Exciton Chirality Method for Establishing Absolute Configuration of 2-Furylcarbinols

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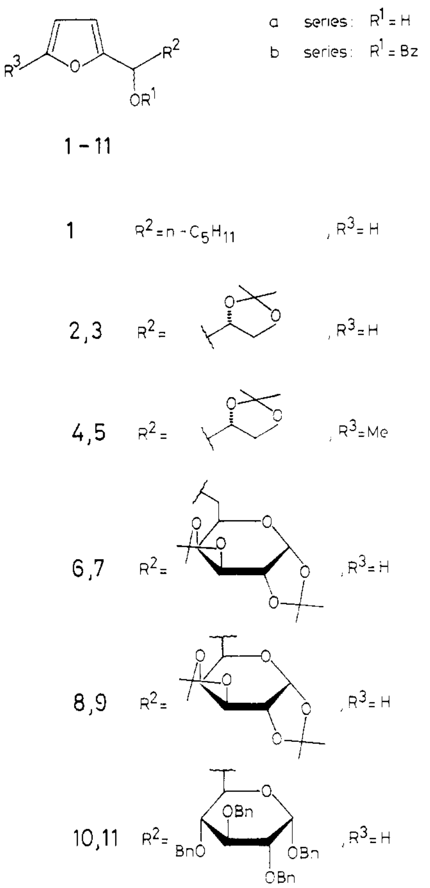
2-Furylcarbinols, versatile chiral building blocks in the synthesis of monosaccharides[1] and polyfunctionalized acyclic compounds, can be prepared in a number of methods. Currently employed ones involve acid- or base-promoted addition of furan to chiral aldehydes,[2,3] kinetic enzymatic[4] or chemical[5] resolution of racemic 2-furylcarbinols, asymmetric reduction of the corresponding 2-acylfurans catalyzed by an alcohol dehydrogenase,[4] aldol reaction of furfural derivatives with a chiral enolate,[6] and the use of chiral starting materials.[7] Despite the growing interest in the preparation and use of optically active 2-furylcarbinols, the methods for determining their absolute configuration are based either on measurement of optical rotation[8] or on chemical correlation with the corresponding α-hydroxy acid.[5]

We have developed a circular dichroic method for the unambiguous assignment of absolute configuration in 2-furylcarbinols. While 2-furylcarbinols display weak Cotton effects ($|\Delta\epsilon|$ ca. 1) in the region of furan chromophore absorption, i.e. below 215 nm,[9] thus discouraging the use of the CD method directly, their *O*-benzoyl derivatives show an enhanced, bisignate Cotton effect in the 230–215-nm range. Within the group of investigated 2-furylcarbinol benzoates of known absolute configuration (**1b**–**9b**), all of those having *R* configuration gave a negative CD band near 230 nm and a positive band between 215 and 220 nm. The opposite sign pattern occurred in 2-furylcarbinol benzoates with *S* configuration (Table I).

Since two Cotton effects are observed within the π-π^* absorption bands of the benzoate (near 228 nm) and 2-alkylfuran chromophore (215–220 nm), the origin of the bisignate 215–230-nm Cotton effect is primarily due to the exciton coupling of the electric transition moments of the two allowed transitions.[10,11] As shown in Figure 1, the electrical transition dipole moments involved in the coupling include that of the benzoate charge transfer π-π^* transition, polarized along the longitudinal benzoate C_2-axis[11] and that of the long-wavelength π-π^* transition in the furan ring,[12] polarized perpendicularly to the C_2-axis.[13]



Molecular mechanics calculations using the MMX routine[14] for the model benzoate **12** reveal several shallow local steric energy minima, the lowest one with the $\phi(1\text{-}2\text{-}6\text{-}7)$ dihedral angle +55° shown in Figure 1. For this conformer the chirality of the electric transition moments is negative ($\theta = -30°$). Other low-energy conformers of **12** with dihedral angles $\phi(1\text{-}2\text{-}6\text{-}7)$ of $-51°$ (relative steric energy 0.18 kcal/mol) and $-173°$ (relative steric energy 0.15 kcal/mol) also have a negative chirality of the electric transition moment system (θ respectively $-70°$ and $-85°$). These data support the rationalization of the experimentally found negative exciton Cotton effect of 2-furylcarbinol benzoates having the *R* configuration.

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[9] (*R*)-Furylalkyl carbinols having no other chiral centers show negative Cotton effect at around 210–215 nm. However, their rotations are positive (see also ref 8).

