-dioxolan-4-ones show long-range coupling between C–2 and C–5 protons,[7–9] however the controversy about the utility of such coupling to assign relative geometries of 2-H and 5-H exists.[8,9] The data collected in Table 1 suggest that $J_{2,5}$ is influenced by electronegativity of substituents.

1a, R₁=Me; R₂=R₃=H
1b, R₁=Me; R₂=R₃=Me
1c, R₁=Me; R₂=R₃=Et
2a, R₁=i-Pr; R₂=R₃=H
2b, R₁=i-Pr; R₂=R₃=Me
3a, R₁=i-Bu; R₂=R₃=H
3b, R₁=i-Bu; R₂=R₃=Me
4a, R₁=CH₂Ph; R₂=R₃=H
4b, R₁=CH₂Ph; R₂=R₃=Me
5a, R₁=Ph; R₂=R₃=H
5b, R₁=Ph; R₂=R₃=Me
6a, R₁=Me; R₂=t–Bu; R₃=H
6b, R₁=Me; R₂=H; R₃=t–Bu
7a, R₁=i-Pr; R₂=t–Bu; R₃=H
7b, R₁=i-Pr; R₂=H; R₃=t–Bu
8a, R₁=Ph; R₂=t–Bu; R₃=H
8b, R₁=Ph; R₂=H; R₃=t–Bu

9a, R₁=Ph; R₂=CCl₃; R₃=H
9b, R₁=Ph; R₂=H; R₃=CCl₃
10, R=Me
11, R=n-Pr

†Recently D. Seebach and R. Naef, *Helv. Chim. Acta* **64**, 2704 (1981) assigned *trans* configuration for **6b** and **8b** by NOE experiments.

Table 1. NMR data for diastereoisomers of
1,3-dioxolan-4-ones (chemical shifts in δ, J in
Hz)

Comp.	5-H	2-H	Ph[a]	J_{2H-5H}
6a[b,c]	4.25	5.14		1.3
6b[b]	4.18	4.98		1.1
7a[b]	3.99	5.13		1.5
7b[b]	3.91	4.96		1.2
8a[d]	5.24	5.28	7.27(m)	1.2
8b[d]	5.12	5.20	7.33(s)	1.3
9a[d]	5.43	5.88	7.35(m)	1.1
9b[d]	5.57	5.97	7.29(s)	1.5

[a]s—singlet, m—multiplet; [b]in CCl₄; [c]measured for the mixture of diastereoisomers; [d]in CDCl₃.

Table 2. CNDO/2 results for the conformers of 1,3-dioxolan-4-one[a]

Form	E_t	E_n	E_{el}	ΔE	μ
A	−2168.4056	3620.2769	−5788.6824	6.365	2.70
B	−2168.3653	3602.2068	−5770.5721	6.362	2.20
C	−2168.3382	3621.1471	−5789.4852	6.390	2.39

[a]E_t, E_n, E_{el} and ΔE—total, nuclear, electronic and transition energy in eV; μ—dipole moment in D.

Conformational considerations

The five-membered ring in γ-lactones is known to occur in envelope form, in which the α- and γ-carbon atoms along with the O=C–O group, all lie in one plane, and the β-atom lies above or below this plane.[10] The same conformation (A and enantiomeric A') with O-1 atom deviated from the ring plane can be considered for structurally related 1,3-dioxolan-4-ones (Fig. 1). The ring chirality is determined by steric effect of bulky 5-substituent, which tends to occupy quasi-equatorial position and then prefers A over A' form. Since, the displacement of C-atom by O-atom in γ-lactone ring reduces the torsional strain (by two pairs of CH–CH interactions) responsible for the puckering of the ring,[11] the existence of planar or near planar conformation B in solution is also very probable. However, conformation B seems to be more crowded and then less preferred in case of bulky substituents which occupy bissectional positions. The X-ray data for trans-2,5-bis-(trichloromethyl)-1,3-dioxolan-4-one show that the dioxolanone ring is near planar with C-2 atom little deviated from the ring plane in crystal state.[12] Inspection of Drieding stereomodels and X-ray data, suggests that second envelope conformation (C and enantiomeric C') with C-2 atom deviated from the ring plane should also be taken into consideration although distortion of the ester group from planarity leads to substantial strain energy in this conformation despite some diminished substituent interactions. These considerations have been confirmed by CNDO/2 calculations of conformational energies (Table 2). These calculations show that the unsubstituted 1,3-dioxolan-4-ones are the most stable in envelope A conformation and that conformation C is less stable than other forms are.

