

GRAPHICAL ABSTRACTS

Tetrahedron, 1993, 49, 9151

ISOLATION OF DOLASTATINS 10-15 FROM THE MARINE MOLLUSC

DOLABELLA AURICULARIA

George R. Pettit, Yoshiaki Kamano, Cherry L. Herald,
Youichi Fujii, Haruhisa Kizu, Fred E. Boettner, Dennis
L. Doubek, Jean M. Schmidt and Claude Michel

Cancer Research Institute and Department of Chemistry, Arizona State University, Tempe,
Arizona 85287 USA

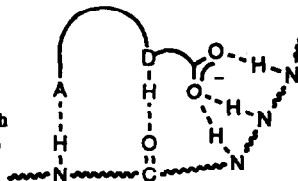
Intensive study of the cell growth inhibition and antineoplastic constituents of the sea hare Dolabella auricularia provided the structurally unique peptides designated dolastatins 1-15.

Tetrahedron, 1993, 49, 9171

RATIONAL DESIGN AND BINDING OF MODIFIED CELL-WALL PEPTIDES TO VANCOMYCIN-GROUP ANTIBIOTICS: FACTORISING FREE ENERGY CONTRIBUTIONS TO BINDING

Stephen E. Holroyd, Patrick Groves, Mark S. Searle, Ute Gerhard & Dudley H. Williams
Cambridge Centre for Molecular Recognition,
University Chemical Laboratories, Lensfield Road,
Cambridge CB2 1EW, UK.

Modified cell-wall peptides have been rationally designed and studied in a semi-quantitative approach to factorising free energy contributions in binding to ristocetin A in aqueous solution.

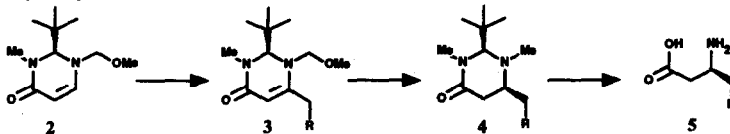


Tetrahedron, 1993, 49, 9183

SELF-REPRODUCTION OF CHIRALITY. ASYMMETRIC SYNTHESIS OF β -ALKYL- β -AMINO ACIDS FROM ENANTIOMERICALLY PURE DIHYDROPYRIMIDINONES

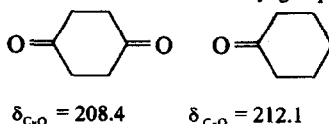
Kent S. Chu and Joseph P. Konopelski*
Department of Chemistry, University of California, Santa Cruz, CA 95064

Deprotonation at C6 of 2 affords a vinyl anion which can be alkylated or acylated in good to excellent yield, providing a route to β -alkyl- β -amino acids in enantiomerically pure form.



Transannular Orbital Interaction in Diketones Detected by ^{13}C NMR Spectroscopy. Jerome E. Gurst,* Ernest M. Schubert, Stefan E. Boiadjiev and David A. Lightner, Departments of Chemistry, The University of West Florida, Pensacola, FL 32514-5751 and The University of Nevada, Reno, NV 89514-0020 USA.

^{13}C NMR spectra of acyclic, monocyclic and polycyclic ketones and diketones demonstrate transannular orbital interaction in diketones. The shielding of the $^{13}\text{C}=\text{O}$ resonance frequency of the diketone relative to the monoketone depends on factors such as the number of intervening σ -bonds, relative orientation of the carbonyl groups and intervening σ -bonds.



Structural Determinants of Basicities of Peptides

Zhuchun Wu and Catherine Fenselau*

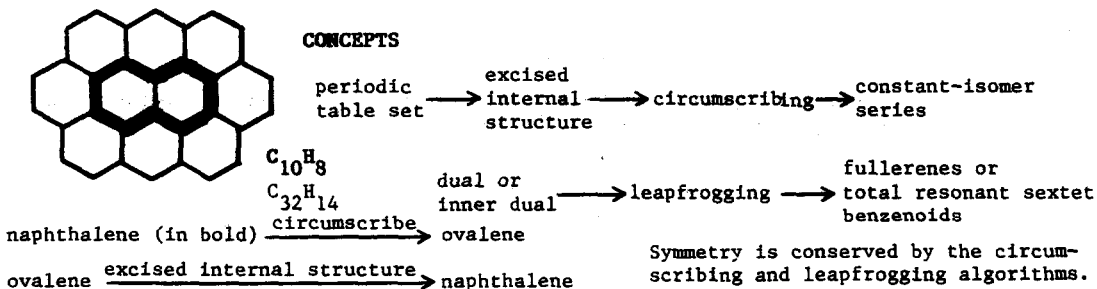
Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, MD 21228

Gas phase basicities have been measured for a series of peptides using the kinetic method illustrated here for glycylglycylalaline and glycylglycylvaline.



