GRAPHICAL ABSTRACTS

FARNESYL CHAIN MODIFICATION OF SQUALENE SYNTHASE INHIBITOR BENZYLFARNESYLAMINE: CONVERSION TO THE TERMINAL BIS(TRIFLUOROMETHYL) DERIVATIVE

Charles F. Jewell Jr.,* John Brinkman, Russell C. Petter and James R. Wareing

Department of Atherosclerosis and Vascular Biology, Preclinical Research

Sandoz Research Institute, Sandoz Pharmaceuticals Corporation

East Hanover, NJ 07936

PPh₃ I
$$\Theta$$
TEOC $\frac{1. \text{BuLi}}{2. \text{Dec}}$
F₃C Θ
TEOC

61%

Prepared from benzylfarnesylamine in 7 steps (29% overall)

TEOC group removed with BF₃•Et₂O (60%) with no isomerization of sensitive (F₃C)₂-olefin

CONFORMATIONAL ANALYSIS OF DIRITHROMYCIN AND EPI-DIRITHROMYCIN

John M. McGill and Ross A. Johnson Lilly Research Laboratories, Eli Lilly and Company Lafayette, IN 47902

The solution conformation of dirithromycin and epi-dirithromycin was determined using NMR spectroscopy in conjunction with molecular mechanics calculations. In solution, dirithromycin exists in a "folded-in" conformation, while epi-dirithromycin exists in a "folded-out" conformation.

Tetrahedron, 1994, 50, 3857

Tetrahedron, 1994, 50, 3849

CH₃OCH₂CH₂OCH₂ 22 NHH

HO
OH
OH
OCH₃
OCH

Isolation and Relay Synthesis of 11α-Hydroperoxy Diacetyl Hederagenin,

a Novel Triterpenoid Derivative from Serjania triquetra (Sapindaceae). Biogenetic Implications.

María Isabel Chávez and Guillermo Delgado*

Instituto de Química de la UNAM. Ciudad Universitaria, Circuito Exterior. Coyoacán 04510. México, D. F.

The novel triterpenoid derivative and key biogenetic and chemical intermediate 3, was isolated, and synthesized from 1. via 2.

Configurational Analysis of New Furanosesquiterpenes from *Dysidea herbacea*. Assignment of Absolute Stereochemistry.

Tetrahedron, 1994, 50, 3879

Tetrahedron, 1994, 50, 3869

Philip A. Searle, Naser M. Jamal, Greg M. Lee and Tadeusz F. Molinski*, Department of Chemistry, University of California, Davis, CA 95616

Isomeric acetates (+)-1 and (+)-2 and their respective enantiomers, 17 and 18, were isolated from two samples of the marine sponge *Dysidea herbacea* which appears to have a dual capacity for antipodal cyclization of geranyl pyrophosphate to furodysin or furodysinin and elaboration of these oxidized derivatives.

SYNTHETIC STUDIES ON THE KEY COMPONENT OF THE NEW GENERATION OF QUINOLONECARBOXYLIC ACID, DU-6859. 1.

Tetrahedron, 1994, 50, 3889

SYNTHESIS OF (1R,2S)-2-FLUOROCYCLOPROPYLAMINE BY THE USE OF OPTICAL RESOLUTION

Osamu Tamura, a) Masaru Hashimoto, a) Yuko Kobayashi, a) Tadashi, Katoh, a) Kazuhiko Nakatani, a)

Masahiro Kamada, b) Isao Hayakawa, c) Toshifumi Akiba, b) and Shiro Terashima**

Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan^{a)}; Production Technology Research Laboratories, ^{b)} Exploratory Research Laboratories, ^{c)} Daiichi Pharmaceutical Co., Ltd., Kita-Kasai, Edogawa, Tokyo 134, Japan

SYNTHETIC STUDIES ON THE KEY COMPONENT OF THE NEW GENERATION OF QUINOLONCARBOXYLIC ACID, DU-6859. 2.

Tetrahedron, 1994, 50, 3905

ASYMMETRIC SYNTHESIS OF (1R,2S)-2-FLUOROCYCLOPROPYLAMINE
Toshifumi Akiba, a) Osamu Tamura, b) Masaru Hashimoto, b) Yuko Kobayashi, b) Tadashi, Katoh, b) Kazuhiko Nakatani, b)

Masahiro Kamada. a) Isao Havakawa. c) and Shiro Terashima *b)

Production Technology Research Laboratories, a) Exploratory Research Laboratories, c) Daiichi Pharmaceutical Co., Ltd.,

Kita-Kasai, Edogawa, Tokyo 134, Japan; Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan^{b)}

HO
$$\mathbb{R}^2 \mathbb{R}^1$$
 O $\mathbb{R}^2 \mathbb{R}^1$ O $\mathbb{R}^2 \mathbb{R}^2$ O $\mathbb{R}^2 \mathbb{R}^2$ O \mathbb{R}^2 O

SYNTHESIS OF SAFRAMYCINS, IX, AN EFFICIENT SYNTHESIS OF THE ABC RING OF SAFRACINS.