Obviously the substituents can modify conformational energy. Since the C–O bond is shorter by 0.10 Å than C–C bond, the substituents at C-2 and C-5 are closer to each other in dioxolanone ring than in γ-lactones, the 2,5-transannular interactions should determine the ring conformation of 1,3-dioxolan-4-ones at first rate. This is close analogy to 1,3-dioxanes, where 2-axial methyl group has larger conformational energy (3.6 kcal/mol) than an axial methyl in cyclohexane (1.7 kcal/mol).[13] Based on these considerations, 2- and 5-bulky substituents should favor A conformation for cis-substitution and B conformation for trans-substitution. In case of 5- and 2,2,5-substituted compounds the equilibrium between A and B forms is predicted. Bulky substituents should prefer puckered A conformation over B, and A' form with 5-substituent in quasi-axial position, should be negligible in conformational equilibrium.

Circular dichroism spectra

The CD method seems to be well suited for verification of these conformational predictions, because chiroptical properties are extremely sensitive to conformational changes.

The CD data of 1,3-dioxolan-4-ones are summarized in Table 3. The results of chiroptical studies point to the existence of conformational equilibrium in solutions of these compounds. This is shown by bisignate curves in the n→π* region, and by the strong substituent and solvent effects on the shape of these curves (Fig. 2).

For stereochemical correlations the CE sign should be assigned for each conformation. The CE of lactones can be related to the spatial configuration of atoms or groups by several rules. According to an earlier approach, the ring chirality determines the lactone CE sign.[14,15] Another approach is based on several sector rules proposed by Klyne,[1,16] Snatzke,[17] and more recently by Weigang.[18] The latest are the most general and can explain optical activity of lactones and lactams. The lactone chromophore with C_s symmetry is treated as a perturbed carboxylate anion which itself has C_{2v} symmetry and the static coupling is responsible for the symmetry lowering.[18,19] According to the Weigang's sector rule the sign of lactone rotatory strength is predicted by antioctant rule and since the postulated spherical distortion of xy nodal plane is symmetric with regard to z axis, it is insignificant for sign predictions. This rule predicts negative CD for A, positive CD for B and C conformations
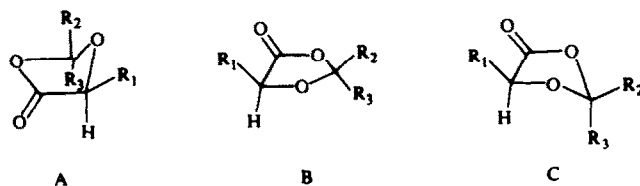

Fig. 1. Conformations of 1,3-dioxolan-4-ones. Enantiomeric forms are denoted by primes in the text.

Table 3. CD data for 1,3-dioxolan-4-ones ([θ] in deg. mole⁻¹ cm², λ in nm)

Comp.	Solv.[a]	λ_{max}	$[\theta]\cdot 10^{-3}$	Comp.	Solv.[a]	λ_{max}	$[\theta]\cdot 10^{-3}$
1a	C	206 233[b]	-0.16 0.18	1b	C	207 234[b]	-0.43 0.14
	A	225	0.45		A	227	0.38
	M	224	0.61		M	225	0.51
				1c	C	213	-1.09
					M	213	-0.67
2a	C	217	-1.06	2b	C	211 242	-1.02 0.08[b]
	M	212 236	-0.50 0.07		M	212 232	-0.40 0.29
3a	C	219	-1.03	3b	C	215	-1.0
	M	212	-0.64		M	212 233	-0.50 0.06
4a	C	224 262[b]	-3.8 -0.22	4b	C	220 262[b]	-4.35 -0.26
5a	C	222 250[b]	6.33 -0.29	5b	C	222 257[b]	12.9 -0.17
	M	221 263[b]	12.2 -0.27[b]		M	221 263[b]	15.0 -0.29
				6b	C	226	1.80
					M	223	1.96
7a	C	219	-4.0	7b	C	226	1.88
	M	219	-3.59		M	223	2.03
8a	C	223 234 257[b]	0.59 -3.52 -0.18	8b	C	222 263[b]	16.5 -0.17
	M	222 237 256[b]	3.73 -1.33 -0.23		M	221 263[b]	15.5 -0.30
9a	C	223 256[b]	12.3 -0.20	9b	C	223 263[b]	14.9 -0.40
	M	222 263[b]	36.0 -0.25		M	223 263[b]	21.0 -0.50
10	A	218	-1.43[c,d]				
11	A	218	-1.87[b,e]				

