#### **GRAPHICAL ABSTRACTS**

#### A NEW STEREOSELECTIVE APPROACH TO THE TRANS-PERHYDROAZULENE SKELETON

Tetrahedron: Asymmetry 1993, 4, 281

Brigitta Popp, Frank Sönnichsen and Werner Tochtermann

Institut für Organische Chemie der Universität, Olshausenstr. 40, D-2300 Kiel, FRG

The synthesis of (-)-4 from the di-O-isopropylideneα-D-glucofuranosyl diester (-)-1a is described

ROOC
$$(CH_2)_6 \longrightarrow \begin{pmatrix} H \\ G_6 \\ G_7 \end{pmatrix} \longrightarrow \begin{pmatrix} CH_3 \\ C=0 \\ COOCH_3 \end{pmatrix}$$

$$RO = DIG \qquad (-)-4$$

Tetrahedron: Asymmetry 1993, 4, 285

A Homoannularly Bridged Hydroxyamino Ferrocene as an Efficient Catalyst for the Enantioselective Ethylation of Aromatic and Aliphatic Aldehydes. Hans Wally, Michael Widhalm, Walter Weissensteiner, and Karl Schlögl Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria.

$$R - C \xrightarrow[H]{OH} R - C \xrightarrow[H]{OH} + R - C \xrightarrow[H]{OH}$$

R = aromatic, aliphatic (straight chain or branched)

(S) maior (R)

e.e. 66 - 97%

minor

Tetrahedron: Asymmetry 1993, 4, 289

Novel Enantioselective Syntheses of Optically Active (1R)-cisand (1R)-trans-Chrysanthemic Acids.

Alain Krief \*, Dominique Surleraux and Nathalie Ropson

Department of Chemistry, Facultés Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000, Namur (Belgium).

Dimethyl dimedone, a non chiral and cheap compound, has been converted to the optically actives 1-(R)-cis- and 1-(R)-trans-chrysanthemic acids possessing high economic value. These processes involve as the key steps (i) a cyclopropanation reaction (ii) a Grob fragmentation and (iii) a lipase monitored hydrolysis of a prochiral discetate,

### HIGHLY STEREOSELECTIVE SYNTHESIS OF β-GLYCOSIDES OF

3-DEOXY-2-HEXULOSONATES Ioncho R. Vlahov, Petinka I. Vlahova, and Richard R. Schmidt

Fakultaet Chemie, Universitaet Konstanz, D-7750 Konstanz, Germany  $(X = N_3, Y = H)$ AcO BnO BnO (X = H, Y = OH)

OR

Tetrahedron: Asymmetry 1993, 4, 293

Optically Active Spirosulfuranes via Nonclassical Resolution with 2,2'-Dihydroxy-1,1'-Binaphthol

Tetrahedron: Asymmetry 1993, 4, 297

J.Drabowicz<sup>a</sup>, J.C.Martin<sup>b</sup>

\*\*Center of Molecular and Macromolecular Studies, PAS, 90-363 Lodz, Sienkievicza 112, Poland Department of Chemistry, Vanderbilt University, Nashville, 37-235 TN, USA.

Resolution of the racemic sulfurane 4a with optically active 2,2'-dihydroxy-1,1'-binaphthol 5 afforded for the time both enantiomers of a spirosulfurane containing a tridentate ligand.

STEREOSELECTIVE REDUCTION OF SUBSTITUTED BENZOPHENONES

Tetrahedron: Asymmetry 1993, 4, 301

BY MICROORGANISMS - p-Cl SUBSTITUTED. I.

Grigor Spassov, Velichka Pramatarova, Radoslav Vlahov and Günter Snatzke<sup>†</sup>
Institute of Organic Chemistry, Bulg. Acad. Sci., 1113 Sofia, BULGARIA

† Ruhr-Universität Bochum, Fakultät für Chemie, Postfach 102148, D-4630 Bochum, FRG

Stereoselective reduction of p-Cl benzophenones by Debaryomyces marama DSM 70250.

STRUCTURE AND SYNTHESIS OF ARTHONIN, A LICHEN METABOLITE FROM ARTHONIA ENDLICHERI

Tetrahedron: Asymmetry 1993, 4, 303

S. Huneck, A. Porzel, J. Schmidt

Institute of Plant Biochemistry, Weinberg 3, D-O-4050 Halle/Saale

Arthonin (1) has been structurally elucidated as (-)-N-benzoyl-L-valinyl N'-benzoyl-L-isoleucinate.

The syntheses of arthonin and iso-arthonin (2) are described.

