

The sensitivity and ruggedness of chiroptical detectors have improved considerably during the past decade. In this article, the authors examine more than 230 chiral compounds using the latest laser-based polarimetry detector for high performance liquid chromatography (HPLC). They also examine the relationship between optical rotation at the detector wavelength of 675 nm and the sodium D line. In addition, the authors consider the sensitivity, linear dynamic range, and effect of solvent composition on rotation and its general use as an HPLC detector for chiral compounds.

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HPLC Detection and Evaluation of Chiral Compounds with a Laser-Based Chiroptical Detector

he high performance liquid chromatography (HPLC) separation of enantiomers has developed into a mature field used in many branches of science and technology (1-3). Its great success has spurred development in a variety of other areas, including in detectors for optically active or chiral compounds. Chiroptical detectors are based on optical rotation (polarimetry) or circular dichroism. Since 1980 several research groups have adopted various forms of micropolarimetry (4–14) and circular dichroism (15–24) into HPLC detector formats. Researchers have published a few reviews on chiroptical detection and the general analytical use of polarimetry and circular dichroism (25-28).

Over the past 10 years, a few commercial versions of these detectors have appeared. During the course of our research we had the opportunity to use or evaluate many of these detectors. Using chiroptical detectors provides both advantages and disadvantages. Some of the beneficial aspects are listed in the accompanying sidebar, "Uses and Beneficial Aspects of Chiroptic Detection." Of these, the most important benefits seem to be the validation of enantiomeric separations and quality control applications. Also, because only chiral compounds are detected, a chromatogram can be simplified greatly. The elimination of interfering peaks from nonchiral compounds allows analysts to focus on the chiral analytes of interest.

Far and away, the major disadvantage of all chiroptical detectors has been their poor sensitivity. Baseline drift and occasional artifact peaks often were related problems. The earliest chiroptical detectors also had difficulties with the instability of seals and other instrumental parts in the presence of certain solvents. Indeed, we considered the earliest chiroptical detectors to be two to three orders of magnitude less sensitive than necessary for most routine analytical separations. This sensitivity left a lot of room for improvement. Most of the advances in commercial chiroptical detectors during the past decade focused on increasing their sensitivity and ruggedness. These improvements have come from using better light sources that provide higher power and greater stability, better optics, and electronic systems optimized to reduce noise.

In this article we examine one of the latest chiroptical detectors. In addition to the usually reported parameters considered in studies involving these detectors, we evaluated its use and sensitivity for a very wide variety of chiral compounds; the relationship, if any, between optical rotation at 675 nm and that of the sodium D line at 589.3 nm; the linear dynamic range of this chiroptical detector; and the effect of different solvents on the relative response of this detector.

EXPERIMENTAL

Materials: We obtained all HPLC columns from Advanced Separation Technologies, Inc. (Whippany, New Jersey). The liquid chromatography (LC) columns we used included 25 cm \times 4.6 mm native β -cyclodextrin Cyclobond I 2000, 25 cm \times 4.6 mm 2-hydroxypropyl- β cyclodextrin Cyclobond I 2000 RSP, and 5 cm \times 4.6 mm, 5- μ m d_p C18 columns. We purchased methanol, acetonitrile, glacial acetic

USES AND BENEFICIAL ASPECTS OF CHIROPTIC DETECTION

- Validation of enantioseparations
- Quality control applications
- Reasonable sensitivity for chiral compounds that lack a UV chromophore; for example, carbohydrates and certain amino acids
- Determining enantiomeric excess without separation, at moderate levels only
- Monitoring conformation of chiral polymers
- Selectivity for chiral analytes simplifies chromatograms by not detecting nonchiral compounds
- Follow or assess racemization
- Demonstrating that an asymmetric synthetic transformation has occurred

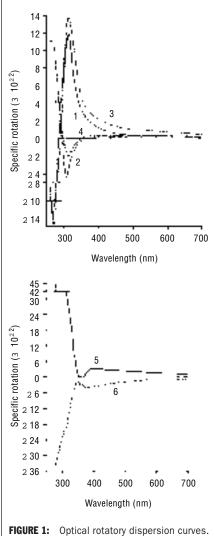
TABLE I: Alphabetical Listing of Chiral Compounds Detected After Reversed-Phase HPLC and Their Measured Relative Response Optical Rotations, Specific Rotations at 675 nm*, and Specific Rotations at the Sodium D Line†