[a]C—cyclohexane, M—methanol, A—acetonitrile; [b]the highest intensity vibronic band; [c]A. J. Meyers, Y. Yamamoto, E. D. Mihelich and R. A. Bell, J. Org. Chem. 45, 2792 (1980); [d]70% optical purity; [e]73% optical purity.

(Fig. 3). For A and C conformations it was assumed that the chiral ring contribution chiral second sphere outweighs the alkyl substituent contribution to the magnitude of CE, according to the Snatzke doctrine of spheres.[20] The same signs can be obtained with the Klyne sector rule, because this rule assumes the same symmetry of lactone chromophore. Inspection of CD data in Table 3 confirms the influence of substituent interaction on conformational equilibrium of 1,3-dioxolan-4-ones. Comparison of the spectra of 1–4 shows that the magnitude of negative CD band becomes greater with the increase of 5-substituent size in accordance with assumption that bulky substituents favor puckered A conformation. The increase of the solvent polarity causes decrease of intensity of this band and the increase or emergence of a positive CD band. This indicates that polar solvents favour the planar B form, which in case of small substituents predominates in equilibrium (1a and 1b). This result is surprising, in view of CNDO/2 calculations, showing a slightly greater dipole moment for A than for B. The influence of 2-substituents on the conformation of the ring is distinctly observed (latic acid derivatives; Fig. 2). Compounds 1a and 1b in polar solvents show only positive CD band in n→π* region, which is characteristic for domination of B conformation, however the non-Gaussian shape of this band in-

dicates that form A gives a minute contribution to the equilibrium. In non-polar solvents these compounds show bisignate CD curves and the magnitude of positive CD band decreases with increase of bulkiness of the 2-substituent. Substitution at C-2 by ethyl groups causes complete disappearence of the positive band even in polar solvents and spectrum of 1c becomes very similar to 2a, as a result of diminished contribution of B form. The existence of bisignate curves shows that conformers A and B have different spectroscopic characteristics. The flattened B form shows CD band at longer wavelengths than A and vibronic structure of this band is distinctly visible. Probably, the last feature can, be attributed to the higher symmetry of planer form. The difference of n→π* transition energies for both conformers is so great that even positive CD band of 1a and 2a in methanol (despite solvent hypsochromic shift) appears at longer wavelength than negative CD of 2a in cyclohexane. However, it is known that in case of superposition of bands with opposite signs, the positions of overlapping CD bands do not correspond to absorption maxima.[21]