Tetrahedron: Asymmetry 1993, 4, 313

ENANTIOSELECTIVE HYDROLYSIS OF SOME 3-(2'-NITROPHENOXY)BUTANOATES CATALYZED BY PSEUDOMONAS SP. AND PSEUDOMONAS FLUORESCENS LIPASE

S. Knezović, V. Šunjić, A. Levài\*

"Ruder Bošković" Institute, P.O.B. 1016,, 41001 Zagreb, Croatia

\*Department of Organic Chemistry, University of Debrecen, P.O B. 20, H-4010 Debrecen, Hungary

Racemic methyl, ethyl and cyanomethyl 3-(2'-nitrophenoxy butanoates I, chiral precursors of 2,3-dihydro-1,5-benzoxazepin-4(5H)-ones were submitted to kinetic resolution by  $Pseudomonas\ fluorescens$  and  $Pseudomonas\ sp.$  lipase, to afford S-(+)-acids and R-(-)-esters, the optical purities of the latter were determined (e.e.'s 69-99 %).

 $R = H_1, 4$ '- $CH_3, 5$ '- $CH_3$  $R' = CH_1, CH_2CH_3, CH_2CN$ 

# CIRCULAR DICHROIC STUDIES OF 2-AMINO-2-DEOXY-GALACTOPYRANOSIDES - CONFORMATIONS OF THE 2-(N-ACETYL-p-BROMOBENZAMIDO) GROUP

Lee-Chiang Lo, <sup>1</sup> Nina Berova, <sup>1,2</sup> Koji Nakanishi, <sup>1</sup> Ezequiel Q. Morales <sup>3</sup> and Jesús T. Vázquez <sup>3</sup>; <sup>1</sup>Department of Chemistry, Columbia University, New York, New York 10027; <sup>2</sup>On leave from the Institute of Organic Chemistry, Bulgarian Academy of Sciences, BG-1113 Sofia; <sup>3</sup>Centro de Productos Naturales Organicos Antonio González, Universidad de La Laguna-C.S.I.C., Carretera de La Esperanza 2, 38206 La Laguna, Tenerife, Spain

The CD spectra of 2-N-acetyl-p-bromobenzamides of galactopyranoside are dependent upon the anomeric configuration. These differences in CD have been accounted for by the different conformations of the 2-NAcBz group.

R = p-Br- $C_6$ H<sub>4</sub>-COR = AcO or BrBzO

Tetrahedron: Asymmetry 1993, 4, 331

### STEREOCHEMISTRY OF THE ENANTIOSELECTIVE REDUCTIVE ALKYLATION OF PROLINE WITH KETONES

Gábor Tóth,\* Attila Kovács, Tibor Tamai and Antal Tungler Technical University Budapest, Hungary

Catalytic hydrogenation of pyruvic acid ethyl ester with Pd/C in the presence of (S)-proline resulted in 1 with S,S configuration.

### LIPASE-CATALYZED KINETIC RESOLUTION OF (±)-2-HYDROXY-METHYL-1,4-BENZODIOXANE

Sándor Antus<sup>xa</sup>, Ágnes Gottsegen<sup>a</sup>, Judit Kajtár<sup>b</sup>, Tibor Kovács<sup>a</sup>, Tamás S.Tóth<sup>a</sup> and Hildebert Vagner<sup>c</sup>
Research Group for Alkaloid Chemistry, Hungarian Academy of Sciences, H-1521
Budapest, POB 91 (Hungary)<sup>a</sup>, Institute of Organic Chemistry, L. Ebtvös
University, H-1518 Budapest 112, POB 32 (Hungary) Institut für Pharmazeutische Biologie der Universität München, D-8000 München 2, Karlstrasse 29 (FRG)<sup>c</sup>

Syntheses of (-)-1 was carried out from (±)-1 by lipase catalyzed transesterification with vinyl acetate in organic solvents.

### Tetrahedron: Asymmetry 1993, 4, 339

lipase, VA organic solvent

$$\bigcirc_{H}^{0} \longrightarrow_{H}^{0} \longrightarrow_{H}^{0} \longrightarrow_{H}^{0}$$

$$(\pm) - \underline{1} \longrightarrow_{H}^{0} \longrightarrow_{H}^{0} \longrightarrow_{H}^{0}$$

KINETIC RESOLUTION IN DIELS-ALDER PROCESSES BERND WEGENER, MARTIN HANSEN, EKKEHARD WINTERFELDT INST. F. ORG. CHEMIE, UNIVERS. HANNOVER, SCHNEIDERBERG 1B, GERMANY

Examples for highly kinetic resolutions with the bioyclic chiral cyclopentadiene 1 and several selected cyclic dienophiles are reported. In combination with a thermal retro-Diels-Alder process this procedure provides easy access to both enantiomeres of these dienophiles.