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[14] MMX^{FM}, Serena Software, P.O. Box 3076, Bloomington, IN; 30° dihedral drive applied to C(2)–C(6) bond rotation. θ is calculated as the angle between two vectors, one connecting C(1′) and C(4′) in the benzene ring and the other connecting midpoints of the furan C=C bonds.

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Table I. Chiroptical Data for O-Benzoylated 2-Furylcarbinols in Acetonitrile Solution

benzoate	config	CD Δε (nm)	UV ε (nm)
1b	*R*	−2.6 (231), +4.6 (215) −1.0 (260)	16200 (229) 1270 (273)
2b	*R*	−2.6 (229), +5.2 (215) −1.4 (253)	17700 (228) 980 (273)
3b	*S*	+4.5 (230), −5.5 (215) +0.6 (260)	18800 (229) 1400 (273)
4b	*R*	−1.0 (234), +4.7 (220) −0.5 (262), +0.6 (241)	18200 (224) 900 (270)
5b	*S*	+5.0 (235), −5.6 (219) +0.8 (265)	19200 (229) 1400 (270)
6b	*R*	−2.0 (229), +5.5 (216) −0.8 (262), +0.8 (241)	17000 (227) 1000 (273)
7b	*S*	+1.6 (231), −5.5 (217) +0.8 (260)	16200 (227) 970 (272)
8b	*R*	−12.6 (237), *a* +1.5 (263)	18000 (229) 1150 (270)
9b	*S*	+1.8 (233), −8.3 (217) +1.6 (253)	18100 (227) 1200 (270)
10b	*R*	−4.2 (228), ca. 0 (215–220) −1.5 (255)	18500 (227) 1600 (260)
11b	*S*	+7.0 (231), −4.0 (214) +0.8 (260)	18700 (227) 1500 (260)

[a] Short-wavelength exciton band covered by a negative Cotton effect at shorter wavelength.

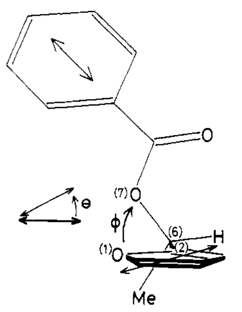

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Figure 1. Negative chirality of the benzoate–furan transition moments in the low-energy conformer of (*R*)-2-furylmethylcarbinol benzoate (12), $\phi(1\text{-}2\text{-}6\text{-}7) = +55°$.

To test the scope of the present CD method for establishing the absolute configuration of 2-furylcarbinols we have prepared the two diasteroisomeric carbinols **10a** and **11a**, having benzyl protecting groups in the D-glucopyranose ring. These compounds were obtained by oxidation of benzyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**13**) to aldehyde **14**, followed by chloroacetic acid catalyzed condensation of the latter with furan[2] (Scheme I).

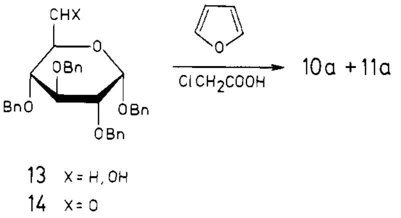
In order to remove the contribution of the benzyl chromophores to the CD spectrum of the benzoate derivatives **10b** and **11b**, we have subtracted the short-wavelength Cotton effect of **10a** (Δε −3.9 at 216 nm) from the Cotton effect of the benzoate **10b** (Table I). The resulting exciton Cotton effect of **10b**, −4.2 (228 nm) and +3.9 (216 nm), clearly indicates an *R* configuration in **10a**. Similar application of this procedure to **11a** (Δε +1.0 at 218 nm) and **11b** gives the exciton Cotton effect of **11b**: +7.0 (231 nm) and −4.5 (216 nm), thus establishing an *S* configuration for **11a**.

In summary, measurement of the CD spectrum of a 2-furylcarbinol benzoate provides a facile method for determining its absolute configuration, even where benzyloxy substituents are present.

Experimental Section

Melting points were determined on a hot stage microscope apparatus and are uncorrected. Optical rotations were measured with a Polamat polarimeter at 20 °C. CD and UV spectra were recorded in spectrograde acetonitrile on a Jobin-Yvon III dichrograph and on a Shimadzu UV 160 spectrophotometer, respectively. ^{1}H NMR spectra were obtained with a JEOL FX 90Q spectrometer in $CDCl_3$ solution, using TMS as an internal standard. Elemental analyses were performed on a Perkin-Elmer 240 CHN analyzer.