For to obtain a clearer picture of spectroscopic properties of A and B, compounds 7a and 7b were synthesized. For cis-substituted 7a the form A should be the most stable and for trans-7b predomination of B conformation is expected. In fact, 7a shows negative CD and
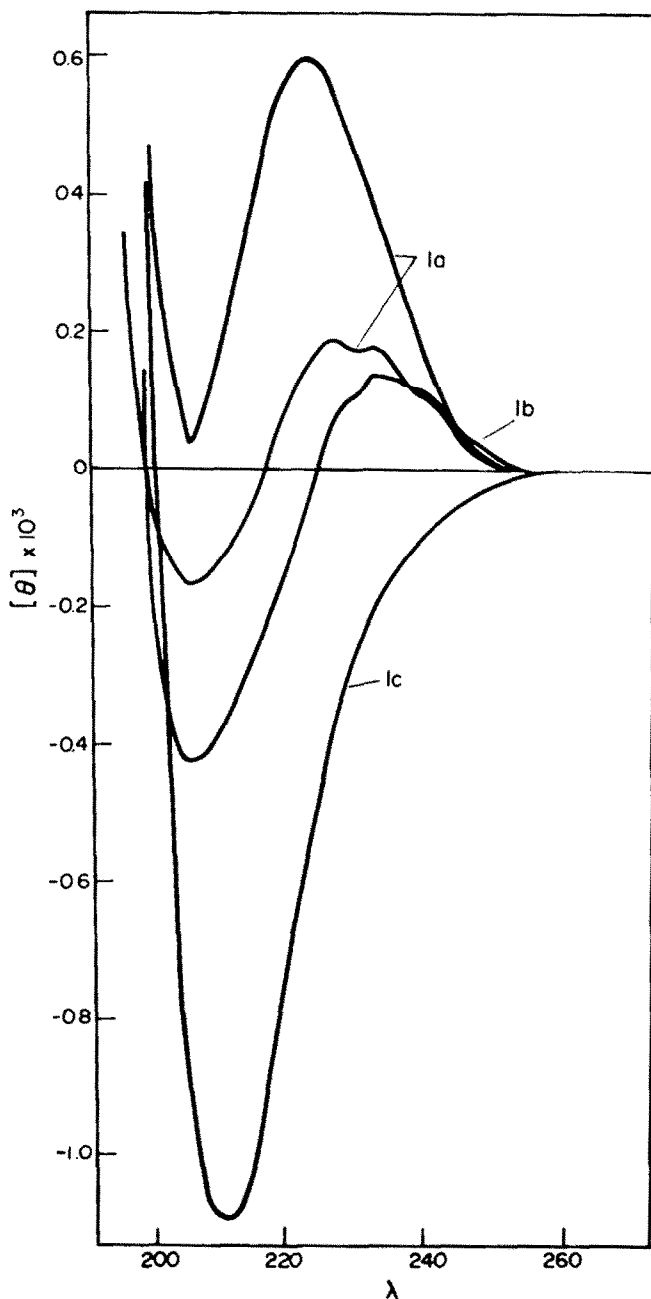
Fig. 2. Circular dichroism spectra of (5S)-5-methyl-1,3-dioxolan-4-one (1a) in methanol (upper curve) and cyclo-
hexane, (5S)-2,2,5-trimethyl-1,3-dioxolan-4-one (1b) and (5S)-2,2-diethyl-5-methyl-1,3-dioxolan-4-one (1c) in cyclo-
hexane.

7b positive CD and moreover, *trans*-**7b** shows CD at longer wavelengths than *cis*-**7a** and the magnitudes of CE is only slightly changed by solvents. The strong magnitude, near Gaussian shape of bands and absence of solvent effect points to existence of **7a** and **7b** (also **6b**) in almost pure conformational states in solution. Because of the stronger chiral ring than substituent contribution to the CE, **7a** shows CD about two times more intense than **7b**. Additionally the marked fine structure of CD band of **6b** proves that this band represents B form. The CD spectra of **7a**, **7b** and also **6b** confirm the configurations predicted for these compounds by NMR spectroscopy.

Some comments are due to the existence of C conformation in equilibrium. CD spectra of δ-lactones,[22]

INDO calculations,[23] and authors CNDO/2 calculations (Table 2) demonstrate that the lactones with non-planar ester group show CD at shorter wavelengths than those with planar groups. As Fig. 1 shows, C form with positive CD may be expected for 5-, 2,2,5-, and *cis*-2,5-substituted compounds and enantiomeric C' with negative CD for *trans*-2,5-substituted compounds. Nevertheless, the CD spectra of corresponding compounds show that these forms do not give significant contribution to the conformational equilibrium.