Tetrahedron: Asymmetry 1993, 4, 345

### Configurational Assignment at C - 2' of some Strigol Analogues

K. Frischmuth, U. Wagner, E. Samson, D. Weigelt, P. Koll, H. Meuer, W. Sheldrick, and P. Welzel\* Fakultät für Chemie der Ruhr-Universität, Postfach 102148, D-4630 Bochum (Germany)

Configurational assignment at C-2' of several strigol analogues by

- (i) X-ray analysis.
- (ii) chemical correlation, and
- (iii) circular dichroism

is described.

Tetrahedron: Asymmetry 1993, 4, 361

Synthetic Sulfur Carotenoids II: Optically Active Carotenoid Thiols

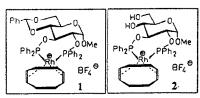
Hans-Richard Sliwka\* and Synnøve Liagen-Jensen
Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Syntheses of optically active carotenoid thiol derivatives by Mitsunobu reactions with (3R,3'R)-zeaxanthin

Application of the Term "Relative Enantioselectivity" as Useful Measure for Comparison of Chiral Catalysts, Demonstrated on Asymmetric Hydrogenation R. Selke, H. Foken, C. Facklam

Max-Planck-Gesellschaft, Arbeitsgruppe Asymmetrische Katalyse, Universität Rostock

Maximum enantioselectivity of up to 99 % ee shows unexpected permutation comparing the catalysts 1 and 2 regarding the type of substrate, and is mathematically conceivable by formation of the quotient of the anantiomeric ratios for two experiments.



Tetrahedron: Asymmetry 1993, 4, 369

Tetrahedron: Asymmetry 1993, 4, 383

CHIROPTICAL PROPERTIES OF BENXENE CHROMOPHORE

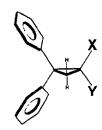
UN SUBSTITUTED 1,1-DIPHENYLCYCLOPROPANES

J. Gawronski , K. Gawronska, D. Radocki

Department of Chemistry, A. Mickiewicz University, 60-780 Poznan, Poland and H. M. Walborsky

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-3006, USA

The CD data on 29 substituted 1,1-diphenylcyclo propanes of known absolute configuration and "perpendicular" conformation are interpreted in terms of relative contributions of X and Y substituents differing in size and donor character.



### SYNTHESIS AND CIRCULAR DICHROISM OF

CHOLESTENO[2,3-d]PYRIDAZINES György Hajós

Central Research Institute for Chemistry, Hungarian Academy of Sciences. H-1525 Budapest, P.o.box 17

Synthesis of 1 and interpretation of its UV and CD spectra. Experimental evidence of a new n- $\pi^*$ transition.

#### Iterative Syn-1,3,5-Triol Synthesis Utilizing the Reaction of \( G-\) (Trimethylsilyi) alkyl Phenyl Sulphones with Oxiranes

B. Achmatowicz and J. Wicha, Institute of Organic Chemistry, Polish Academy of Sciences

Tetrahedron: Asymmetry 1993, 4, 399

Tetrahedron: Asymmetry 1993, 4, 393

Tetrahedron: Asymmetry 1993, 4, 411

Circular Dichroism of Steroidal and Related Cisoid CL, B-Unasaturated Ketones. Part I.

Jadwiga Frelek \*, Wojciech J. Szczepek \*,b, and Hans Peter Weiß \*

- a Institute of Organic Chemistry, Polish Academy of Sciences, PL-01-224 Warsaw
- b Department of Chemistry, Warsaw University, PI-02-093 Warsaw
- <sup>C</sup> Lehrstuhl für Strukturchemie, Ruhr-Universität, D-4630 Bochum 1

Synthesis and chiroptical properties of 23 cisoid α, β-unsaturated ketones have been described. The relation between structure and observed Cotton effects is discussed in terms of previously published rules. It is shown that CD spectra of these compounds are influenced by substituents located in the allylic axial or equatorial as well as α'-axial or equatorial position(s).