DECIPHERING THE INFORMATION CONTENT OF POLYCYCLIC CONJUGATED HYDROCARBON FORMULAS - FROM BENZENOIDS TO FULLERENES

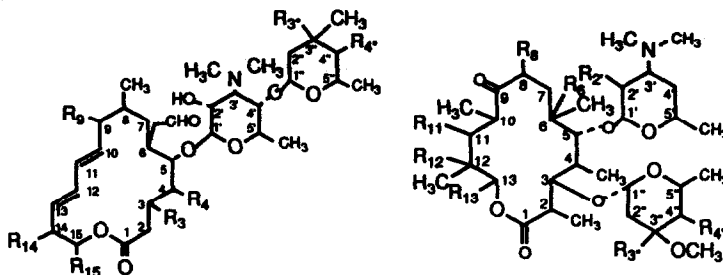
Jerry Ray Dias, Department of Chemistry, University of Missouri, Kansas City, MO 64110-2499



MACROLIDE ANTIBIOTIC STRUCTURE DETERMINATION BY FAST ATOM BOMBARDMENT/TANDEM MASS SPECTROMETRY

Y. Shida^{1,2}, L.J. Deterding¹, K. O'Hara², M. Kono², and K.B. Tomer¹ - ¹NIEHS, P.O. Box 12233, Res. Tri. Pk., NC 27709, ²Tokyo College of Pharmacy, Tokyo 192-03, Japan

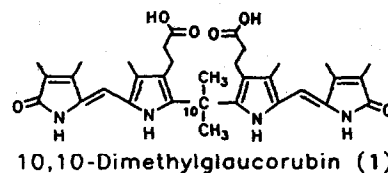
The MS/MS fragmentations of a series of 14- and 16-membered ring macrolide antibiotics are reported.



BILIRUBIN CONFORMATION AND INTRAMOLECULAR STERIC BUTTRESSING. C(10)-*gem*-DIMETHYL EFFECT

Meiqiang Xie, Darren L. Holmes and David A. Lightner*
Department of Chemistry, University of Nevada, Reno

An amphiphilic analog (1) of bilirubin with a *gem*-dimethyl group at C(10) adopts a folded intramolecularly hydrogen-bonded conformation similar to, but apparently flatter than, the most stable ridge-tile conformation of bilirubin or glaucorubin (2) (2 = 1 without the *gem*-dimethyls)—as determined by molecular dynamics calculations, ¹H-NMR analyses and circular dichroism spectroscopy.



LIQUID CHROMATOGRAPHY/MASS SPECTROMETRIC DETECTION OF ANATOXIN-A, A NEUROTOXIN FROM CYANOBACTERIA

Ken-ichi Harada, Hidetoshi Nagai, Yukio Kimura and Makoto Suzuki, Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

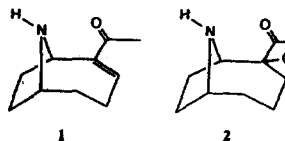
Ho-Dong Park, Department of Hygiene, School of Medicine, Shinshu University, Matsumoto, 390 Japan

Mariyo F. Watanabe, Tokyo Metropolitan Research Laboratory of public health, shinjuku, Tokyo 169, Japan

Raija Luukkainen and Kaarina Sivonen, University of Helsinki, Department of Microbiology, SF-00710, Finland

Wayne W. Carmichael, Department of biological Sciences, Wright State University, Dayton, Ohio 45435, U.S.A.

For a sensitive and specific detection of anatoxin-a (1), a neurotoxin from a cyanobacterium *Anabaena flos-aquae* and its degradation product (2), TSP-LS/MS was established. The method was successfully applied to trace analysis of 1 and 2 in laboratory and bloom cells and made possible the first detection of them in Japanese samples.



Tetrahedron, 1993, 49, 9261

Iridoid Glycosides from *Linaria* Species

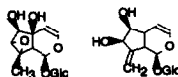
Nedjalka V. Handjieva, Emilia I. Ilieva, Stefan L. Spassov, Simeon S. Popov*

Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Helmut Duddeck

Institute of Organic Chemistry, University of Hannover, 3000 Hannover

The structure of two new iridoid glucosides, 7,8-*epi*-antirrinoside, from *L. dalmatica* and 6 β -hydroxyantirride from *L. genistifolia* and *L. peloponnesiaca*, were determined using spectroscopic techniques and molecular mechanics calculations.