Compound	Relative Response‡	$[\alpha]_{675}^{22}$ (degrees)	Published $[\alpha]_D^{20}$ Value (degrees)	Solvent Used to Obtain Published Value
Compound	iicopolioc ₊	(ucgrocs)	value (degrees)	
(1 <i>R</i> ,4 <i>S</i>)- <i>cis</i> -4-Acetoxy-2-cyclopenten-1-ol (1 <i>S</i> ,4 <i>R</i>)- <i>cis</i> -4-Acetoxy-2-cyclopenten-1-ol	-12.36 12.59	-59.4 63.5	-67 68	Chloroform Chloroform
(R)-(-)-O-Acetylmandelic acid	-22.14	-115.6	-147.5	Acetone
(S)-(+)-O-Acetylmandelic acid	21.80	105.3	147.5 ¹⁹	Acetone
N-(4-Aminobenzoyl)-L-glutamic acid diethyl ester	5.45	28.5	17.9 ²¹	Chloroform
(S)-(+)-2-Amino-1-butanol	2.09	8.9	10 20.4	Neat 5 N Hydrochloric acid
$L - \alpha$ -Amino- <i>n</i> -butyric acid $D - \alpha$ -Amino- <i>n</i> -butyric acid	1.83§ -1.94§	9.76§ -10.57§	-7.94	Water
(S)-2-Amino-4-butyrolactone hydrobromide	-10.34	-50.9	-21	Water
(1 <i>S</i> ,2 <i>R</i>)-(+)-2-Amino-1,2-diphenylethanol	2.85	16.4	7	Ethanol
(1 <i>R</i> ,2 <i>S</i>)-(-)-2-Amino-1,2-diphenylethanol	-2.89	-14.5	-7	Ethanol
(1R,2S)-(+)-2-Amino-1-phenyl-1,3-propanediol (R)-(+)-2-Amino-3-phenyl-1-propanol	4.09 4.30	24.4 15.1	28 23	Methanol 1 N Hydrochloric acid
(S)-(-)-2-Amino-3-phenyl-1-propanol	-4.64	-16.6	-22.822	1 N Hydrochloric acid
(R)-(-)-1-Amino-2-propanol	-8.63	-38.4	-23.5	Methanol
(S)-(+)-1-Amino-2-propanol	8.78	39.5	23.5	Methanol
(R)-(+)-3-Aminoquinuclidine dihydrochloride (S)-(-)-3-Aminoquinuclidine dihydrochloride	9.28 9.31	43.1 42.5	24 24	Water Water
1,6-Anhydro-3,4- <i>O</i> -isopropylindene-2-tosyl-D-galactose	-14.05	-42.5	-24 -60^{23}	Chloroform
(R)-(-)-1-(9-Anthryl)-2,2,2-trifluoroethanol	-7.95	-39.2	-25.5	Chloroform
(S)-(+)-1-(9-Anthryl)-2,2,2-trifluoroethanol	7.77	42.5	25.5	Chloroform
L-Arginine	3.30b	16.7	26.1	6 N Hydrochloric acid
D-Asparagine monohydrate (1R)-(-)-2-Azabicyclo[2.2.1]hept-5-en-3-one	-2.15§ -125.74	-10.12§ -629.7	-27 -565	1 N Hydrochloric acid Chloroform
(1S)-(+)-2-Azabicyclo[2.2.1]hept-5-en-3-one	126.44	634.8	565	Chloroform
(S)-(-)-2-Azetidine carboxylic acid	-31.14§	-152.9§	-120	Water
(S)-(+)-Benzoin	41.96	235.6	115 ¹⁹	Acetone
(S)-(+)-Benzoyl-2-tert-butyl-3-methyl-4-imidazolidinone	27.17	133.1	125 ²⁶	Methylene chloride
(R)-(+)-4-Benzyl-5,5-dimethyl-2-oxazolidinone (S)-(-)-4-Benzyl-5,5-dimethyl-2-oxazolidinone	31.94 	128.1 	96 98 ²²	Chloroform Chloroform
Benzyl (R)-(-)-glycidyl ether	-3.10	-15.2	-54	Toluene
(+)-2,3-o-Benzylidene-D-threitol	3.32	15.2	11 ¹⁸	Methanol
(-)-2,3-o-Benzylidene-L-threitol	-3.41	-14.6	-10.5	Methanol
N-Benzyl-α-methylbenzylamine	-6.74	-32.4	-40 ¹⁹	Neat Methanol
(S)-(+)-N-Benzyl-1-(1-naphthyl)-ethylamine hydrochloride (R)-(-)-N-Benzyl-1-(1-naphthyl)-ethylamine hydrochloride	8.17 	59.1 	61 61	Methanol
(R)-(+)-4-Benzyl-2-oxazolidinone	4.02	24.5	64 ¹⁸	Chloroform
(S)-(-)-4-Benzyl-2-oxazolidinone	-3.91	-23.4	-63	Chloroform
(R)-(+)-3-(Benzyloxycarbonyl)-4-oxazolidine carboxylic acid		101.5	92	Chloroform
(R)-(-)-Benzyloxy-3-(p-tosyloxy)-2-propanol (S)-(+)-Benzyloxy-3-(p-tosyloxy)-2-propanol	-2.88 2.87	-14.5 11.6	-7 7	Toluene Toluene
(R)-(-)-4-Benzyl-3-propionyl-2-oxazolidinone	-34.50	-179.0	-102	Ethanol
(S)-(+)-4-Benzyl-3-propionyl-2-oxazolidinone	33.54	177.6	97	Ethanol
(R)-(+)-1,1'-Bi-2-naphthol	5.03	30.2	34 ²¹	Tetrahydrofuran
(S)- $(-)$ -1,1'-Bi-2-naphthol	-4.93	-30.5	-34 ²² -146 ²³	Tetrahydrofuran
 (R)-(-)-1,1'-Bi-2-naphthol bis(trifluoromethanesulfonate) (S)-(+)-1,1'-Bi-2-naphthol bis(trifluoromethanesulfonate) 	-34.87 34.53	-176.5 174.5	- 146 148 ²¹	Chloroform Chloroform
(R)- $(-)$ -Binaphthyl-2,2'-diyl hydrogen phosphate	-138.25	-622.1	-607.1 ¹⁹	Methanol
(S)-(+)-Binaphthyl-2,2'-diyl hydrogen phosphate	139.22	626.5	595 ²²	Methanol
2,6-Bis[(4R)-(+)-isopropyl-2-oxazolin-2-yl]pyridine	31.68	163.4	118	Methylene chloride
2,6-Bis[(4S)-(-)-isopropyl-2-oxazolin-2-yl]pyridine {Bis-[(2S,3aR,4S,7aR)-octahydro-7,8,8-trimethyl-4,7- methanabaarafusan 2, yl] athar	-31.89 -43.49	-156.1	-118 ²⁵	Methylene chloride Tetrahydrofuran
methanobenzofuran-2-yl]-ether} [(1 <i>S</i>)- <i>endo</i>]-(-)-Borneol	-43.49 -9.05	-229.6 -45.0	-202	Ethanol
(+)-Borneol	9.75	48.9	36	Ethanol
(2R,3R)-3-(4-Bromophenyl)-glycidol	11.09	51.1	33	Chloroform
(2 <i>S</i> ,3 <i>S</i>)-(+)-2,3-Butanediol	2.14	10.2	13	Neat
(2 <i>R</i> ,3 <i>R</i>)-(-)-2,3-Butanediol (<i>R</i>)-(+)-1,2,4-Butanetriol	-2.07 8.78	-9.2 42.5	-13.2 ²³ 26	Neat Methanol
(S) - (-) - 1, 2, 4-Butanetriol	-9.70	-47.6	-27 ¹⁹	Methanol
(R)-(-)-2-Butanol	-11.28	-58.7	-12.6 ²²	Neat
tert-Butyl-(R)-(+)-lactate	2.82	13.1	7.3	Methylene chloride
(+)-Camphor	10.29	53.9	44.1 ²⁵	Ethanol
(-)-Camphor (1 <i>S</i> ,3 <i>R</i>)-(-)-Camphoric acid	-10.32 -13.18	-52.1 -67.2	-30.7 -48	Methanol Ethanol
(18,57)-(-)-Camphorquinone	-20.49	-94.4	-101	Toluene
(1R)-(+)-2,10-Camphorsultam	7.73	54.3	32	Chloroform
(1S)-(-)-2,10-Camphorsultam	-8.08	-49.0	-32 ¹⁹	Chloroform
(1 <i>S</i>)-(+)-3-Carene	6.05	29.5	17	Neat
D-Carnitine (R)-()-Carvone	4.24 	22.8 -80.4	30.9 61	Water Neat
(<i>S</i>)-(+)-Carvone	16.66	80.6	61	Neat
(+)-β-Cedrene	4.28	21.6	13	Neat
(R)-(+)-4-Chloro-3-hydroxybutyronitrile	5.52	31.2	11 ²⁵	Neat
(S)-(-)-4-Chloro-3-hydroxybutyronitrile	-5.37	-25.2	-8^{25} 36^{23}	Neat
Cholic acid (+)-β-Citronellene	10.15 11.16	50.2 54.0	36	95% Ethanol Neat
(S) - $(-)$ - β -Citronellol	-1.26	-6.3	-5.3	Neat
(1R,2R)-trans-1,2-Cyclopentanediol	-8.43	-41.7	-21	Chloroform
(1 <i>S</i> ,2 <i>S</i>)- <i>trans</i> -1,2-Cyclopentanediol	8.22	45.8	19	Chloroform
(1R,3S)-(+)-4-Cyclopentane-1,3-diol-1-acetate	13.03	67.3	68	Chloroform Water
3,4-Dehydro-2-proline (R)-(+)-1,2-Diaminopropane dihydrochloride	-79.31 8.42	-375.1 46.2	-385 4	Water Water
(S) - (-) - 1,2-Diaminopropane dihydrochloride	-8.51	-40.2	-4	Water
(-)-2,3-Dibenzoyl-L-tartaric acid	-24.32	-109.5	-116	Ethanol
(+)-2,3-Dibenzoyl-D-tartaric acid	24.31	109.4	116 ²⁸	Ethanol

* All samples were measured in a methanol mobile phase (unless mentioned otherwise) at a concentration of 3 mg/mL, and with 1 μ L of solution injected onto the reversed-phase HPLC column. † All values of $[\alpha]_{D}^{20}$ were obtained from references 30 and 31.

‡ Relative responses of peak area of the chiral detector at 675 nm compared with L-valine.

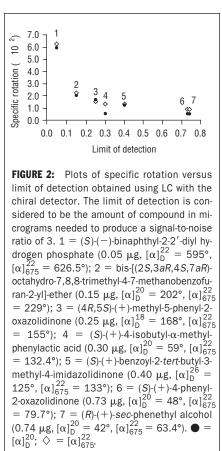
§ Responses measured in water.



1 = B-norcholestan-3-one in methanol, 2 = Bnorcoprostan-3-one in methanol, 3 = trans-8methylhydrindan-5-one in methanol, 4 = cis-8-methylhydrindan-5-one in dioxane, 5 = (5*S*,10*S*)-5-hydroxy-10-methyl- $\Delta^{1(9)}$ -2-octalone in dioxane, 6 = (5S, 10R)-5-hydroxy-10-methyl- $\Delta^{\rm 1(9)}\mbox{-}2\mbox{-}octalone$ in dioxane. (Reproduced with permission from reference 33.)

acid, and triethylamine from Fisher Scientific (St. Louis, Missouri). All chiral compounds were purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin); Sigma Chemical Co. (St. Louis, Missouri); and Fluka Chemical Corp. (Ronkonkoma, New York).

Apparatus: We performed LC separations using a LC-6A pump, a CR601 Chromatopac integrator, a SPD-2AM spectrophotometric detector, and a RID-10A refractive index detector (all from Shimadzu Scientific Instruments, Columbia, Maryland) and an Advanced laser polarimeter (PDR-Chiral, Inc., Palm Beach Gardens, Florida). The specifications for this laser-based polarimeter-chiral detector indicate that it routinely provides sensitivity levels of less than 25×10^{-6} ° using a 675-nm diode laser, a new modulation scheme, and window materials that enable performance independent



of operating pressure, solvent composition, or flow rate (29).

The UV detection wavelength was set at 190 nm for cyclodextrins and sugars or 254 nm for the enantiomeric separations of aromatic compounds. The LC chromatograms for all chiral compounds were obtained by using two LC-10AT pumps, a SIL-10A autoinjector, a SLC-10A system controller, and a CR501 Chromatogram of the chiral detector (PDR-Chiral). All chromatograms were obtained at ambient temperature (22 °C). Table I lists the experimental conditions for more than 200 commercially available chiral compounds (30,31).

Specific rotation measurements: We calculated each compound's specific rotation at 675 nm using chromatographic peaks generated with the chiral detector and equation 1, outlined by Bobbitt and co-workers (32) as

$$\left[a\right] 5 \frac{v a}{lm F_{G}}$$
[1]

where $[\alpha]$ is the specific rotation in degrees, v is the detector flow cell volume in milliliters, α is the observed rotation in degrees, l is the detector path length in decimeters, m is the injected mass in grams, and F_G is the Gaussian fraction (that is, the fraction of injected mass present in the flow cell [32]).

The chiral detector's flow cell volume and path length are 56 μ L and 5.17 cm, respectively.