Naoki Saito, Yasuko Obara, Tomoko Aihara, Shunji Harada, Yukiko Shida, and Akinori Kubo*

Meiji College of Pharmacy, 1-35-23 Nozawa, Setagaya-ku, Tokyo 154, Japan

1,2,3,4,5,6-Hexahydro-10-hydroxy-1,5-imino-9-methoxy-3,8,11-trimethyl-3-benzazocine 1 embodying all of the skeletal features of the ABC ring of safracins has been synthesized from compound 2 via a direct regioselective bromination, followed by the sequence reduction, metal-halogen interchange, and reaction of the organometallic intermediate with nitrobenzene. And the conversion of 2 to a p-quinone 3 is also described.

Tetrahedron, 1994, 50, 3915

Highly Diastereoselective Formation of Bicyclic Compounds by Intramolecular Cycloaddition of Chiral Thiaalkenyl Nitrones

Tetrahedron, 1994, 50, 3929

Hans Günter Aurich*, Jose-Luis Ruiz Quintero Fachbereich Chemie der Philipps-Universität Marburg, D-35032 Marburg, Germany

Bicyclic compounds with four or five contiguous chiral centers arose by spontaneous intramolecular cycloaddition of the corresponding alkenyl nitrones.

BZ

R²

R1

NR7

Effects of Configuration and N-Substitution on the Formation of β-Lactams from Bicyclic Cyano-substituted Isoxazolidines

Tetrahedron, 1994, 50, 3943

Hans Günter Aurich*, Jose-Luis Rniz Onintero

Fachbereich Chemie der Philipps-Universität Marburg, D-35032 Marburg, Germany

Treatment of 4-cyano-3-oxa-7-thia-2-azabicyclo[3,3,0]octanes with lithium diisoproylamide afforded bicyclic 8-lactams.

CLAISEN REARRANGEMENT OF N-SILYL KETENE N,O-ACETALS GENERATED FROM ALLYL N-PHENYLIMIDATES

Tetrahedron, 1994, 50, 3951

Peter Metz* and Cornelia Linz

Organisch-Chemisches Institut der Universität Münster, Corrensstraße 40. D-48149 Münster, Germany

Highly diastereoselective Claisen rearrangements yielding anilides 3 via deprotonation / silylation of allyl N-phenylimidates 1 are reported. Additionally, NOE difference studies of educts and N-silyl ketene N,O-acetals are described.

REACTIVITY OF PYRROLE PIGMENTS: PART 16.

MESOBILIVERDIN IXa AND MESOBILIRUBIN IXa

BRIDGED BETWEEN THE PROPIONIC ACID SUBSTITUENTS.

Josep M. Ribó*, Joaquim Crusats, and Montserrat Marco.

Departament de Ouímica Orgànica, Universitat de Barcelona, c/ Martí i Franquès I. E-08028, Catalonia, Spain

For n = 1 reactivity towards hu, Nu , H+, B , Zn(II)

is compared with that of mesobiliverdin IXa dimethyl ester.

For n = 1 the corresponding mesobilirubin is also obtained

and compared to mesobilrubin IXα dimethyl ester.

Tetrahedron, 1994, 50, 3975

Tetrahedron, 1994, 50, 3967

AN EXPEDITIOUS ASYMMETRIC SYNTHESIS OF ALLOPHENYLNORSTATINE

Mark E. Bunnage, Stephen G. Davies, * Christopher J. Goodwinb and Osamu Ichihara

a The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY, UK

b Fisons plc, Pharmaceutical Division, Research and Development Laboratories, Bakewell Road, Loughborough, LE11 ORH, UK

Allophenylnorstatine, the pivotal amino acid in the kynostatin HIV-1 protease inhibitors, has been prepared in 39% overall yield via a tandem lithium amide conjugate addition-electrophilic hydroxylation protocol.

