

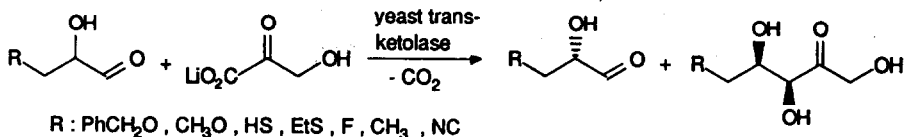
GRAPHICAL ABSTRACTS

Tetrahedron Lett. 1992, 33, 5157

PREPARATION OF OPTICALLY PURE L-2-HYDROXYALDEHYDES WITH YEAST TRANSKETOLASE

Franz Effenberger*, Volker Null and Thomas Ziegler, Institut für Organische Chemie, Universität Stuttgart

L-2-Hydroxyaldehydes and 5-substituted 2-ketoses are obtained via transketolase-catalyzed reaction of racemic 2-hydroxyaldehydes with lithium hydroxypyruvate.

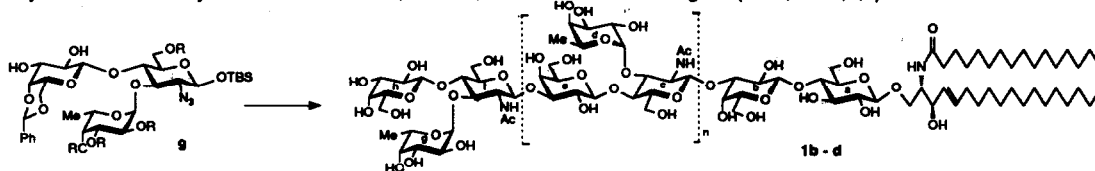


Tetrahedron Lett. 1992, 33, 5161

AN EFFICIENT SYNTHESIS OF THE LEWIS X (Le^x) ANTIGEN FAMILY

Alexander Toepfer and Richard R. Schmidt
Fakultät Chemie, Universität Konstanz, D-7750 Konstanz, Germany

Trisaccharide building block **9**, readily obtained from 2-azido-2-deoxy-D-glucose, L-fucose, and D-galactose, proved to be very versatile for the synthesis of the dimeric, trimeric, and tetrameric Le^x antigens (**1b-d**; n = 1,2,3).

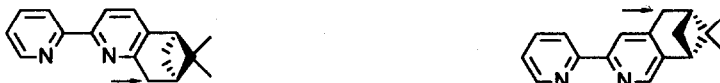


Tetrahedron Lett. 1992, 33, 5165

NEW VERSATILE OPTICALLY ACTIVE BIPYRIDINES AS BUILDING BLOCKS FOR HELICATING AND CAGING LIGANDS

Pascal Hayoz and Alex von Zelewsky*
Institute of Inorganic Chemistry, University of Fribourg, Péroilles, CH-1700 Fribourg, Switzerland

Chiral building blocks for the synthesis of heliacting and caging ligands with rigid frame works. The new bipyridines are easily prepared in two step reactions using α -pinene as source of chirality. They can be transformed by alkylation etc. at the indicated positions.

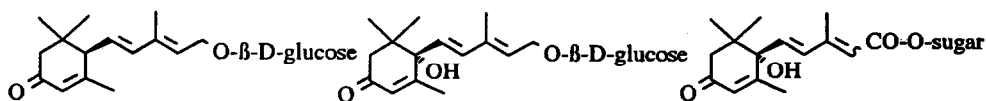


Tetrahedron Lett. 1992, 33, 5169

BIO-OXIDATIVE CLEAVAGE OF CAROTENOIDS: IMPORTANT ROUTE TO PHYSIOLOGICAL ACTIVE PLANT CONSTITUENTS

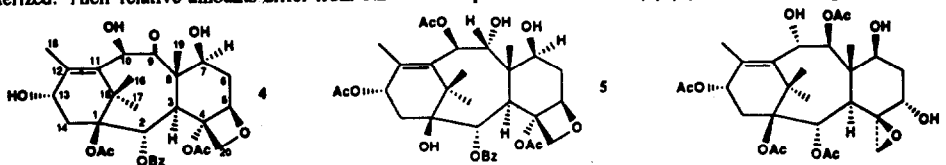
Andrea Lutz and Peter Winterhalter, Lehrstuhl für Lebensmittelchemie der Universität Würzburg
Am Hubland, 8700 Würzburg, Germany

New C₁₅-constituents in quince fruit:



TAXANES ISOLATED FROM TAXUS CANADENSIS

Lolita O. Zamir^{a,b}, Maria E. Nadea^a, Sophie Bélair^a, Françoise Sauriol^a, Orval Mamer^a, Emile Jacquain^d, France I. Jean^a, and François X. Garneau^a. Université du Québec: Institut Armand Frappier^a and Chicoutimi^c, McGill University^{b,c}, Jardin Botanique de Montréal^d. Eight taxanes isolated from *Taxus canadensis* have been rigorously characterized. Their relative amounts differ from other *Taxus* species. Metabolites (4,5,8) had not been reported in other yews.