TABLE I: Continued

Compound	Relative Response‡	[α] ²² 675 (degrees)	Published $\left[\alpha ight]_{D}^{20}$ Value (degrees)	Solvent Used to Obtain Published Value		
(-)-N,N'-Dibenzyl-p-tartramide	-22.73	-109.3	-83	Pyridine		
(+)-N,N'-Dibenzyl-D-tartramide	24.27	117.9	83	Pyridine		
(-)-3,9-Dibromocamphor	-20.33	-106.0	-100 ¹⁹	Chloroform		
(+)-3,9-Dibromocamphor	20.56	110.2	100 ¹⁹	Chloroform		
(1R,2S)-(+)-2-(Dibutylamino)-1-phenyl-1-propanol	3.01	14.7	21	Chloroform		
(-)-10-Dicyclohexylsulfamoyl-D-isoborneol	-6.39	-30.1	-25	Ethanol		
(+)-10-Dicyclohexylsulfamoyl-L-isoborneol	5.92	33.9	25	Ethanol		
(3 <i>R</i> - <i>cis</i>)-(-)-2,3-Dihydro-3-isopropyl-7 <i>a</i> -methylpyrrolo- [2,1-B]oxazol-5(7 <i>aH</i>)-one	18.59	94.9	41	Chloroform		
(3 <i>S</i> - <i>cis</i>)-(+)-2,3-Dihydro-3-isopropyl-7 <i>a</i> -methylpyrrolo-	10.39	54.5	41	Childroidhin		
[2,1-β]oxazol-5(7 <i>aH</i>)-one	-18.44	-89.4	-3722	Chloroform		
(3 <i>S</i> - <i>cis</i>)-(+)-2,3-Dihydro-7 <i>a</i> -methyl-3-phenylpyrrolo-	10.44	03.4	51	Childroidhin		
[2,1-β]oxazol-5(7 <i>aH</i>)-one	38.10	195.8	124	Chloroform		
(3 <i>R-cis</i>)-(-)-2,3-Dihydro-7 <i>a</i> -methyl-3-phenylpyrrolo-	00.10	155.0	124	Gilloroform		
$[2,1-\beta]$ oxazol-5(7 <i>aH</i>)-one	-39.67	-199.9	-124	Chloroform		
Diisopropyl-p-tartrate	-5.98	-23.0	-17^{23}	Neat		
Diisopropyl-L-tartrate	5.81	24.1	17 ²⁴	Neat		
(1S)-(+)-Dimenthyl succinate	24.81	125.1	89	Chloroform		
(1R)-(-)-Dimenthyl succinate	-24.59	-131.6	-89	Chloroform		
(+)-trans-α,α'-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)-						
bis(diphenylmethanol)	17.23	90.6	67 ¹⁹	Chloroform		
(-)-trans-α,α'-(2,2-Dimethyl-1,3-dioxolane-4,5-diyl)bis-	-	-				
(diphenylmethanol)	-17.37	-86.4	-62.6^{19}	Chloroform		
(R)-(-)-2,2-Dimethyl-1,3-dioxolane-4-methanol	-3.75	-17.6	-13.7	Neat		
(+)-Dimethyl-2,3- <i>o</i> -isopropylidene-D-tartrate	18.79	81.7	55	Neat		
(−)-Dimethyl-2,3- <i>o</i> -isopropylidene-L-tartrate	-18.92	-82.5	-54	Neat		
(1 R, exo, exo)-3-[N-(3,5-Dimethylphenyl)-benzene-						
sulfonamido]-isoborneol	10.59	77.4	65	Chloroform		
(4S,5R)-(+)-1,5-Dimethyl-4-phenyl-2-imidazolidinone	16.58	81.7	45	Methanol		
(4R,5S)-(-)-1,5-Dimethyl-4-phenyl-2-imidazolidinone	-16.43	-74.6	-42	Methanol		
(S)-(+)-N,S-Dimethyl-S-phenylsulfoximine	37.92	187.9	140 ²⁴	Methanol		
(R)-(-)-N,S-Dimethyl-S-phenylsulfoximine	-37.63	-182.3	-140^{24}	Methanol		
(7S)-(-)-10,10-Dimethyl-5-thia-4-azatricyclo[5.2.1.0]-						
dec-3-ene-5,5-dioxide	-9.86	-46.4	-34	Chloroform		
(7R)-(+)-10,10-Dimethyl-5-thia-4-azatricyclo[5.2.1.0]-						
dec-3-ene-5,5-dioxide	9.75	52.1	34	Chloroform		
№-(3,5-DinitrobenzoyI)-L-leucine	-3.28	-17.3	-14.3	Ethanol		
(R)-(-)-N-(3,5-Dinitrobenzoyl)-α-methylbenzylamine	-7.95	-37.3	-46 ¹⁸	Acetone		
(S)-(+)-N-(3,5-Dinitrobenzoyl)-α-methylbenzylamine	6.27	36.2	46.2	Acetone		
(R)-(-)-N-(3,5-Dinitrobenzoyl)-α-phenylglycine	-18.86	-94.3	-98.1 ¹⁹	Tetrahydrofuran		
(4R,5R)-(+)-cis-4,5-Diphenyl-2-oxazolidinone	17.69	88.2	56 ²²	Chloroform		
(4S,5R)-(-)-cis-4,5-Diphenyl-2-oxazolidinone	-17.09	-86.4	-56^{22}	Chloroform		
(+)-(S)-1-[(R)-2-(Diphenylphosphino)ferrocenyl]ethyl						
methyl ether	65.89	335.4	337	Chloroform		
(-)-(R)-1-[(R)-2-(Diphenylphosphino)ferrocenyl]ethyl						
methyl ether	-64.78	-331.0	-337	Chloroform		
(1 <i>S</i> ,2 <i>R</i>)-(+)-Ephedrine hydrochloride	8.95	43.9	34.3 ²³	Water		
(S)-(+)-Epichlorohydrin	9.96	46.6	34	Methanol		
(R)- $(-)$ -Epichlorohydrin	-9.95	-47.2	-34	Methanol		
Ethyl (S)-(-)-2-(<i>tert</i> -butyl-dimethylsilyloxy)propionate	-8.63	-41.0	$-30 \\ -50.5^{24}$	Chloroform		
(1R)-(-)-Fenchone	-18.18	-79.4	-50.5 18.7-~52.7	Neat		
β-D-(+)-Glucose (R)-(+)-Glycidyl triryl ether	16.77§	82.1§		Water		
(S) - (+) - 4.4a, 5.6, 7, 8-Hexahydro-4 <i>a</i> -methyl-2(3 <i>H</i>)-	1.46	7.8	10.5	Chloroform		
	20.15	000.6	011.1	Ethonol		
naphthalenone	39.15 8.57	200.6	211.1	Ethanol		
(2S,5S)-(+)-Hexanediol	8.57	40.4	34.5 -8.8 ²⁶	Chloroform Water		
L-Homoserine (R,R)-(+)-Hydrobenzoin	-2.69§	-13.3§	-8.8 93 ²⁸			
(R,R)-(+)-Hydrobenzoin (S,S)-(-)-Hydrobenzoin	25.81 	132.6 	-94 ²⁴	Ethanol Ethanol		
(R)-(-)-2-Hydroxy-3,3-dimethyl-y-butyrolactone	-28.23 -5.70	- 141.6	-94	Water		
L – A-Hydroxyisovaleric acid	1.55	- 30.9	18	Chloroform		
(S)-(+)-5-(1-Hydroxy-1-methylethyl)-2-methyl-	1.00	0.1	10	5		
2-cyclohexane-1-one	9.07	46.6	41 ¹⁹	Ethanol		
(S)-(-)-5-(Hydroxymethyl)-2(5H)-furanone	-44.68	-226.8	-144	Water		
(R)-(-)-5-(Hydroxymethyl)-2-pyrrolidinone	-10.79	-50.6	-31	Ethanol		
(S)-(+)-3-Hydroxy-3-methyl-4,4,4-trichlorobutyric						
β-lactone	1.57	6.8	6 ²⁶	Ethanol		
(R)-(-)-3-Hydroxy-3-methyl-4,4,4-trichlorobutyric			-			
β-lactone	-1.64	-7.4	-627	Ethanol		
(R)-(+)-4-Hydroxy-2-pyrrolidinone	15.62	77.8	43 ²³	Ethanol		
(S)-(-)-4-Hydroxy-2-pyrrolidinone	-14.82	-75.9	-43^{23}	Ethanol		
(S)-(+)-3-Hydroxytetrahydrofuran	5.40	31.1	17.5	Methanol		
(R)-(-)-3-Hydroxytetrahydrofuran	-5.47	-32.6	-18	Methanol		
(R)- $(-)$ -1-Indanol	-7.74	-24.6	-29 ²⁰	Chloroform		
(S)-(+)-1-Indanol	7.63	27.8	30	Chloroform		
(S) -(+)-4-lsobutyl- α -methylphenylacetic acid	25.94	132.4	59	Ethanol		
(+)-lsopinocampheol	10.82	48.6	36.2	Ethanol		
(-)-Isopinocampheol	-10.53	-47.4	-36	Ethanol		
(+)-2,3-0-Isopropylidene-L-threitol	-7.44	-32.0	3.1 ⁴²	Ethanol		
(-)-2,3-0-Isopropylidene-D-threitol	7.43	31.2	-2.1 ²⁶	Chloroform		
(S)-(-)-4-Isopropyl-2-oxazolidinethione	-3.52	-16.5	-23	Chloroform		
(4R)-(+)-4-IsopropyI-2-oxazolidinone	7.20	36.7	17	Ethanol		
(4S)-(-)-4-lsopropyl-2-oxazolidinone	-7.32	-35.3	-18	Ethanol		
	-10.12	-49.6	-31.5	Water		
(R)-(-)-3-IsopropyI-2,5-piperazinedione	-10.12	10.0				
	4.93	24.4	22	Neat		
(R)-(-)-3-IsopropyI-2,5-piperazinedione				Neat Neat		

* All samples were measured in a methanol mobile phase (unless mentioned otherwise) at a concentration of 3 mg/mL, and with 1 μL of solution injected onto the reversed-phase HPLC column.