It seems to be interesting to compare the chiroptical properties of 1,3-dioxolan-4-ones and α-substituted γ-lactones. The CD spectra of γ-lactones collected in Table 3, exhibit negative CE in polar solvent for n→π*
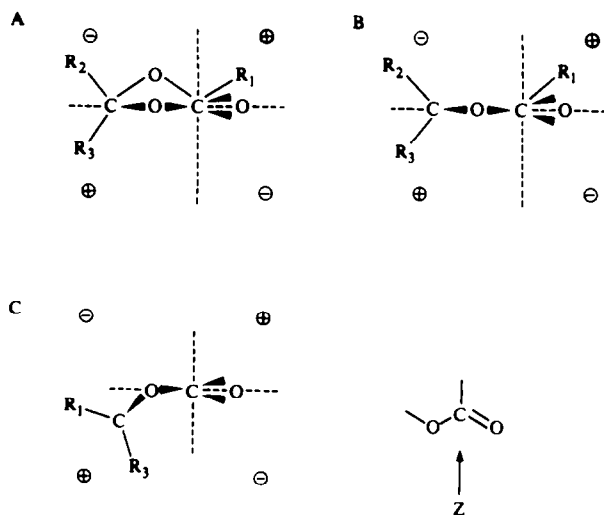
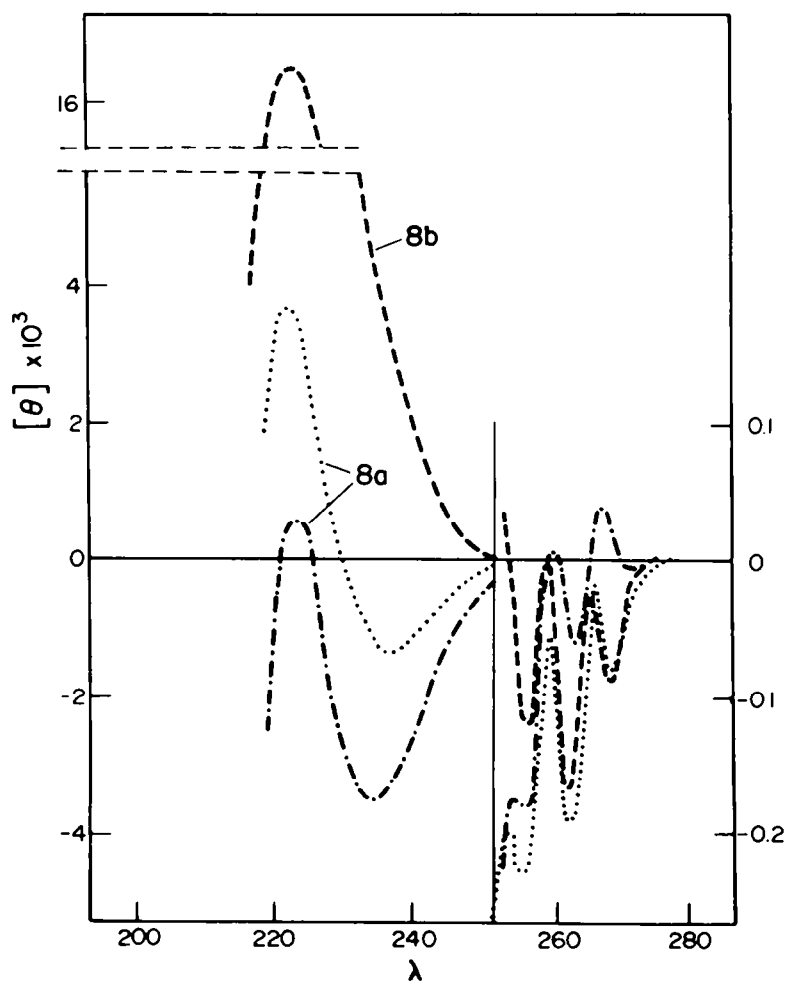Fig. 3. Sector projections of 1,3-dioxolan-4-one conformations. The arrow shows direction of projections.

Fig. 4. Circular dichroism spectra of cis-**8a** in methanol (————) cis-**8a**(—·—·—) and trans-**8b** (........) in cyclohexane.

transition and its magnitude becomes greater with the increase of α-substitutent size. This observation and the relatively strong magnitude of CE confirms the existence of γ-lactones mainly in envelope A conformation.