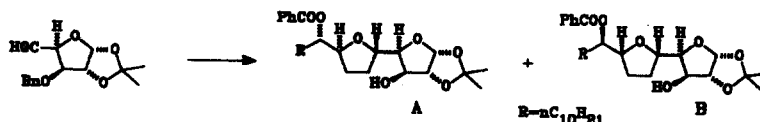


APPROACH TO THE SYNTHESIS OF ANNONACEOUS ACETOGENINS FROM D-GLUCOSE.

Philippe Bertrand and Jean-Pierre Gesson

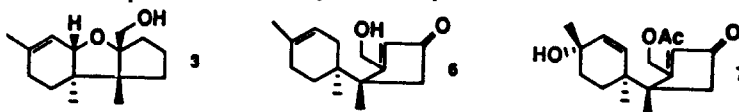
Laboratoire de Chimie 12, Associé au CNRS, 40, Avenue du Recteur Pineau, F-86022 Poitiers.

The conversion of D-Glucose to the *cis* and *trans* fused acetogenin synthons A and B has been carried out using as the key step an epoxidation-cyclization.



STRUCTURES OF NEW METABOLITES FROM FUSARIUM SPECIES: AN APOTRICHOTHECENE AND OXYGENATED TRICHODIENES.

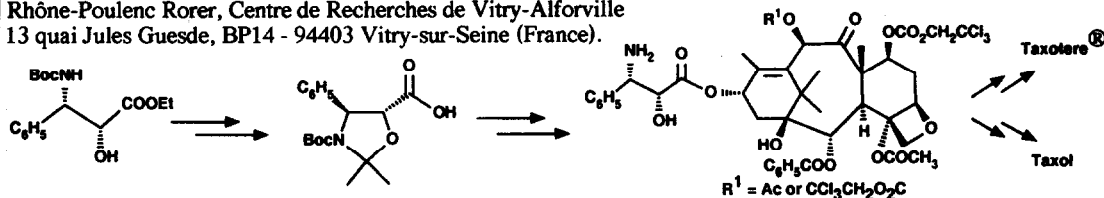
Lolita O. Zamir^{a,b}, Kenneth A. Devor^a, Anastasia Nikolakakis^a, Yves Nadeau^{a,c}, Françoise Sauriol^a. ^a Centre de recherche en Microbiologie Appliquée, Université du Québec, Institut Armand Frappier, 531, boul. des Prairies, Laval, Québec, Canada, H7N 4Z3; ^b Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6; ^c Presently at Merck Frosst, Pointe-Claire. Three new metabolites were isolated from *Fusarium spp*, one apotrichothecene 3 and two oxygenated derivatives 6, 7 of trichodiene. The apotrichothecene was a precursor to apotrichodiol and sambucinol.



IMPROVED PROTECTION AND ESTERIFICATION OF A PRECURSOR OF TAXOTERE[®] AND TAXOL SIDE CHAINS

A. Commerçon, D. Bézard, F. Bernard and J.D. Bourzat

Rhône-Poulenc Rorer, Centre de Recherches de Vitry-Alforville 13 quai Jules Guesde, BP14 - 94403 Vitry-sur-Seine (France).

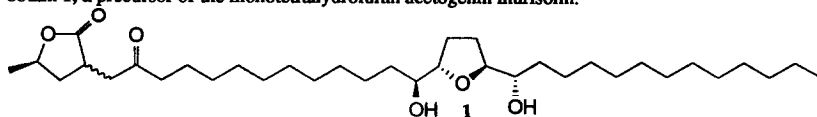


Synthesis of 2,3,3-Dihydro-4-Oxo-Murisolin : Conjugate Addition of Primary Alkyl Iodides to α,β -Unsaturated Ketones

Bruno Figadère*, Jean-Christophe Harmange, Liu Xiao Hai and André Cavé

Laboratoire de Pharmacognosie, associé au C.N.R.S. Faculté de Pharmacie 92296 Châtenay-Malabry(France)

The conjugate addition of an highly functionalized primary alkyl iodide to an enone allows us to obtain 1, a precursor of the monotetrahydrofuran acetogenin murisolin.

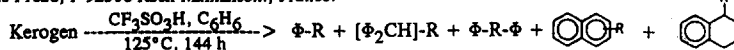


Chemical Characterization of Oil Shale Kerogens Using A Transalkylation Reaction

A. Ambès^a, N. Baudet^a, J.C. Jacquesy^a, A. Kribii^a and M. Vandenbroucke^b

a) Laboratoire de Chimie 12, 40 Av. du Recteur-Pineau, F-86022 Poitiers.

b) I.F.P., 2-4 Av. de Bois-Préau, F-92506 Rueil-Malmaison., France.



The sequence $\phi\text{-Cx} \rightarrow [\text{tetraline}]\text{-Cx-4} \rightarrow [\text{naphthalene}]\text{-Cx-4}$ and $\phi\text{-Cx} \rightarrow [\phi_2\text{CH}]\text{-Cx-1}$ was demonstrated in the same conditions. The distribution of alkyl chains substituting initially the aromatics of kerogens and transferred on benzene was then established in the two studied kerogens.