† All values of $\left[\alpha\right]_{D}^{20}$ were obtained from references 30 and 31.

‡ Relative responses of peak area of the chiral detector at 675 nm compared with L-valine.

§ Responses measured in water

TABLE I: Continued

Compound Relative Response: [0,7] (degrees) Published (o) Value (degrees) Solvent Utack to Dbain Published Value (-):						
Compound Response: (degrees) Value (degrees) Published Value (+)-Linement oxic 17.47 80.9 6^{27} Not (+)-Mandolic and 22.94 180.0 11 Water (+)-Mandolic and 22.94 180.0 11 Water (+)-Mandolic and 20.81 17.37 98.3 40 Example (+)-Mandolic and 10.93 -11.13 0.11 Water Nation (5)-(-)-Mandolic and monomic 11.37 98.3 -11.13 0.11 Nation (5)-(-)-Mandolic and monomic 11.37 93.9 94 Obiordorm (4)-(-)-(-)-(-)-Mandolic and monomic 11.37 93.8 94 Obiordorm (4)-(-)-(-)-(-)-Mandolic and monomic 11.37 93.8 94 Obiordorm (4)-(-)-(-)-(-)-Mandolic and monomic 11.37 93.8 94 Obiordorm (4)-(-)-(-)-(-)-(-)-Mandolic and monomic 11.37 93.8 0.00000000000000000000000000000000000		Polotivo	L. 122	Published [120	Solvent Used to Obtain	
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$ \begin{array}{c} (\dot{r}) (-) Authyl mandelse & -43.72 & -200.2 & -14.4 & Methanol \\ (55.7) (-) Authyl mandelse & -43.72 & -200.3 & 32.94 & Methanol \\ (15.27) (-) 2.75 & -23.54 & Methanol & -23.63 & -23.64 & Methanol \\ (15.25) (-) 2.74 & -44.04thyl -5phenyl 2-oxazolidinone & -33.69 & -150.4 & -16.89 & Dibordorm \\ (7) (-) Authyl 5-spheryl 2-oxazolidinone & -31.50 & -16.84 & -16.89 & Dibordorm \\ (7) (-) Authyl 5-spheryl 2-oxazolidinone & -0.150 & -16.85 & -145 & Acotone \\ (7) (-) Authyl 5-spheryl 2-oxazolidinone & -0.160 & -16.85 & -145 & Acotone \\ (7) (-) Authyl 5-spheryl 2-oxazolidinone & -21.84 & -111.5 & 93 & Dibordorm \\ (7) (-) Authyl 5-spheryl 2-oxazolidinone & -21.84 & -111.5 & 93 & Dibordorm \\ (7) (-) Authyl 5-spheryl 2-oxazolidinone & -15.57 & -77.8 & -88^{12} & Methanol \\ (7) (-) 2-27.04 & -10.33 & -10.54 & -16.85 & -145 & Acotone \\ (7) (-) 2-27.04 & -10.33 & -10.55 & -16.84 & -14.3^{23} & Methanol \\ (7) (-) 2-27.04 & -10.33 & -10.55 & -17.73 & -88^{12} & Methanol \\ (7) (-) 2-27.04 & -10.33 & -10.55 & -19.3 & -10.84 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 & -10.16 $						
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17.42.7.1						
i(4.8.5) i(-) -148thyl-5penyl-2-acazildinone 30.8 155.0 168 Chloroform (R) -Nathyl-ophylacitoxia 40.10 184.1 145 Acetone (R) -Nathyl-ophylacitoxia 40.10 184.1 145 Acetone Mone-(TS) -Nathyl-ophylacitoxia -40.60 -185.5 -200 Tetrahydrofuran (R) -Nathyl-ophylacitoxia -41.62 -266.5 -200 Tetrahydrofuran (R) -Systematedia 18.64 83.9 98.8 Chloroform (R) -Systematedia 15.14 75.7 10.9 Natl (S) -Seri-Phentifyl alcohol -15.57 -77.3 -88.27 Methanol (S) -Seri-Phentifyl alcohol -12.67 -63.4 -43.33 Natl (R) +Seri-Phentifyl alcohol -81.5 -59.3 -61.67 Chloroform (R) -Seri-Phentifyl alcohol -81.5 -59.3 Toluene Chloroform (R) -Seri-Phentifyl alcohol -81.5 -59.3 Toluene Chloroform (S) -Ser	(1S,2R)-(+)-trans-2-(1-Methyl-1-phenylethyl)cyclohexaneol		36.3		Methanol	
(S5.57)-(-)-4.Hethyl-5.polysillatoxia -13.0 -15.0 -168 ²⁵ Chloroform (S)-(-)-Methyl-polysillatoxia -40.0 -18.5 -14.5 Acetone (S)-(-)-Methyl-polysillatoxia -40.0 -18.5 -14.5 Acetone (-)Mose-latol dimer -49.22 -266.5 -20.0 Tetrahydrohran (17.555)-(+)-2-obabicroli 3.0.10c+6-n-3-one 29.99 148.6 102.5 Methanol (S)-(-)-Periniyl alcohol 15.14 77.7 -98 ²² Methanol (S)-(-)-Periniyl alcohol -15.57 -77.8 -88 ²² Methanol (S)-(-)-Periniyl alcohol -8.15 -9.93 -48.6 ²¹ Chloroform (S)-(-)-Periniyl-butanol -8.15 -9.93 -48.6 ²¹ Chloroform (S)-(-)-Periniyl-butanol -8.15 -9.93 Toluene (S)-(-)-Periniyl-butanol -8.15 -9.93 Toluene (S)-(-)-Periniyl-butanol -8.15 -9.33 Toluene (S)-(-)-Periniyl-butanol -8.15 -9.34 Refa ²¹ Chloroform (S)-(-)-Perinyl-butanol 14.33 71.6 6 Methanol (S)-(-)-Periniyl-butanol	(1R,2S)-(-)-trans-2-(1-Methyl-1-phenylethyl)cyclohexaneol	-8.28	-33.6			
(S5.57)-(-)-4.Hethyl-5.polysillatoxia -13.0 -15.0 -168 ²⁵ Chloroform (S)-(-)-Methyl-polysillatoxia -40.0 -18.5 -14.5 Acetone (S)-(-)-Methyl-polysillatoxia -40.0 -18.5 -14.5 Acetone (-)Mose-latol dimer -49.22 -266.5 -20.0 Tetrahydrohran (17.555)-(+)-2-obabicroli 3.0.10c+6-n-3-one 29.99 148.6 102.5 Methanol (S)-(-)-Periniyl alcohol 15.14 77.7 -98 ²² Methanol (S)-(-)-Periniyl alcohol -15.57 -77.8 -88 ²² Methanol (S)-(-)-Periniyl alcohol -8.15 -9.93 -48.6 ²¹ Chloroform (S)-(-)-Periniyl-butanol -8.15 -9.93 -48.6 ²¹ Chloroform (S)-(-)-Periniyl-butanol -8.15 -9.93 Toluene (S)-(-)-Periniyl-butanol -8.15 -9.93 Toluene (S)-(-)-Periniyl-butanol -8.15 -9.33 Toluene (S)-(-)-Periniyl-butanol -8.15 -9.34 Refa ²¹ Chloroform (S)-(-)-Perinyl-butanol 14.33 71.6 6 Methanol (S)-(-)-Periniyl-butanol	(4R,5S)-(+)-4-Methyl-5-phenyl-2-oxazolidinone	30.98	155.0	168 ¹⁸	Chloroform	
(P) (+) Methyl-polysillatöxie 40.10 184.1 145 Acetane Mone-(15) (+) menthyl phthalate 21.64 111.2 93 Chicorotorn (-) Noel-atal dimer -49.20 -266.5 -200 Tetrahydrohran (18,555) (+) -2-Oxabicyciol (3.0) tot-en-3-one 29.99 146.6 102.5 Methanol (25,45) (+) -Pennihyl alcohol 15.14 75.7 109 Neat (5) (-) -seer-branethyl alcohol -12.67 -63.4 -41.323 Neat (5) (-) -seer-branethyl alcohol -12.67 -53.4 -46.857 Chicoroforn (5) (-) -seer-branethyl alcohol -12.67 -53.4 -46.857 Chicoroforn (5) (-) -seer-branethyl alcohol -83.7 -59.3 Tolane -59.3 Tolane (7) (-) -Praneyn-1-butanol 8.19 54.4 55 Chicoroforn -59.3 Tolane (18,26) (+) -traze-2-Pranyn-1-sycoloxane -10.69 -53.1 -54.5 Neat (18, (-) + -Pranyn-1-3-dixane -10.69 -53.1 -54.5 Neat <		-31.30	-150.4	-168^{25}	Chloroform	
(S)-(-)-Methyl-problemic decision -145 Actone (-)-Noe-latol dimer -1452 -266.5 -200 Tetrahydorburan (125,SS)+(-)-2-babicy(013,0)cf-6-n-3-one 29.99 148.6 102.5 Methanol (125,SS)+(-)-2-babicy(013,0)cf-6-n-3-one 29.99 148.6 102.5 Methanol (15,SS)-(-)-2-babicy(013,0)cf-6-n-3-one 29.99 148.6 102.5 Methanol (S)-(-)-2-brainyl alcohol -15.57 -77.8 -88 ²³ Methanol (S)-(-)-2-brainyl alcohol -81.5 -99.3 -48.8 ²¹ Chioroform (S)-(-)-2-brainyl-1-buanol -81.5 -99.3 -68.8 ²¹ Chioroform (S)-(-)-2-brainyl-1-buanon 95.1 49.0 54.5 Meat (S)-(-)-2-brainyl-1-buanon 95.1 49.0 54.5 Meat (S)-(-)-4-brainyl-1-buanon 95.1 49.0 54.5 Meat (S)-(-)-4-brainyl-1-buanon 16.85 -73.9 -06 Chioroform (S)-(-)-4-brainyl-1-buanon 16.85 -73.9 -49 Chioroform	(R)-(+)-Methyl-p-tolylsulfoxide	40.10	184.1		Acetone	