CD of mandelic acid derivatives

Recently Sutsumabayashi *et al.* measured CD spectra of 5-phenyl substituted 1,3-dioxolan-4-ones and stated that the positive CD cannot be explained by any semiempirical rules.[24] The chiroptical properties of 5-phenylsubstituted 1,3-dioxolan-4-ones differ considerably from the CD of those with aliphatic side chains. Compounds **5**, **8** and **9** exhibit weak CD band near 250 nm with distinct vibronic structure which corresponds to the ^1L_b excitation of phenyl moiety, and intense band near 220 nm. The origin of the last band, general for α-substituted phenylacetic acid derivatives, is uncertain,[25-28] since the ^1L_a phenyl transition and $n\rightarrow\pi^*$ carboxylate transition occur in the same region. The transitions involving both carboxylate and aromatic orbitals are also possible.[26,27] CNDO/S–CI calculations reveal that the rotatory strength of ^1L_a excitation is relatively weak and should be of the same order as ^1L_b.[26] Inspection of CD data for compounds **5a** and **5b** shows, that the 220 nm band cannot be assigned to the pure $n\rightarrow\pi^*$ transition, because firstly, the hyposochromic shift caused by polar solvents is absent, and secondly the strong positive CD should correspond to predominance of B conformation, which is improbable for such compounds. The comparison of the CD for **5a** and **5b** reveals that the substitution of hydrogen atoms at C–2 by methyl groups causes about twofold enhancement in intensity of the 220 nm band. This can be attributed to the hindered rotation of the phenyl moiety caused by near bulky substituent, as it is also evident from the NMR spectrum. The solvent dependence of CD arrives at the same conclusion.

The magnitude of CE at 220 nm for **5a** and **5b** increases in going from cyclohexane to methanol because more crowded B conformation of the dioxolanone ring is preferred in polar solvents and then phenyl rotation is hindered. On the contrary, the spectrum of *trans*-**8b** is only slightly dependent on solvent polarity, since this compound exists in almost pure B conformational state similarly to **7b**. Both carboxyl and phenyl groups can then be tentatively treated as homoconjugated β,γ-unsaturated lactone inherently dissymmetric chromophore and CD sign should be determined by helicity of this arrangement. This conclusion is supported by CD of related 4-oxazolidiones, which show the same CD sign, contrary to 4-oxazolidinones with aliphatic side chains, which show CD of opposite sign to related 1,3-dioxolan-4-ones.[28] The chiroptical properties of α-phenylacetic acids are similarly treated by Barth *et al.*,[27] and α-phenoxypropionic acids by Fredga *et al.*[29]

Surprising, at first sight, is the CD spectrum of *cis*-**8a**, which shows only very low positive CD at 223 nm and more intense, broad, negative CD band at 234 nm (Fig. 4), which resemble the spectrum of *cis*-**7a**. The strong interaction between *cis*-phenyl and t-butyl groups probably causes such orientation of aromatic ring, which diminishes interaction with lactone group, and spectra of **9a** and **7a** with aliphatic side chain become similar. The weak 223 nm band corresponds probably to the ^1L_a transition, whose low rotatory strength is in accordance with Richardson's prediction,[26] and negative 234 nm band corresponds to $n\rightarrow\pi^*$ lactone transitions. This

example points to interaction between phenyl and lactone chromophores, however CNDO/S–CI calculations,[23,26] and the author's CNDO/2–CI calculations show that the $n\rightarrow\pi^*$ transition is almost localized in the ester group.

EXPERIMENTAL

CD spectra were recorded on JASCO J–20 spectropolarimeter. NMR spectra were taken with Tesla BS–487 (80 MHz) spectrometer with TMS as internal standard. The CNDO/2–CI calculations have been performed for geometries of 1,3-dioxolan-4-one derived from X-ray data,[11] with standard parameterization of Pople *et al.*[30] The dihedral angle was assumed 20° and 18° for A and C conformations respectively.

1,3-Dioxolan-4-ones were obtained by refluxing of 1:1.2 molar mixture of corresponding α-hydroxy acids and carbonyl compounds (paraformaldehyde was used as source of CH_2O) respectively in benzene solution with catalytic amount of toluene-p-sulphonic acid for 1 h. Water was trapped with Dean–Stark apparatus. The reaction mixture was washed with aqueous $NaHCO_3$, dried (Na_2SO_4) and benzene was evaporated at reduced pressure. The residue was distilled. Column chromatography was performed on silicagel (MN-Kieselgel 60, 200 mesh, Macherey Nagel).