Scheme I



Benzyl 2,3,4-Tri-*O*-benzyl-6-*C*-(2-furyl)-α-D- and -L-glycero-D-glucopyranosides (10a and 11a). To a cooled (−40 °C) solution of oxalyl chloride (0.37 mL) in dichloromethane (10 mL) was slowly added a solution of dimetyl sulfoxide (0.7 mL) in CH_2Cl_2 (2 mL) followed by addition of benzyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**13**)[18] (2.0 g) in CH_2Cl_2 (5 mL). After 15 min of stirring triethylamine (2.6 mL) was added, and the mixture stirred for an additional 5 min. After attaining room temperature, water (25 mL) was added, and the product was extracted with chloroform. The extract was washed with 1 N hydrochloric acid and with water. After drying ($MgSO_4$) and concentration to dryness, the remaining syrup was purified by chromatography on silica gel with hexane–ethyl acetate (7:3) as eluent to yield aldehyde **14**, 1.6 g (80%).

To a solution of aldehyde **14** (1.35 g) in furan (5 mL) chloroacetic acid (650 mg) was added, and the solution was refluxed for 4 h.[2] The mixture was cooled, concentrated to dryness, dissolved in ether, and washed with saturated sodium bicarbonate solution. Drying ($MgSO_4$) and concentration to dryness left a product which was chromatographed on silica gel in toluene–ethyl acetate, 9:1.

Eluted first was **10a** (0.2 g, 13.6%): $[\alpha]_D$ +61° (*c* 1.8, $CHCl_3$); ^{1}H NMR (500 MHz), inter alia, δ 6.34, 6.30 (q and d, 2 H, furan H-4 and H-3), 4.95 (d, 1 H, $J_{5,6}$ = 5.1 Hz, H-6), 4.82 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1), 4.15 (dd, 1 H, $J_{5,4}$ = 9.9 Hz, H-5), 4.11 (t, 1 H, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.1 Hz, H-3), 3.49 (dd, 1 H, H-2), 3.45 (dd, 1 H, H-4).

Eluted second was **11a** (0.33 g, 22.5%): $[\alpha]_D$ +55° (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz), inter alia, δ 6.37, 6.33 (q and dt, 2 H, furan H-4 and H-3), 5.01 (d, 1 H, $J_{6,5}$ = 1.2 Hz, H-6), 4.72 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 4.10 (t, 1 H, $J_{3,4}$ = 9.3 Hz, H-3), 4.08 (dd, 1 H, $J_{5,4}$ = 9.9 Hz, H-5), 3.76 (dd, 1 H, H-4), 3.51 (dd, 1 H, $J_{2,3}$ = 9.6 Hz, H-2). Anal. Calcd for $C_{38}H_{38}O_7{\cdot}H_2O$: C, 73.06; H, 6.45. Found: C, 73.37; H, 6.00.

Preparation of Benzoates 1b–11b. Benzoyl derivatives **1b**–**11b** were prepared from the corresponding 2-furylcarbinols **1a**,[15] **2a**,[16] **3a**,[16] **4a**,[3] **5a**,[3] **6a**,[17] **7a**,[17] **8a**,[2] **9a**,[2] **10a**, and **11a** by the standard benzoylation procedure (0.5 mmol of carbinol, 5 mg of 4-(dimethylamino)pyridine, and 0.09 mL, i.e. 0.75 mmol, of benzoyl chloride in 0.5 mL of pyridine overnight at room temperature) followed by treatment with aqueous acetone (3 h) and standard workup. The benzoates (crude yield in excess 90%) were purified by short-column chromatography on silica gel (eluent 1:1 hexane–dichloromethane).

1b: oil; $[\alpha]_D$ +69° (*c* 1.4, $CHCl_3$); ^{1}H NMR δ 8.0–8.1 (m, 2 H), 7.3–7.7 (m, 4 H), 6.35 (m, 2 H), 6.09 (t, 1 H, *J* = 7 Hz), 2.04 (m, 2 H), 1.35 (m, 6 H), 0.87 (t, 3 H, *J* = 6 Hz). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.71; H, 7.63.

2b: mp 68–71 °C; $[\alpha]_D$ +82° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 8.0–8.2 (m, 2 H), 7.4–7.7 (m, 4 H), 6.42 (d, 1 H, *J* = 3 Hz), 6.32 (dd, 1 H, *J* = 2, 3 Hz), 6.20 (d, 1 H, *J* = 6 Hz), 4.63 (dt, 1 H, *J* = 6 Hz),

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(15) We thank Prof. F. Sato for a sample of the carbinol **1a** (ref 5).

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4.20 (d, 2 H, J = 6 Hz), 1.37 (s, 6 H). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.41; H, 6.05.