Tetrahedron: Asymmetry 1993, 4, 425

#### RESOLUTION OF METHYL CIS-3-CHLOROMETHYL-2-TETRAHYDROFURANCARBOXYLATE VIA ENZYMATIC HYDROLYSIS

J. H. Udding, J. Fraanje, K. Goubitz, H. Hiemstra\* and W. N. Speckamp\*, University of Amsterdam, The Netherlands; B. Kaptein, H. E. Schoemaker and J. Kamphuis, DSM Research, The Netherlands

racemic cis-1

(+)-(25,3R)-1

(-)-(3aR,6aR)-2

Enzymatic hydrolysis of racemic cis-1 gives optically active lactone 2 and ester 1. Acylase-I and α-chymotrypsin show the highest selectivity (E = 51 resp. 28).

ABSOLUTE HELICITIES OF TWISTED 9,10-PHENANTHRENEQUINONES: CIRCULAR DICHROISM AND CHEMICAL CORRELATION TO BIPHENYLS

Rainer Fritsch, Erwin Hartmann, Gert Brandl and Albrecht Mannschreck\*

Institut für Organische Chemie, Universität Regensburg, D-8400 Regensburg, Germany

Quinone 1 is chemically correlated to biphenyl (M)-2. CD of quinones related to 1 is discussed.

FIRST ASYMMETRIC SYNTHESIS OF (+)- AND (-)-ROCCELLARIC ACID AND DIHYDROPROTOLICHESTERINIC ACID

Tetrahedron: Asymmetry 1993, 4, 457

Johann Mulzer\*, Nabiollah Salimi, Hans Hartl, Institut für Organische Chemie der Freien Universität Berlin, Takustrasse 3, W-1000-Berlin 33, FRG

Syntheses of stereopure roccellaric acid (1) and dihydroprotolichesterinic acid (2) via Claisen Rearrangement, iodolactonization and deiodination in form of both enantiomers are described, e.g.

Harry P.J.M. Dekkers and Perry F. Moraal

Tetrahedron: Asymmetry 1993, 4, 473

Tetrahedron: Asymmetry 1993, 4, 479

C7H12O cis-3,4-Dimethylcyclopentanone RING INVERSION BARRIER IN THE S1 (nm\*) STATE OF cis-3,4-DIMETHYLCYCLOPENTANONE

> Me Me

barrier:  $12 \pm 1.5 \text{ kJ/mol}$ 

The Effect of the Benzene Ring on 1,5-Electrocyclization:

Synthesis and Thermolysis of Optically Active Benzohomofuran.

Benzohomothiophene, N-Carbmethoxyhomoindole, Benzohomophosphole and Homoindene.

F.-G. Klärner\*, A. E. Kleine, D. Oebels, F. Scheidt, Fakultät für Chemie, Ruhr-Universität Bochum, PO 102148, D-4630 Bochum 1, Germany

X: O, S, N-CO<sub>2</sub>CH<sub>3</sub>, P-Ph, CH<sub>2</sub> Racemization of optically active benzobicyclo[3.1.0]hexenes SYNTHESIS, INTRAMOLECULAR HYDROGEN BONDING AND CONFORMATION OF OPTICALLY ACTIVE BILIRUBIN AMIDES. ANALYSIS BY CIRCULAR DICHROISM AND NMR

Tetrahedron: Asymmetry 1993, 4, 491

Stefan E. Boiadjiev, Richard V. Person and David A. Lightner\* Department of Chemistry, University of Nevada, Reno

Optically active bilirubin amides of  $(\beta S_*\beta'S)$ -dimethylmesobilirubin-XIII $\alpha$  were prepared by total synthesis from monopyrroles. Like the parent acid, 1 and 2 exhibit intense exciton coupling CD Cotton effects associated with the long wavelength transition near 430 nm:  $\Delta \epsilon_{430}^{\rm max} - 436$ ,  $\Delta \epsilon_{388}^{\rm max} + 178$  for 1 and  $\Delta \epsilon_{432}^{\rm max} - 410$ ,  $\Delta \epsilon_{381}^{\rm max} + 161$  for 2 in CCl<sub>4</sub>. The CD and NMR data support intramolecularly hydrogen-bonded ridge-tile shaped M-chirality conformations.

Tetrahedron: Asymmetry 1993, 4, 511

BACKSCATTERING DUAL CIRCULAR POLARIZATION RAMAN OPTICAL ACTIVITY IN EPHEDRINE MOLECULES

G.-S. Yu, D. Che, T. B. Freedman and L. A. Nafie, Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100 USA

The in-phase dual circular polarization Raman optical activity spectra of the hydrochloride salts of ephedrine molecules in H<sub>2</sub>O solution provide configurational and conformational markers for rotamers I and II for 1 and 2, and I' for 3 and 4.