(5*S*)-5-*Methyl*-1,3-*dioxolan-4-one* (**1a**), bp 95–98°/120 Torr, (lit[31] bp 79.5°/27 Torr); $[\alpha]_D^{20}$ = + 44.2° (neat); NMR (δ, CCl_4): 5.35 (s, 1H) and 5.25 (s, 1H), 4.12 (q, 1H).

(5*S*)-2,2,5-*Trimethyl*-1,3-*dioxolan-4-one* (**1b**), bp 88–90°/65 Torr, $[\alpha]_D^{20}$ = + 34.9° (neat); NMR (δ, CCl_4): 4.28 (q, 1H), 1.19 (s, 3H) and 1.13 (s, 3H); (Found: C, 55.30; H, 7.75; $C_6H_{10}O_3$ requires: C, 55.37; H, 7.74).

(5*S*)-2,2-*Diethyl*-5-*methyl*-1,3-*dioxolan-4-one* (**1c**) bp 96–98°/22 Torr; $[\alpha]_D^{20}$ = + 19.9° (neat); (Found: C, 60.59; H, 8.95; $C_8H_{14}O_3$ requires: C, 60.74; H, 8.92).

(5*S*)-5-*Isopropyl*-1,3-*dioxolan-4-one* (**2a**) b.p. 98–100°/50 Torr, (lit[4] racemate b.p. 172.2–173.4/756 Torr); $[\alpha]_D^{20}$ = – 24.4° (neat); NMR (δ, CCl_4): 5.31 (s, 1H) and 5.23 (s, 1H), 3.83 (d, 1H).

(5*S*)-5-*Isopropyl*-2,2-*dimethyl*-1,3-*dioxolan-4-one* (**2b**), b.p. 82–84°/30 Torr; $[\alpha]_D^{20}$ = – 15.4° (neat); NMR (δ, CCl_4): 4.05 (d, 1H), 1.44 (s, 3H) and 1.38 (s, 3H); (Found: C, 60. 80; H, 9.01; $C_8H_{14}O_3$ requires: C, 60.74; H, 8.92).

(5*S*)-5-*Isobutyl*-1,3-*dioxolan-4-one* (**3a**), b.p. 87–89°/12 Torr (lit)[31] racemate b.p. 84.0–86.0°/9 Torr); $[\alpha]_D^{20}$ = – 15.2° (neat); NMR (δ, CCl_4): 5.35 (s, 1H) and 5.24 (s, 1H), 4.03 (m, 1H).

(5*S*)-5-*Isobutyl*-2,2-*dimethyl*-1,3-*dioxolan-4-one* (**3b**), b.p. 94–96°/12 Torr; $[\alpha]_D^{20}$ = – 9.9° (neat; NMR (δ, CCl_4): 4.15 (m, 1H), 1.41 (s, 3H) and 1.37 (s, 3H); (Found: C, 62.55; H, 9.40; $C_9H_{16}O_3$ requires: C, 62.77; H, 9.36).

(5*S*)-5-*Benzyl*-1,3-*dioxolan-4-one* (**4a**), b.p. 148°/12 Torr; $[\alpha]_D^{20}$ = – 86.8° (neat); NMR (δ, CCl_4): 7.02 (s, 5H), 5.01 (s, 1H) and 4.98 (s, 1H); 4.13 (m, 1H), 2.88 (m, 2H); (Found: C, 67.45; H, 5.61; $C_{10}H_{10}O_3$ requires: C, 67.41; H, 5.66).

(5*S*)-5-*Benzyl*-2,2-*dimethyl*-1,3-*dioxolan-4-one* (**4b**), b.p. 156–158°/12 Torr; m.p. 61–62° (from hexane); $[\alpha]_D^{20}$ = – 82° (c1, CCl_4) NMR (δ, CCl_4): 4.38 (m, 1H), 2.88 (m, 2H), 1.26 (s, 3H) and 1.11 (s, 3H); (Found: C, 73.91; H, 7.95, $C_{12}H_{14}O_2$ requires: C, 74.13; H, 7.92).