3b: syrup; $[\alpha]_D$ −50.5° (*c* 1.6, $CHCl_3$); ^{1}H NMR δ 8.0–8.2 (m, 2 H), 7.4–7.8 (m, 4 H), 6.48 (d, 1 H, J = 3 Hz), 6.34 (dd, 1 H, J = 2, 3 Hz), 6.13 (d, 1 H, J = 8 Hz), 4.75 (dt, 1 H, J = 6, 8 Hz), 4.02 (dd, 1 H, J = 6, 9 Hz), 3.78 (dd, 1 H, J = 6, 9 Hz), 1.43 (s, 3 H), 1.38 (s, 3 H). Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.21; H, 5.88.

4b: oil; $[\alpha]_D$ +90.6° (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 8.0–8.2 (m, 2 H), 7.3–7.8 (m, 3 H), 6.34 (d, 1 H, J = 3 Hz), 6.17 (d, 1 H, J = 5.5 Hz), 5.93 (dd, 1 H, J = 1, 3 Hz), 4.60 (dt, 1 H, J = 5.5, 6 Hz), 4.23 (d, 2 H, J = 6 Hz), 2.27 (s, 3 H), 1.37 (s, 6 H). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.01; H, 6.17.

5b: oil; $[\alpha]_D$ −50.4° (*c* 1.5, $CHCl_3$); ^{1}H NMR δ 8.0–8.2 (m, 2 H), 7.4–7.7 (m, 3 H), 6.35 (d, 1 H, J = 3 Hz), 6.05 (d, 1 H, J = 8 Hz), 5.92 (dd, 1 H, J = 1, 3 Hz), 4.72 (ddd, 1 H, J = 6, 8 Hz), 4.01 (dd, 1 H, J = 6, 9 Hz), 3.77 (dd, 1 H, J = 6, 9 Hz), 2.33, 1.44 and 1.38 (3 s, 9 H). Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.24; H, 6.11.

6b: syrup; $[\alpha]_D$ +3.0° (*c* 2.1, $CHCl_3$); ^{1}H NMR δ 8.0–8.1 (m, 2 H), 7.3–7.6 (m, 4 H), 6.25–6.45 (m, 3 H), 5.51 (d, 1 H, J = 5 Hz), 4.58 (dd, 1 H, J = 2.5, 8 Hz), 3.8–4.3 (m, 3 H), 2.3–2.5 (m, 2 H), 1.45, 1.35, 1.20, and 0.99 (4 s, 12 H). Anal. Calcd for $C_{24}H_{28}O_8$: C, 64.85; H, 6.35. Found: C, 64.54; H, 6.08.

7b: syrup; $[\alpha]_D$ −114.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 8.0–8.1 (m, 2 H), 7.3–7.6 (m, 4 H), 6.50 (d, 1 H, J = 3 Hz), 6.33 (dd, 1 H, J = 2, 3 Hz), 6.25 (t, 1 H, J = 7 Hz), 5.50 (d, 1 H, J = 5 Hz), 4.56 (dd, 1 H, J = 2, 8 Hz), 4.1–4.3 (m, 2 H), 3.64 (dt, 1 H, J = 2, 7 Hz), 2.45 (t, 2 H, J = 7 Hz), 1.46, 1.33, 1.26, and 1.16 (4 s, 12 H). Anal. Calcd for $C_{24}H_{28}O_8$: C, 64.85; H, 6.35. Found: C, 64.65; H, 6.30.

8b: mp 206–9 °C; $[\alpha]_D$ −140.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 7.9–8.1 (m, 2 H), 7.3–7.5 (m, 4 H), 6.54 (s, 2 H), 6.18 (d, 1 H, J = 9 Hz), 5.43 (d, 1 H, J = 5 Hz), 4.2–4.7 (m, 4 H), 1.63, 1.43, 1.28, and 1.25 (4 s, 12 H). Anal. Calcd for $C_{23}H_{26}O_8$: C, 64.18; H, 6.09. Found: C, 63.83; H, 5.98.

9b: syrup; $[\alpha]_D$ −87.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 8.0–8.1 (m, 2 H), 7.3–7.5 (m, 4 H), 6.57 (d, 1 H, J = 3 Hz), 6.34 (dd, 1 H, J = 2, 3 Hz), 6.18 (d, 1 H, J = 9 Hz), 5.49 (d, 1 H, J = 5 Hz), 4.3–4.8 (m, 4 H), 1.65, 1.48, 1.34, and 1.27 (4 s, 12 H). Anal. Calcd for $C_{23}H_{26}O_8$: C, 64.18; H, 6.09. Found: C, 63.92; H, 6.10.