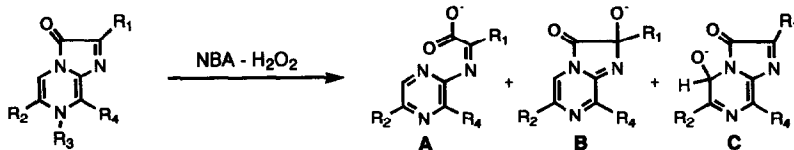
Tetrahedron, 1993, 49, 9267

Mass Spectrometric Studies on Chemiluminescence of Coelenterate Luciferin Analogues

Takashi Hirano, Sadatoshi Nishibuchi, Michiaki Yoneda, Kazuo Tsujimoto, and Mamoru Ohashi*

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

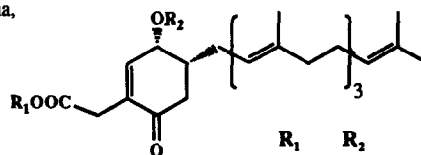
On the basis of the results of LSIMS under chemiluminescence conditions, the oxygenated ions of coelenterate luciferin analogues were observed, whose structures have been deduced as A, B, and C.



Tetrahedron, 1993, 49, 9277

EUNICENONES A AND B: DITERPENOID CYCLOHEXENONES OF A RARE SKELETAL CLASS FROM A NEW SPECIES OF THE CARIBBEAN GORGONIAN *EUNICEA*.

J. Shin and W. Fenical* Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0236



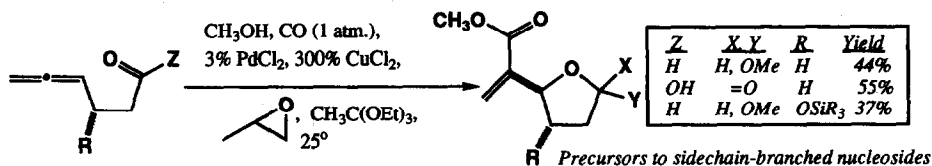
Eunicenones A and B (1, 2), compounds of a mixed biosynthetic origin, have been isolated from a new species of the Caribbean *Eunicea*. The structures of the new compounds were described by spectroscopic means and through chemical interconversions. The absolute stereochemistries of 1 and 2 were determined by a CD measurement of a corresponding benzoate derivative.

	R ₁	R ₂
1	Me	H
2	H	Ac

FURANOSIDES AND FURANONES BEARING ACRYLATE SIDECHAINS VIA PALLADIUM-MEDIATED CYCLIZATIONS OF γ -OXOALLENES

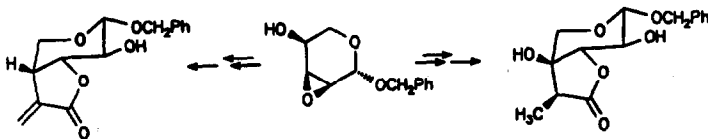
Robert D. Walkup* and Michael D. Mosher

Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, TX 79409-1061

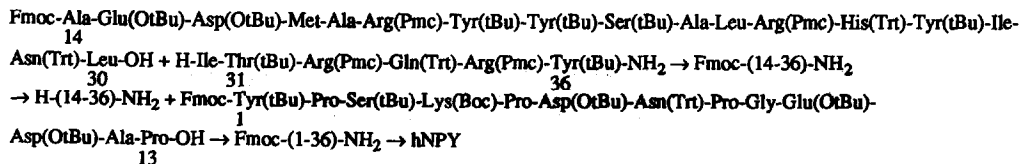

Stereoselective Synthesis of β -Oxy- and α -Methylene- γ -Butyrolactones on Pyranose Templates

Yousef Al-Abed, Taleb H. Al-Tel and Wolfgang Voelter*

Abteilung für Physikalische Biochemie des Physiologisch-chemischen Instituts der Universität Tübingen, Hoppe-Seyler-Straße 4, D-7400 Tübingen, Germany.


A GENERAL STRATEGY FOR THE SYNTHESIS OF LARGE PEPTIDES: THE COMBINED SOLID-PHASE AND SOLUTION APPROACH.
Bernhard Riniker, Andreas Florschütz, Heinz Fretz, Peter Sieber, and Bruno Kamber
Pharmaceutical Division, Ciba-Geigy Limited, Basle, Switzerland

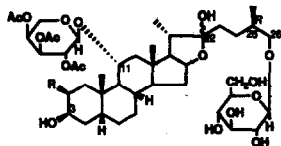
Large peptides are built up in solution from smaller segments with lipophilic protecting groups, which can be prepared by solid-phase synthesis. The scheme below depicts the synthesis of human NPY using this method.



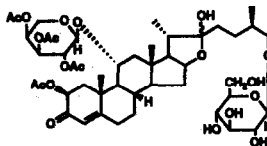
**STRUCTURE ELUCIDATION OF FUROSTANOL GLYCOSIDES
USING LIQUID SECONDARY ION MASS SPECTROMETRY**

Yuji Ikenishi, Shinya Yoshimatsu, Ken'ichi Takeda* and Yuzo Nakagawa*
Shionogi Research Laboratories, Shionogi & Co., Ltd., Fukushima-ku, Osaka 553, Japan
* Deceased on 14th April, 1991.