$ \begin{array}{llllllllllllllllllllllllllllllllllll$						
[-)-local-table dimer - 49.22 - 266.5200 Temperature (CR 555) + -2-20ablyce(13.31) etc302 - 29.9 148.6 102.5 (CR 555) + -2-20ablyce(13.31) etc303 - 27.9 -38.7 Methanol (CR 5))-2-Perilyl acholo - 15.57 - 7.7.8 - 8852 Methanol (S))-2-Perilyl acholo - 12.67 - 63.4 - 41.353 - 10.4 Methanol (S))-2-Perilyl acholo - 12.67 - 63.4 - 41.354 Methanol - 12.67 - 63.4 - 41.354 Methanol - 12.67 - 63.4 - 41.354 Methanol - 27.7.8 - 48.651 Chioroform		21.64	111.2	93	Chloroform	
[1A558]+(-)=2-0xabicycli3.3/joch-6-en-3-one 2.9.99 144.6 102.5 Methanol [25:45]+(-)=Preinblanded) 15.14 75.7 109 Neat [5]-(-)=Preinbly alcohol -15.57 -77.8 -88.27 Methanol [5]-(-)=Preinbly alcohol -12.67 -63.4 -41.3 ²³ Neat [6]-(-)=breinbly alcohol -2.63 -2.79 -33.7 Vater [6]-(-)=Preinbly alcohol -81.5 -59.3 -48.6 ⁶¹ Ohoroform [6]-(-)=Preinblaytic acid -23.33 -120.5 -33 Toluna [5]-(-)=Preinblaytic acid -23.33 -120.5 -43 Methanol [6]-(-)=Preinblaytic acid -23.33 -160.5 Methanol Methanol [6]-(-)=Preinblaytic acid -13.03 -16.5 Methanol Methanol [6]-(-)=Preinblaytic acid -10.69 Ohoroform Methanol Methanol [6]-(-)=Preinblaytic acid -15.51 -61.9 Methanol Methanol [6]-(-)=Preinblaytic acid -15.55 -73.3 -64.5 Methanol [6]-(-)=Preinblaytic acid -55.7 -28.1 <td></td> <td>-49.22</td> <td>-266.5</td> <td>-200</td> <td>Tetrahydrofuran</td>		-49.22	-266.5	-200	Tetrahydrofuran	
(25.45)(+)-Pentaneloi 18.64 83.9 39.8 Chordrom (S)(-)-Pertifyl acholo -15.57 -77.8 -88 ²² Methanol (S)(-)-Pertifyl acholo -12.57 -77.8 -88 ²² Methanol (P)(-)-Pertifyl acholo -12.67 -63.4 -41.3 ³⁰ Vater (S)(-)-Pertifyl acholo -81.5 -53.3 -48.6 ³¹ Obsordrom (S)(-)-Pertifyl acholo -23.73 -120.5 -93 Tolusene (S)(-)-Pertifyl acholo -23.73 -120.5 -93 Tolusene (S)(-)-(+) frams-2-Prenyl acholon 14.33 71.6 58 Metanol (S)(-)-(+) +Prenyl+1-2-vitanediol -15.01 -61.9 -61 Nat (S)(-)-(+) +Prenyl+1-2-vitanediol 14.70 67.7 69 Chioroform (S)(-)-(+) +Prenyl+1-2-vitanediol 14.70 67.7 69 Chioroform (S)(-)-(+) +Prenyltalyricai 16.85 73.9 -49 Chioroform (S)(-)-(+) +Prenyltalyricai 16.85 73.6 17.4 Ethanol <td></td> <td>29.99</td> <td></td> <td></td> <td></td>		29.99				
$ \begin{array}{c} r _{1} + (-)^{-1}p^{-1} $						
$ \begin{aligned} S_1()=2e^{-1}p + larked larke$						
$(S_1 \leftarrow -)$ sac-Phenetylationia -12.67 -63.4 -41.3^{23} Water $(R_1 \leftarrow +)$ + Phenyl-1-butanol 8.19 54.4 55 $Chloroform$ $(R_1 \leftarrow +)$ + Phenyl-1-butanol -8.15 -59.3 $-74.6.8^{21}$ $Chloroform$ $(R_1 \leftarrow +)$ - Phenyl-butyric acid 22.33 -120.5 -33 $Toluene$ $(S_1 \leftarrow +)$ - Phenyl-1-butyric acid 22.33 120.5 -33 $Toluene$ $(S_2 \leftarrow +)$ + Phenyl-1-bytholycic acid 23.43 175.1 8.8 Methanol $(R_1 \leftarrow +)$ - Phenyl-1-syntholycic acid -10.69 -53.1 -54.5 Neat $(R_1 \leftarrow +)$ - Phenyl-1-3-dinamediol -15.01 -61.9 -69 $Chloroform$ $(S_1 \leftarrow +)$ - Phenyl-1-2-sthanediol -16.55 -73.9 -49 $Chloroform$ $(S_2 \to +)$ - Phenyl-1-2-sthanediol -16.55 -73.9 -49 $Chloroform$ $(S_2 \to +)$ - Phenyl-2-soxzoldinone -16.55 77.4 48 $Chloroform$ $(S_2 \to +)$ - Phenyl-2-soxzoldinone -16.55 79.7 48 $Chloroform$ $(S_1 \leftarrow +)$ - Phenyl-2-soxzoldinone <t< td=""><td></td><td></td><td></td><td></td><td></td></t<>						
i-Phenylatanine -5.08 -27.9 -33.7 Water (S) (-) +1Phenyl +1butanol -8.15 -53.3 -46.6 ²¹ Chloroform (S) (-) +2Phenylbutyric acid 23.43 125.1 92 ¹⁸ Toluene (S) (+) +2Phenylbutyric acid 23.43 125.1 92 ¹⁸ Methanol (S) (+) +2Phenylbutyric acid 23.43 125.1 92 ¹⁸ Methanol (S) (+) +4Phenyl-1.2 ethanediol 14.43 71.6 6.8 Methanol (S) (+) +4Phenyl-1.2 ethanediol -15.01 -61.5 Neat (S) (+) +4Phenyl-1.2 ethanediol 14.70 67.7 6.9 Chloroform (S) (+) +4Phenyl-1.2 ethanediol 14.70 67.7 6.9 Chloroform (S) (+) +4Phenyl-1.2 ethanediol 16.55 73.2 -49 Chloroform (S) (+) +4Phenyl-1.2 ethanediol 16.55 73.2 -49 Chloroform (S) (+) +4Phenyl-1.2 ethanediol 16.55 73.7 4.8 Chloroform (S) (+) +4Phenyl-2.0 exacildinone 15.6 79.7 4.8 Chlorofor						
$\begin{aligned} R + (-) + Phenyl-1-butanol & R.19 & 5.4 & 5.5 & Chlordorm \\ R - (-) + Phenylbutyric acid & -2.3.73 & -120.5 & -9.3^{11} & Chlordorm \\ R - (-) + Phenylbutyric acid & -2.3.73 & -120.5 & -9.3^{11} & Toluene \\ (52R) + (+) + Phanyl-1-cyclohexanol & 14.33 & 71.6 & 5.8 & Methanol \\ R + (-) + Phanyl-1 - Siloxane & 3.51 & 49.0 & 54.5 & Neat \\ R + (-) + Phanyl-1 - Siloxane & -10.69 & -3.31 & -54.5 & Neat \\ R + (-) + Phenyl-1 - Siloxane & -10.69 & -3.31 & -54.5 & Neat \\ R + (-) + Phenyl-1 - Siloxane & -10.69 & -3.31 & -54.5 & Neat \\ R + (-) + Phenyl-1 - Siloxane & -10.69 & -3.31 & -54.5 & Neat \\ R + (-) + Phenyl-1 - Siloxane & -10.69 & -3.31 & -54.5 & Neat \\ R + (-) + Phenyl-1 - Siloxane & -10.65 & 77.9 & -49 & Chlordorm \\ S + (-) + Phenyl-1 - Siloxane & -16.55 & -73.9 & -49 & Chlordorm \\ S + (-) + Phenyl-1 - Siloxane & -16.55 & -73.9 & -49 & Chlordorm \\ 22.33) + (-) + Shenylylociol & -16.55 & -73.9 & -49 & Chlordorm \\ 22.33) + (-) + Shenylylociol & -16.55 & -73.9 & -49 & Chlordorm \\ 22.35) + (-) + Shenylylociol & -16.56 & 70.7 & 48 & Chlordorm \\ S + (-) + Phenyl-2 + Oxazolidinone & -16.66 & 79.7 & 48 & Chlordorm \\ S + (-) + Phenyl-2 + Oxazolidinone & -16.56 & 79.7 & 48 & Chlordorm \\ S + (-) + Phans-Pinane & 2.74 & 14.4 & 17 & Neat \\ R + (+) + Phans-Pinane & 2.74 & 14.4 & 17 & Neat \\ R + (+) + Phans-Pinane & 2.74 & 14.4 & 17 & Neat \\ S + (-) + Phans-Pinane & -2.75 & -12.3 & -17 & Neat \\ S + (-) + Phenolecci & -2.25 & -12.6 & 8.5 & Toluene \\ S + (-) + Phenolecci & -2.27 & -38.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.266 & -35.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.266 & -35.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.268 & -35.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.268 & -35.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.268 & -35.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.268 & -35.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.268 & -35.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.268 & -35.6 & -26.4^{53} & Water \\ Phepcilc acid & -7.268 & -35.6 & -26.4^{53}$						