Tetrahedron: Asymmetry 1993, 4, 517

Circular Dichroism of Oriented Molecules

Electric dipole/magnetic dipole and electric dipole/electric quadrupole contribution for cholest-4-en-3-one

Hans-Georg Kuball\*a, Bernd Schultheisa, Melanie Klasena, Jadwiga Frelekb, Alfred Schönhoferc

a FB Chemie Universität Kaiserslautern, D-6750 Kaiserslautern, FRG; b Institute of Organic Chemistry, Polish Academy of Sciences, PL-01-224 Warsaw, PL; c Technische Universität Berlin, D-1000 Berlin 12, FRG

The circular dichroism along three mutually perpendicular axes of cholest-4-ene-3-one is calculated from measurements of oriented molecules. It is shown that not only the magnitudes but also the signs of three quantities are different. Thus, by looking at the molecule from different directions, chirality information may be obtained.

## THE CIRCULAR DICHROISM OF ORIENTED & SHEETS: THEORETICAL PREDICTIONS

Robert W. Woody

Department of Biochemistry, Colorado State University, Fort Collins, Colorado 80523

Calculation of circular dichroism spectra for light propagating along x,y,z directions of antiparallel and parallel \( \beta \)-structures

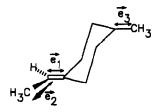
Tetrahedron: Asymmetry 1993, 4, 529

## COUPLED OSCILLATOR CALCULATIONS OF CIRCULAR DICHROISM INTENSITIES: STRUCTURAL APPLICATIONS IN ORGANIC CHEMISTRY.

Carlo Rosini, Maurizio Zandomeneghi and Piero Salvadori.

Centro CNR Macromolecole Stereordinate Otticamente Attive, Dipartimento di Chimica e Chimica Ind.le, via Risorgimento 35, 56126 Pisa, ITALY.

Within a general coupled oscillator model it is possible to calculate the circular dichroism of electrically allowed transitions. To this end a molecule is represented as an aggregate of interacting dipoles.



Tetrahedron: Asymmetry 1993, 4, 555

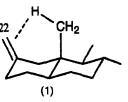
## EFFECT OF $CH/\pi$ INTERACTION ON THE CHIROPTICAL PROPERTIES OF OLEFINS AND DIENES

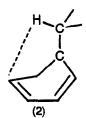
S. Araki, T. Seki, K. Sakakibara, M. Hirota, Y. Kodama, and M. Nishio,

a) Yokohama National University, Hodogaya-ku, Yokohama 240

b) Pharmaceutical Research center, Meiji Seika Ltd., Yokohama 222

Rotational strengths of exo-methylenesteroids (1) and  $\alpha$ -phellandrene (2) were calculated. Axial-alkyl effect on CD was explained in terms of CH/ $\pi$  interaction.





CHIROPTICAL, STRUCTURAL AND CATALYTIC PROPERTIES OF S-a-METHYL-(1-(SUBSTITUTED-PHENYL)-2-(2'-PYRIDO)--1-ETHYLIDEN) BENZYLAMINES AND THEIR Rb(i) AND Cu(i) COMPLEXES

Vıtomır Šunjıć, Dragan Šepac, Biserka Kojjić Prodić, Rudolf Kiralj, Katica Mlinarić-Majerski, Vladimir Vinković

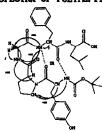
"Ruder Bošković" Institute, P.O.B. 1016, 41001 Zagreb, Croatia

Structure and conformation of chiral 1,5-bidentate nitrogen ligands I and their Rh(I) (NBD) complexes II are discussed. On binding to Rh(I), the ligands I change their structure (enamine-imine shift), and nearly invert conformation. In situ prepared Cu(I) complexes of I exhibited low enantioselectivity in cyclopropanation of styrene.

Tetrahedron: Asymmetry 1993, 4, 575

Tetrahedron: Asymmetry 1993, 4, 591

## FT-IR SPECTROSCOPY GUIDED ANALYSIS OF THE CIRCULAR DICHROISM SPECTRA OF POLYPEPTIDES.



A.Perczel<sup>a</sup>, Zs.Majer<sup>a</sup>, S.Holly<sup>b</sup>, D.Machytka<sup>b</sup>, G.D.Fasman<sup>C</sup> and M.Hollósi<sup>ax</sup>

Dep. of Org. Chem., Eötvős Univ.Budapest 112, POB. 32, Cent. Res. Inst. for Chem. 1525 Budapest POB. 17, H<sup>b</sup> Dep. of Biochem., Brandeis Univ. Waltham, MA 02254, USA