ALKALOIDS FROM THE ANTARCTIC SPONGE KIRKPATRICKIA VARIALOSA. PART 1: VARIOLIN B, A NEW ANTITUMOUR AND ANTIVIRAL COMPOUND

Nigel B. Perry, *Laurent Ettouati, *Marc Litaudon, *John W. Blunt, *Murray H. G. Munro, *Sean Parkin *‡ and Hakon Hope. *‡

^oDepartment of Chemistry, University of Canterbury, Christchurch, New Zealand and [†]Department of Chemistry, University of California, Davis, CA 95616, USA

The title compound has been characterised by X-ray crystallography, and a degradation product, variolin D, identified from its spectral data.

Tetrahedron, 1994, 50, 3993

CH₃ NH₂ OH NH₂ CH₃ OH NH₂ NH₂ NH₂

variolin A N(3')-methyl tetrahydrovariolin B ALKALOIDS FROM THE ANTARCTIC SPONGE KIRKPATRICKIA VARIALOSA. PART 2: VARIOLIN A AND N(3')-METHYL TETRAHYDRO-VARIOLIN B

Golakoti Trimurtulu,* D. John Faulkner,* Nigel B. Perry, * Laurent Ettouati, * Marc Litaudon. * John W. Blunt, * Murray H. G. Munro* and Geoffrey B Jameson. *

**Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0212, USA, **Department of Chemistry, University of Canterbury, Christchurch, New Zealand and **Department of Chemistry, Georgetown University, Washington, DC 20057, USA

The title compounds, which are both cytotoxic, have been characterised by X-ray crystallography and interpretation of spectral data.

Tetrahedron, 1994, 50, 4001

RADICAL-CHAIN ADDITION OF BENZENETHIOL TO ALLENIC ESTERS: EPR AND PRODUCT STUDIES

Salvatore Cabiddu, Claudia Fattuoni*

Dipartimento di Scienze Chimiche, Università, via Ospedale 72, I-09124 Cagliari, Italy

Marco Lucarini, Gian Franco Pedulli

Dipartimento di Chimica Organica "A. Mangini", Università, via S. Donato 15, I-40127 Bologna, Italy

The radical addition of benzenethiol to the title compounds has been studied. The reaction products have been identified by ¹H NMR and the intermediate radicals detected by EPR spectroscopy.

$$R_1$$
 $C=C=C$ R_2 R_1 $COOCH_3$ $PhSH$ R_2 $Products$

SYNTHESIS AND COMPLEMENTARY COMPLEX FORMATION PROPERTIES OF OLIGONUCLEOTIDES COVALENTLY LINKED TO NEW STABILIZING AGENTS.

Tetrahedron, 1994, 50, 4009

A. Balbi*, E. Sottofattori, T. Grandi, M. Mazzei -Institute of Pharmaceutical Sciences, Viale Benedetto XV, 3 - Genoa (Italy); T.V. Abramova, S.G. Lokhov, A.V. Lebedev*-Institute of Bioorganic Chemistry, Novosibirsk (Russia).

Oligodeoxyribonucleotides (ODNs) of different lengths have been linked to the new stabilizing agents (SAs) 2-5 related to the coumarin family and tested against acridine connected oligomers of the

same sequence. Melting temperature experiments demonstrated that all ODNSAs formed complexes of increased stability with complementary sequences of deoxyribo-20-mer.

LACCASE ENZYME CATALYSED EFFICIENT SYNTHESIS OF

Tetrahedron, 1994, 50, 4019

3-SUBSTITUTED-1,2,4-TRIAZOLO(4,3-b)(4,1,2)BENZOTHIADIAZINE-8-ONES

U.T. BHALERAO*, C. MURALIKRISHNA & B. RADHA RANI

Organic Division II, Indian Institute of Chemical Technology, Hyderabad - 500 007, INDIA.

Full details of an efficient one step synthesis of 3-substituted-1,2,4-triazolo(4,3-b)(4,1,2)benzothiadiazine-8-ones(4) by Laccase enzyme (E.C.1.10.3.2) mediated reaction of various 5-substituted-4-amino-3-mercapto-1,2,4-triazoles (1) and hydroquinone(2) is described.

EFFICIENT SYNTHESIS OF 3-MONO AND DISUBSTITUTED

Tetrahedron, 1994, 50, 4025

LACTAMS USING MEERWEIN ESCHENMOSER [3,3] SIGMATROPIC REARRANGEMENTS.

Brian Coates, David Montgomery and Paul J. Stevenson.* School of Chemistry, The Queen's University of Belfast, Belfast, BT9 5AG, N. Ireland.

Methoxymethyleniminium triflate or methylsulphate salts react with allyl alkoxides to give 3-allyl substituted lactams in good yield. Twelve examples given.

$$(CH_2)_n$$
 N^+ OMe $(CH_2)_n$ N OMe $(CH_2)_n$ N O

64% yield R^{1} =Me, n = 1.