$ \begin{aligned} & (S) (-) (-) + Phenyl-1-butani & -8.15 & -59.3 & -48.6^{21} & Chloroform \\ & (S) (+) + Phenylburylic acid & -23.73 & -120.5 & -93 & Toluene \\ & (S) (-) + 2+Phenylburylic acid & 23.43 & 125.1 & 92.19 & Toluene \\ & (15.2R) (+) + Frans 2-Phenyl-1-cyclohexanol & 14.33 & 71.6 & 58 & Methanol \\ & (S) (-) -4+Phenyl 1.3-dioxane & 9.51 & 49.0 & 54.5 & Neat \\ & (S) (-) -4+Phenyl 1.2-dinanediol & -15.01 & -61.9 & -69 & Chloroform \\ & (S) (-) -4+Phenyl 1.2-dinanediol & -15.01 & -61.9 & -69 & Chloroform \\ & (S) (-) +(-) + Phenyl 1.2-dinanediol & -15.01 & -61.9 & -61.24 & Ethanol \\ & (Z3.35) (-) -5-Phenylglycidol & 16.95 & -73.2 & -49 & Chloroform \\ & (Z3.35) (-) -5-Phenylglycidol & -16.55 & -73.9 & -49 & Chloroform \\ & (Z3.35) (-) -5-Phenylglycidol & -16.55 & -73.9 & -49 & Chloroform \\ & (Z3.35) (-) -5-Phenylglycidol & -16.55 & -73.9 & -49 & Chloroform \\ & (S) (-) + (-) + Phenyl - 2-oxazolidinone & -16.43 & -80.6 & -48.25 & Chloroform \\ & (S) (-) + (-) + Phenyl - 2-oxazolidinone & -16.43 & -80.6 & -48.25 & Chloroform \\ & (S) (-) - (-) + Phenyl - 2-oxazolidinone & 15.06 & 25.2 & 24 & Neat \\ & (15) (-) - c-Phinane & -5.13 & -24.1 & -24 & Neat \\ & (15) (-) - c-Phinane & -5.75 & -12.3 & -17 & Neat \\ & (15) (-) - c-Phinane & -2.75 & -12.3 & -17 & Neat \\ & (15) (-) - c-Phinane & -2.75 & -12.3 & -17 & Neat \\ & (15) (-) - c-Phene & -3.26 & -125.6 & 8.5 & Toluene \\ & (12.23.35, S5) (+) - Pinanediol & 25.54 & 120.3 & -8.6^{21} & Toluene \\ & (15.23.37, S3.35, S5) (+) - Pinanediol & 25.6 & -123.6 & 8.5 & Toluene \\ & (15.23.37, S3.35, S5) (+) - Pinanediol & 25.6 & -123.6 & 8.5 & Toluene \\ & (15.23.37, S3.35, S5) (+) - Pinanediol & 25.6 & -123.6 & 8.5 & Toluene \\ & (15.2) (-) - Pinpene & -2.29 & -135.6 & -21 & Neat \\ & (P) (-) - Pinpene & -2.29 & -135.6 & -21 & Neat \\ & (P) (-) - Pinpene & -2.29 & -135.6 & -21 & Neat \\ & (P) (-) - Pinpene & -2.29 & -12.6 & -3.64 & Water \\ & (P) (-) - Pinpene & -2.29 & 12.9 & 6.83 & Water \\ & (P) (-) - Pinpene & -2.84 & 131.3 & 107 & Neat \\ & (P) (-) - Pinpene & -2.84 & 131.3 & 107 & Neat \\ & $						
$ \begin{array}{c} R - (-) - 2 - heny hubry is add \\ S - (+) - 2 - heny hubry is add \\ S - (+) - 1 - 2 - 2 - heny (-) - cyclohexanol \\ A - 3 - 2 - 1 - 2 - 2 - 1 - 2 - 2 - 3 - 2 - 1 - 2 - 2 - 3 - 2 - 1 - 2 - 2 - 3 - 2 - 2 - 3 - 2 - 2 - 2 - 2$						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						
$ \begin{array}{llllllllllllllllllllllllllllllllllll$						
$ \begin{aligned} S -(-)-I+Phenyl-1.2-ethanediol & -10.69 & -53.1 & -54.5 & Neat \\ (P)-(-)-I+Phenyl-1.2-ethanediol & -15.01 & -61.9 & -69 & Chloroform \\ (S)-(-)-Phenyl-1.2-ethanediol & 14.70 & 67.7 & 69 & Chloroform \\ (S)-(-)-Phenyl-1.2-ethanediol & 14.70 & 67.7 & 69 & Chloroform \\ (Z3.37)+(-)-3-Phenylgylciol & 16.95 & 79.2 & 49 & Chloroform \\ (Z3.37)+(-)-3-Phenylgylciol & -16.55 & -7.39 & -49 & Chloroform \\ (Z3.37)+(-)-3-Phenylgylciol & -16.55 & -7.39 & -49 & Chloroform \\ -3-Phenyllactic acid & -6.87 & -28.1 & -20.8^{24} & Water \\ (P)-(-)-4-Phenyl-2-oxazolidione & -16.43 & -80.6 & -48^{25} & Chloroform \\ (S)-(+)-Phenyl-2-oxazolidione & -16.56 & 79.7 & 48 & Chloroform \\ (1P)-(+)-a-Phenyl-2-oxazolidione & -5.16 & 25.2 & 24 & Neat \\ (1R)-(+)-a-Phenyl-2-oxazolidione & -5.16 & 25.2 & 24 & Neat \\ (1R)-(+)-a-Phanel & -5.13 & -24.1 & -24 & Neat \\ (1R)-(+)-rans-Pinane & -5.13 & -24.1 & -24 & Neat \\ (1R)-(+)-rans-Pinane & -5.15 & -21.3 & -17 & Neat \\ (1R)-(+)-rans-Pinane & -2.75 & -12.3 & -17 & Neat \\ (1R)-(+)-rans-Pinane & -2.27 & -12.3 & -16 & -21 & Neat \\ (1R2R-3SSR)-(-)-Pinanediol & 25.54 & 120.3 & -8.8^{23} & Toluene \\ (1S2C3SR,SS)-(+)-Pinanediol & 25.54 & 120.3 & -8.8^{23} & Toluene \\ (1S2C3SR,SS)-(+)-Pinanediol & 25.26 & -123.6 & 8.5 & Toluene \\ (1S2C3SR,SS)-(+)-Pinanediol & 25.26 & -123.6 & 8.5 & Toluene \\ (1S2C3SR,SS)-(+)-Pinanediol & 25.26 & -123.6 & -21 & Neat \\ D-Piocolic acid & 8.278 & 388 & 27^{25} & Water \\ U-Piocolic acid & 8.278 & 388 & 27^{25} & Water \\ U-Piolocic acid & 8.278 & 388 & -26.4 & Water \\ (P)-(+)-Prolylene carbonate & 15.42 & 74.5 & 2 & Neat \\ (S)-(-)-Prolylene carbonate & 15.42 & 74.5 & 2 & Neat \\ (S)-(-)-Prolylene carbonate & 15.42 & 74.5 & 2 & Neat \\ (S)-(-)-Prolylene carbonate & 15.42 & 74.5 & 2 & Neat \\ (S)-(-)-Prolylene carbonate & 15.44 & 9.0 & 33^{18} & Neat \\ (C)-2-(2.4,5,7-Tetranturb-9-Huronyl-Hanol & -10.64 & -23.7 & -22 & Neat \\ (S)-(-)-2-(2.4,5,7-Tetranturb-9-Huronyl-1 & -10.64 & -44.8 & -30^{17} & Chloroform \\ (P)-(-)-2.2,2.4,5,7-Tetranturb-9-Huronyl-1 & -10.64 & -44.8 & -30^{17} & Chloro$						
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$						
$ \begin{array}{llllllllllllllllllllllllllllllllllll$						
$ \begin{aligned} & (s)_{-(-)}^{} + (-1-Phenylethyl)matelimide & -21 02 & -78.3 & -61^{24} & Ethanol \\ & (2R,3R)_{+}(+) -3-Phenylghylidol & 16.95 & 79.2 & 49 & Chloroform \\ & c-3-Phenylghicito aid & -6.65 & -73.3 & -49 & Chloroform \\ & c-3-Phenylghicito aid & -6.65 & -73.8 & -49 & Chloroform \\ & c-3-Phenylghicito aid & -6.65 & 73.7 & 48 & Chloroform \\ & (S)_{+}(+) +4-Phenyl-2-oxazolidinone & 16.56 & 79.7 & 48 & Chloroform \\ & (S)_{+}(+) +4-Phenyl-2-oxazolidinone & 16.56 & 79.7 & 48 & Chloroform \\ & (S)_{+}(+) +4-Phenyl-2-oxazolidinone & -5.13 & -24.1 & -24 & Neat \\ & (1S)_{+}(-) -cis-Pinane & -5.13 & -24.1 & -24 & Neat \\ & (1S)_{+}(-) -cis-Pinane & -5.13 & -24.1 & -24 & Neat \\ & (1S)_{+}(-) -cis-Pinane & -5.13 & -24.1 & -24 & Neat \\ & (1S)_{+}(-) -trans-Pinane & -2.75 & -12.3 & -17 & Neat \\ & (1S2,SAR,SS)_{+}(+) Pinamediol & 25.54 & 120.3 & -8.6^{21} & Toluene \\ & (1S2,SAR,SS)_{+}(+) Pinamediol & -25.26 & -123.6 & 8.5 & Toluene \\ & (1S,C)_{+}(1S,S)_{+}(+) Pinamediol & -25.26 & -123.6 & 8.5 & Toluene \\ & (1S,C)_{+}(-) -p.Pinanediol & -7.268 & -35.68 & -26.4^{25} & Water \\ & (-Proline & -22.33 & -106.8 & -84 & Water \\ & (-Propile aid & -7.268 & -35.68 & -26.4^{25} & Water \\ & (-Propile aid & -7.268 & -35.68 & -26.4^{25} & Water \\ & (-Propile carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -15.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -16.15 & -71.8 & -2 & Neat \\ & (S)_{+}(-) -Propylene carbonate & -16.1$						
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* All samples were measured in a methanol mobile phase (unless mentioned otherwise) at a concentration of 3 mg/mL, and with 1 μ L of solution injected onto the reversed-phase HPLC column. † All values of $[\alpha]_D^{20}$ were obtained from references 30 and 31.