10b: syrup; $[\alpha]_D$ +45.7° (*c* 1.9, $CHCl_3$); ^{1}H NMR δ 8.0–8.2 (m, 2 H), 7.1–7.6 (m, 25 H), 6.57 (d, 1 H, J = 2 Hz), 6.38 (m, 2 H), 4.1–5.0 (m, 10 H), 3.5–3.7 (m, 2 H). Anal. Calcd for $C_{45}H_{42}O_8$: C, 76.04; H, 5.96. Found: C, 75.75; H, 5.88.

11b: syrup, $[\alpha]_D$ +41.8° (*c* 2.1, $CHCl_3$), ^{1}H NMR δ 8.0–8.2 (m, 2 H), 7.1–7.6 (m, 25 H), 6.56 (d, 1 H, J = 3 Hz), 6.42 (d, 1 H, J = 3 Hz), 6.32 (dd, 1 H, J = 2, 3 Hz), 4.0–5.0 (m, 10 H), 3.4–3.6 (m, 2 H). Anal. Calcd for $C_{45}H_{42}O_8$: C, 76.04; H, 5.96. Found: C, 75.91; H, 5.68.

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Ozonolysis of 1,1-Dimethoxyethene, 1,2-Dimethoxyethene, and Vinyl Acetate

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Recent studies of the ozonolyses of methyl vinyl ether[1] and 1-ethoxypropene,[2] which have one alkoxy group at the double bond, have shown that 3-alkoxy-1,2-dioxolanes can be obtained in appreciable yields, along with lesser amounts of 3-alkoxy-1,2,4-trioxolanes (ozonides). These results can be rationalized by a Criegee-like mechanism[3] whereby a carbonyl oxide (CH_2OO) combines either with unreacted alkene or the cogenerated ester (Scheme I). An intramolecular cycloaddition of a carbonyl oxide to a remote ester to give a bicyclic alkoxy ozonide has also been reported.[4] On the other hand, ozonolyses of (Z)-dimethoxystilbene and tetramethoxyethene[5] gave no evidence for the carbonyl oxide intermediate. Neither dioxolanes nor trioxolanes were observed and the alkenes behaved anomalously. This contrast leads us to report on the ozonolyses of several simple alkenes containing two alkoxy substituents at the double bond. We also reexamined the ozonolysis of vinyl acetate, which was reported to produce neither dioxolanes nor trioxolanes[6] in the absence of any trapping agent and obtained different results.

Scheme I

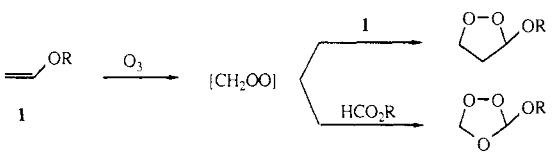

Table I. Ozonolysis of (*E*)- and (*Z*)-1,2-Dimethoxyethene in Various Solvents

alkene	solvent	T (°C)	product	% yield	(cis/trans)
Z	$CDCl_3$	−41	**1, 2**	16	(55/45)
Z	$CDCl_3$	0	**1, 2**	13	(54/46)
Z	MeOH	−41	**6**	72	
E	MeOH	−45	**6**	73	
Z	CH_3CHO/C_5H_{12}	−41	**4, 5**	58	(44/56)
E	CH_3CHO/C_5H_{12}	−41	**4, 5**	56	(45/55)
Z	$(CH_3)_2CHCHO/CDCl_3$	0	**7, 8**	93	(53/47)
Z	$(CH_3)_3CCHO/C_5H_{12}$	−41	**10, 11**	59	(53/47)
E	$(CH_3)_3CCHO/C_5H_{12}$	−41	**10, 11**	69	(48/52)
Z	$(CH_3)_2CO/C_5H_{12}$	0	**9**	10	
Z	CH_3OCHO	−41	**12**	0	

Results and Discussion

A preliminary report of the ozonolysis of (Z)-1,2-dimethoxyethene indicated that small amounts of *cis*- and *trans*-3,6-dimethoxy-1,2,4,5-tetroxane (**1**, **2**) were obtained.[7] These ozonolyses were repeated in reactive solvents as well as in $CDCl_3$ to establish the reaction pathway more clearly. In $CDCl_3$, the average yields of tetroxane and methyl formate were about 15% and 90%, respectively. No dioxolane or trioxolanes could be identified. A soluble peroxidic polymer evidenced by a broad NMR signal around 6.0 ppm was also produced but could not be further characterized. In reactive solvents (Table I), the expected products from trapping a methoxy-substituted carbonyl oxide (CH_3OCHOO) were obtained in appreciable yields. The trapping reactions exhibited little stereospecificity for either alkene configuration. The results are consistent with a Criegee reaction pathway. The ozonolysis leads to the

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