(5*S*)-5-*Phenyl*-1,3-*dioxolan-4-one* (**5a**), b.p. 141°/12 Torr (lit.[32] b.p. 143°/17 Torr; lit.[4] racemate b.p. 125°/2 Torr); $[\alpha]_D^{20}$ = + 57.0° (neat); NMR (δ, CCl_4): 7.09 (s, 5H); 5.28 (s, 1H) and 5.22 (s, 1H), 4.86 (s, 1H).

(5*S*)-5-*Phenyl*-2,2-*dimethyl*-1,3-*dioxolan-4-one* (**5b**), m.p. 71° $[\alpha]_D^{20}$ = + 41° (c2, CCl_4); NMR (δ, CCl_4): 7.26 (m, 5H), 5.16 (s, 1H), 1.49 (s, 1H) and 1.47 (s, 1H); (Found: C, 68.80; H, 6.07; $C_{11}H_{12}O_3$ requires: C, 68.74; H, 6.29).

(2*R*,5*S*)-2-*tert*-*butyl*-5-*methyl*-1,3-*dioxolan-4-one* (**6b**), from the mixture of diastereoisomers b.p. 85–88°/25 Torr obtained after condensation, *trans*-isomer **6b** was separated by cryatallizing at – 5°. The product was purified by two crystallizations from hexane at – 70°C; m.p. below 0°; $[\alpha]_D^{20}$ = +39.2° (neat); (Found: C, 60.92; H, 8.88; $C_8H_{14}O_3$ requires: C, 60.74; H, 8.92).

(2*S*,5*S*)- *and* (2*R*,5*S*)-2-*tert*-*Butyl*-5-*isopropyl*-1,3-*dioxolan-4-ones* (**7a**) and (**7b**), from the mixture of diastereoisomers b.p. 105–108°/20 Torr, *cis*- and *trans*-isomers are separated by column

chromatography. *Cis*-7a, $[\alpha]_D^{20} = -18.6°$ (neat); (Found: C, 64.20; H, 9.75; $C_{10}H_{18}O_3$ requires: C, 64.49; H, 9.74). Diastereoisomer *trans*-7b was additionally purified by crystallization from hexane at $-70°$, $[\alpha]_D^{20} = -3.1°$ (neat); (Found: C, 64.37; H, 9.65; $C_{10}H_{18}O_3$ requires: C, 64.49; H, 9.74).

(2S5S)- and (2R,5S)-2-*tert*-butyl-5-phenyl-1,3-dioxolan-4-ones (8a) and (8b), the condensation gives almost pure *trans*-8b diastereoisomer, which was purified by two crystallizations from hexane; m.p. 137–138°; $[\alpha]_D^{20} = -88°$ (c1, CHCl₃); (Found: C, 70.85; H, 7.37; $C_{13}H_{16}O_3$ requires: C, 70.89; H, 7.32). *Cis*-8a diastereoisomer was obtained from 8b by reflux for 4 h in toluene with catalytic amount of toluene-p-sulphonic acid. The reaction mixture was washed with aqueous NaHCO₃ and dried over Na₂SO₄. After evaporation, hexane was added and crystals of 8b was filtered. The filtrate was evaporated and chromatographed on silica gel. The liquid *cis*-8a has $[\alpha]_D^{20} = +3.9°$ (neat); (Found: C, 70.61; H, 7.33; $C_{13}H_{16}O_3$ requires: C, 70.89, H, 7.32).

(2S,5S)- and (2R,5S)-5-Phenyl-2-trichloromethyl-1,3-dioxolan-4-ones (9a) and (9b), from the mixture of diastereoisomers, purification by two further crystallizations from hexane has m.p. purification by further two crystallizations from hexane has mp 120–121°, $[\alpha]_D^{20} = +21°$ (c1, CHCl₃); (Found: C, 42.70; H, 2.40; $C_8H_7O_3Cl_3$ requires: C, 42.75; H, 2.41). *Trans*-9b was isolated by column chromatography on silicagel and after crystallization from hexane has m.p. 72°; $[\alpha]_D^{20} = +71°$ (c1, CHCl₃); (Found: C, 42.77; H, 2.41; $C_8H_7O_3Cl_3$ requires: C, 42.75; H, 2.41).

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