‡ Relative responses of peak area of the chiral detector at 675 nm compared with L-valine.

§ Responses measured in water

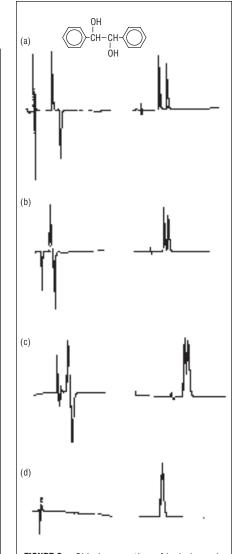


FIGURE 3: Chiral separation of hydrobenzoin enantiomers using optical rotation (left) and UV (right) detection. Column: (a–c) 25 cm imes4.6 mm Cyclobond I 2000 RSP, (d) 5 cm imes4.6 mm C18; mobile phase: (a) 10:90 (v/v)methanol-1% TEAA (pH 4.1), (b) 30:70 (v/v) methanol-1% TEAA (pH 4.1), (c) 50:50 (v/v) methanol-1% TEAA (pH 4.1), (d) methanol; flow rate: 1 mL/min; UV detection wavelength: 254 nm. Resolution: (a) 1.9, (b) 1.4, (c) 0.6, (d) no separation.

RESULTS AND DISCUSSION

As a starting point, we chromatographed more than 230 chiral compounds under identical conditions — or as close to identical as possible given each compound's solubility in the mobile phase. Instead of providing ideal separation conditions for this great variety of compounds, the purpose of chromatography in this exercise was providing fairly rapidly eluted peaks (that is, 0 < k < 1.5) that could be compared directly with others in terms of sensitivity and could be used to calculate the specific rotation of each compound (see Experimental). Table I lists these results. The first column gives the relative response of each compound relative to

Compounds	[α] <mark>20</mark> (°)†	Solvent	Toluene	Chloroform	Methanol	Acetone	Tetrahydrofuran
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R)-(—)-Benzyloxy-3-(<i>p</i> -tosyloxy)-2-propanol	-7	Toluene	_	_	_	_	_
S)-(+)-Benzyloxy-3-(p-tosyloxy)-2-propanol	+7	Toluene	+	+	+	+	+
S)-(+)-3-Hydroxy-3-methyl-4,4,4-trichlorobutyric							
B-lactone	$+6.0^{26}$	Ethanol	_	+	+	+	+
R)-(—)-3-Hydroxy-3-methyl-4,4,4-trichlorobutyric							
3-lactone	-6.0^{27}	Ethanol	+	—	_	_	—
+)-2,3- <i>0</i> -Isopropylidene-∟-threitol	$+3.1^{24}$	Ethanol	+	_	_	+	+
)-2,3- <i>0</i> -Isopropylidene-D-threitol	-2.1^{26}	Chloroform	_	+	+	_	—
R, 2R, 3S, 5R)-(-)-Pinanediol	-8.6^{21}	Toluene	_	_	+	N/D	_
S, 2S, 3R, 5S)-(+)-Pinanediol	+8.5	Toluene	+	+	—	N/D	+
R)-(+)-Propylene carbonate	+2	Neat	+	_	+	N/D	+
S)-($-$)-Propylene carbonate	-2	Neat	_	+	—	N/D	_
7S)-(-)-10,10-Dimethyl-5-thia-4-azatricyclo[5.2.1.0]							
dec-3-ene-5,5-dioxide	-34	Chloroform	-	_	-	-	_
^{7}R)-(+)-10,10-Dimethyl-5-thia-4-azatricyclo[5.2.1.0]							
dec-3-ene-5,5-dioxide	+34	Chloroform	+	+	+	+	+
R)-(-)-2-Azabicyclo[2.2.1]hept-5-en-3-one	-565	Chloroform	_	_	-	-	_
S)-(+)-2-Azabicyclo[2.2.1]hept-5-en-3-one	+565	Chloroform	+	+	+	+	+

† All values of $[\alpha]_{D}^{20}$ were obtained from references 30 and 31.

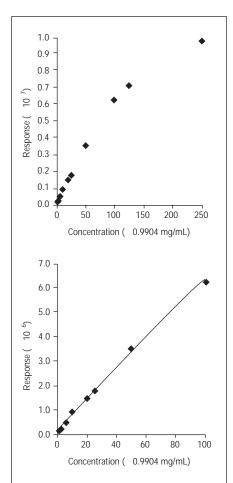


FIGURE 4: Plots of detector response versus concentration for (4R)-(+)-4-isopropyl-2-oxazo-lidinone. $[\alpha]_D = +17^\circ$, $[\alpha]_D^{22} = +36.7^\circ$, $R^2 = 0.997$.