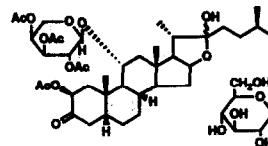
The structure elucidation of five genuine furostanol glycosides by LSIMS and LSIMS/MS and MO calculation for the stabilization feature of $[M + Na]^+$ were carried out.



FG-1 (1) : R=OAc $C_{46}H_{72}O_{19}$ (928)
FG-2 (2) : R=OH $C_{44}H_{70}O_{18}$ (886)
FG-3 (3) : R=H $C_{44}H_{70}O_{17}$ (870)



FG-4 (4) : $C_{46}H_{68}O_{19}$ (924)



FG-5 (5) : $C_{46}H_{70}O_{19}$ (926)

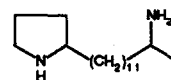
**ALKALOIDS OF THE MEXICAN BEAN BEETLE,
Epilachna varivestis (COCCINELLIDAE)**

Athula B. Attygalle,* Shang-Cheng Xu, Kevin D. McCormick, and Jerrold Meinwald,
Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853

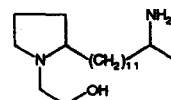
Curtis L. Blankespoor and Thomas Eisner

Section of Neurobiology and Behavior, Cornell University, Ithaca, New York 14853

Several new alkaloids, including 2-(12-aminotridecyl)-pyrrolidine (G) and its 1-(2-hydroxyethyl) derivative (I), are characterized from extracts of adult Mexican bean beetles.



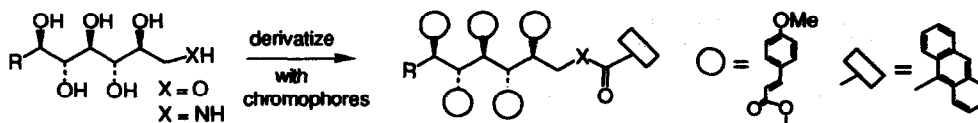
G



I

Assignment of Relative and Absolute Configuration of Acyclic
Polyols and Aminopolyols by Circular Dichroism - Trends Follow Fischer's Sugar Family Tree

Peng Zhou^a, Nikolina Berova^{a,b}, William T. Wiesler^a and Koji Nakanishi, ^{a*} a) Department of Chemistry, Columbia University, New York, N.Y. 10027, USA. b) On leave from the Institute of Organic Chemistry, Bulg. Acad. Sci., BG-1113 Sofia.

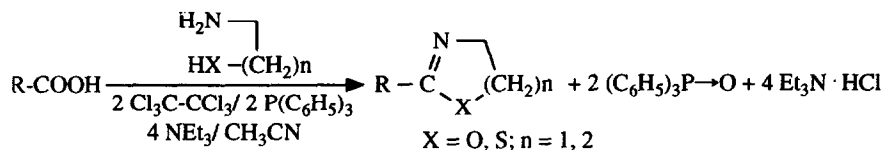


The CD curves of bichromophorically derivatized acyclic 1,2-polyols and 1-aminopolyols, when measured in methylcyclohexane, show a distinct general trend allowing for assignment of configuration in polyols up to 1,2,3,4,5-pentols and 1-amino-2,3,4,5-tetrols. Systematic trends allow one to use these reference curves for assignment of configuration in higher homologs (i.e., 1,2,3,4,5,6-hexols).

A SIMPLE SYNTHESIS OF Δ^2 -OXAZOLINES, Δ^2 -OXAZINES, Δ^2 -THIAZOLINES AND 2-SUBSTITUTED BENZOXAZOLES

Helmut Vorbrüggen and Konrad Krolkiewicz

Research Laboratories of Schering AG; D-1000 Berlin 65; Germany



Carboxylic acids react with amino alcohols, amino mercaptans and o-aminophenols in the presence of triphenylphosphine dichloride and triethylamine at 23°C in acetonitrile to the corresponding Δ^2 -oxazolines, Δ^2 -oxazines, Δ^2 -thiazolines and 2-substituted benzoxazoles in up to 80% yield.

THE SYNTHESIS OF 1R- AND 1S-5-METHYLENYLCAMPHOR AND THEIR EPOXIDATION BY CYTOCHROME P-450-CAM.

David M. Maryniak,¹ Saloumeh Kadkhodayan,¹ George B. Crull,² Thomas A. Bryson¹ and John H. Dawson^{1,3*}
¹Department of Chemistry and Biochemistry and the ³School of Medicine, University of South Carolina,
Columbia, SC 29208 and ²Department of Chemistry, State University of New York, Stony Brook, NY 11794

The syntheses of the title compounds from 5-oxoborneol and their epoxidation by cytochrome P-450-CAM are described.