L-valine, which was assigned the normalized value of +1. The second column lists the calculated specific rotations for each compound at 675 nm and 22 °C. The third and fourth columns provide published values of the specific rotation at the sodium D line and the solvent in which they were measured.

The specific rotation of a chiral compound changes with the wavelength of light used and other environmental conditions. Optical rotatory dispersion spectra essentially are plots of specific rotation versus wavelength, as shown in Figure 1 (33). However, most of the literature about chiral compounds discusses using 589.3 nm (the sodium D line) when giving specific rotations. Modern laser-based micropolarimeters use different wavelengths (λ), which are dictated by the nature of the laser light source used.

Generally, analysts would expect no relationship between the direction of rotation of plane polarized light at 589.3 and 675 nm. As Table I shows, however, more than 98% of the examined compounds had the same direction, although different magnitude, of rotation at 589.3 and 675 nm. The main reason for this correlation is that none of the compounds examined had chromophores in the visible region of the spectrum, although most had absorbance in the UV region.

As Figure 1 shows, the optical rotatory dispersion spectra of compounds far from any absorption bands (that is, the portion in the visible region) tend to be flat and featureless, nearly parallel to the line of zero specific rotation. In fact, theory indicates that rotation changes slowly with wavelength at wavelengths far from an absorption band (29). Hence if the specific rotation of a compound is measured under identical conditions at two wavelengths that are not too distant from one another but are far from an adsorption band, there is a high probability that they will have the same sign of rotation (Table I).

Two pairs of enantiomers in Table I did not rotate plane polarized light in the same direction at both 589.3 and 675 nm. They were the enantiomers of 2,3-*O*-isopropylidenethreitol and pinanediol. In both of these cases, the optical rotation at 589.3 nm was quite small. Indeed, the smaller the optical rotation at either of the wavelengths being compared, the more likely is the occurrence of a discrepancy in their direction of rotation. In addition, compounds with small optical rotations are more likely to change their sign with environmental changes such as solvent, pH, and temperature changes.

Table II shows the solvent effect on the direction of plane polarized light for several compounds. Those compounds with small rotations are most likely to show changes in sign with different solvent types. This result, of course, is eminently logical. If the absolute value of a compound's change in rotation is less than the absolute value of its specific rotation, then its sign or direction of rotation must always be the same. Conversely, if the absolute value of a compound's change in rotation is greater than the absolute value of its specific rotation, then it may or may not show the opposite sign depending on the direction of change.

Sensitivity is one of the most important factors when considering a chiroptical detector. Obviously, the magnitude of a chiral molecule's specific rotation at the wavelength of detection will affect its detectability. Figure 2 shows the limit of detection of seven compounds versus their specific rotation at 675 nm. Also included is the analogous plot that uses

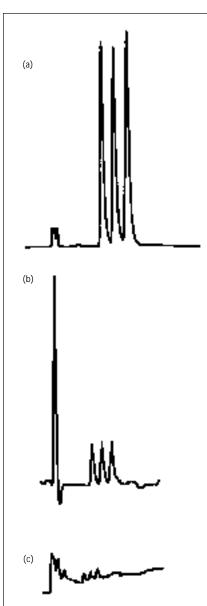
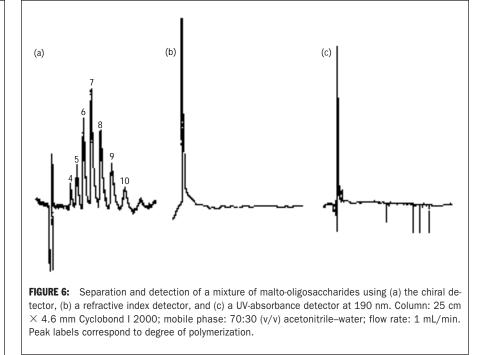


FIGURE 5: Separation and detection of α -, β -, and γ -cyclodextrins using (a) the chiral detector, (b) a refractive index detector, and (c) a UV-absorbance detector at 190 nm. Column: 25 cm \times 4.6 mm Cyclobond I 2000; mobile phase: 75:25 (v/v) acetonitrile–water; flow rate: 1 mL/min.

each compound's specific rotation at the sodium D line. The plot versus $[\alpha]_{675}$ shows the expected correlation of smaller limit of detection with higher specific rotation. The most sensitive determination was for (S)-(-)-binaphthyl-2,2'-diylhydrogen phosphate, which provided a $[\alpha]_{675}$ value of 635°. We were able to detect approximately 50 ng of this compound. Compounds 1 through 7 in Figure 2 span the range of specific rotations found for most compounds of pharmaceutical interest, as well as many chiral synthons, auxiliaries, and catalysts (34,35). The curve for $\left[\alpha\right]_{D}^{20}$ (Figure 2) did not correlate as well; indeed, we would not expect them to because the limits of detection were calculated using a different wave-





length of light. However, we observed the same general trend. Because the specific rotation of most compounds still is reported at the sodium D line and not at other wavelengths, analysts may be able to estimate an approximate limit of detection in some cases.

Figure 3 shows several chromatograms that compare the response from the chiral detector (left) with a standard UV detector (right) for enantiomers of hydrobenzoin at various degrees of resolution. When peaks overlap, the chromatogram developed using any chiroptical detector cannot accurately calculate resolution (R_s), selectivity, or quantitate the enantiomers. As Zukowski, Tang, Berthod, and Armstrong (22) showed, analysts must use an in-line UV detector or other conventional detectors to determine these parameters correctly (22).

The linear dynamic range of the chiral detector covers approximately 2.5 orders of magnitude, although it varies with the specific rotation of each analyte. Figure 4 shows the plot for a typical case of (4R)-(+)-4-isopropyl-2-oxazolidinone. The detector response is no longer linear when the amount of analytes injected exceeds approximately 100 µg (Figure 4).

The chiral detector is not as sensitive for chiral aromatic molecule analysis as are typical UV HPLC detectors. However, this detector tends to be much more sensitive than UV detectors, even when used at low wavelengths, or differential refractometer detectors for various chiral nonaromatic compounds such as carbohydrates and some amino acids (6). Figures 5 and 6 clearly show these results for a chromatographic separation of different cyclodextrins and a series of linear oligosaccharides.

It has been stated in numerous publications that chiroptical detectors coupled with conventional detectors can be used to determine enantiomeric purity without having to perform a chromatographic separation of enantiomers (7,9,10,12,22,23). Although this statement may be true for mixtures of moderate enantiomeric excess, this approach should be avoided in situations involving a large excess of one antipode. Zukowski, Tang, Berthod, and Armstrong (22) demonstrated conclusively that the error for this determination is enormous for mixtures of high or low enantiomeric excess. The error in the coupled detector method is dependent on matching the sensitivity and linear range of the two detectors, as well as their precision and accuracy (22). Because the chiroptical detector always had greater limitations in these areas, it generally imposes the greatest error on this approach (22).

Using enantiomerically pure standards, analysts can construct a calibration curve of the ratio of chiroptical detector peak area to UV detector peak area versus the enantiomeric composition, as shown in Figure 7. The composition of unknown mixtures then can be determined using the standard curve. The chiral

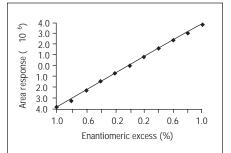


FIGURE 7: Calibration plot of peak area response versus enantiomeric excess for (*S*)-(+)-4-benzyl-3-propionyl-2-oxazolidinone ($R^2 = 0.999$).

detector can be used effectively in this manner if the standards are available (Figure 7). However no chiroptical detector should be used for mixtures of enantiomeric excess greater than 90% because of the escalating error for determining mixtures in that range (22). The most efficient and accurate way to determine enantiomeric excesses is by chromatography or capillary electrophoresis in some cases.

CONCLUSION

Chiroptical detectors can be exceedingly useful for the detection and analysis of various chiral molecules. They also provide a rapid, efficient way to validate enantiomeric separations. Traditionally, the shortcomings of these detectors has been their lack of sensitivity and robustness. Some early detectors also were far too large and complex to be practical HPLC detectors. The chiral detector we used in our study was small, compact, and simple to use.

We were able to couple it with most HPLC systems. Thus far, it is the most stable and sensitive of the chiroptical detectors that we have used. We could detect HPLC enantioseparations at analyte levels that do not overload most chiral stationary phases (this finding was not true of most earlier commercial detectors). However, this detector is still not as sensitive as a typical UV detector for most aromatic compounds.

One aspect of this detector that may prove useful is the unexpected high correlation between the magnitude and direction the specific rotations of molecules at 675 nm and at the sodium D line. This ability allows analysts to estimate a compound's sign of rotation and possibly detector sensitivity from literature values and vice versa. Clearly, chiroptical detector technology is rapidly approaching the point at which the detectors will be useful and perhaps routine devices in laboratories and manufacturing plants in which chiral molecules are prevalent and important compounds.

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