Solid Phase Synthesis of a Cyclic Peptide Derived from a Curaremimetic Toxin

Anne Tromelin*, Marie-Hélène Fulachier, Gilles Mourier and André Ménez

Département d'Etudes et d'Ingénierie des Protéines. Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette Cedex, France

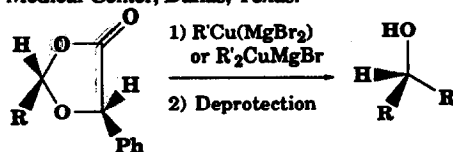
The design and synthesis of a cyclic peptide corresponding to a partial sequence of toxin α of *Naja nigricollis* is described.

c(-Asn-Tyr-Lys-Lys-Val-Trp-Arg-Asp-Ile-Arg-Gly-Thr-Ile-Ile-Glu-Arg-Gly-Pro-)

Nucleophilic Substitution at the Acetalic Center of Mandelate 1,3-Dioxolan-4-ones using Magnesium-Copper Reagents: Application to the Synthesis of Chiral Secondary Alcohols.

B. Heckmann, C. Mioskowski, J. Yu and J.R. Falck, Université Louis Pasteur, Faculté de Pharmacie, Illkirch-France; University of Texas Southwestern Medical Center, Dallas, Texas.

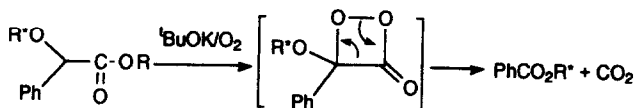
Ethereal magnesium-copper reagents add stereoselectively to mandelic acid derived 1,3-dioxolan-4-ones to afford optically active secondary alcohols after removal of the chiral auxiliary.



OXIDATIVE DECARBOXYLATION OF MANDELATE ETHERS AND α -PHENYLACETATES VIA DIOXETANONE GENERATION

B. Heckmann, C. Alayrac, C. Mioskowski*, S. Chandrasekhar and J.R. Falck*,
Univ. Louis Pasteur, Faculté de Pharmacie, 67401 Illkirch, Fr. and Depts of Molecular Genetics and Pharmacology, Univ. of Texas Southwestern Medical Center, Dallas, Texas 75235 U.S.A.

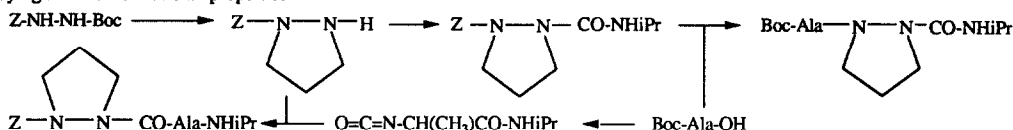
Mandelate ethers are oxidatively decarboxylated via in situ generated dioxetanones using t BuOK and air at ambient temperature leading, after hydrolysis, to the benzoic acid and the corresponding alcohol.



THE COUPLE PRO/AZAPRO : A MEANS OF β -TURN FORMATION CONTROL SYNTHESIS AND CONFORMATION OF TWO AZAPRO-CONTAINING DIPEPTIDES

Alain Lecoq, Guy Boussard*, André Aubry and Michel Marraud
CNRS-URA-494, ENSIC-INPL, BP 451, 54001 Nancy, France

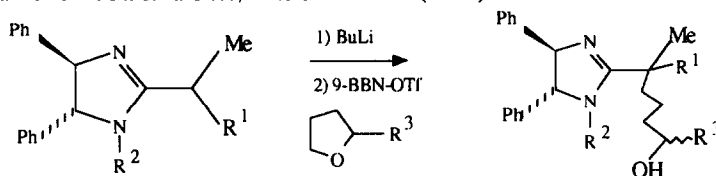
Combining peptide synthesis methods and the use of appropriate isocyanates, two AzaPro-containing dipeptides have been prepared before studying their conformational properties.



9-BBN Triflate Mediated Stereoselective Alkylation of 2-alkyl Imidazolines with Tetrahydrofurans

Peter I. DALKO and Yves LANGLOIS*

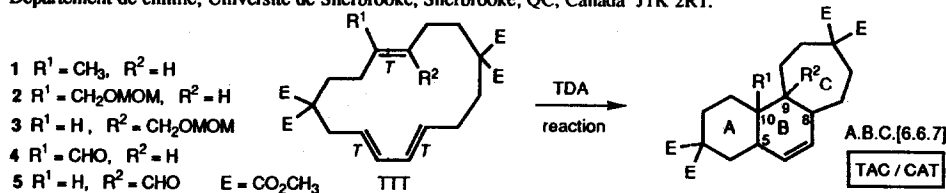
Laboratoire de Synthèse des Substances Naturelles, associé au CNRS, ICMO,
Bât. 410 - Université de Paris-Sud, 91405 ORSAY Cedex (France)



TRANSANNULAR DIELS-ALDER REACTION OF TRANS-TRANS-TRANS 15-MEMBERED MACROCYCLIC TRIENES.

Dennis G. Hall, Renate Müller and Pierre Deslongchamps.

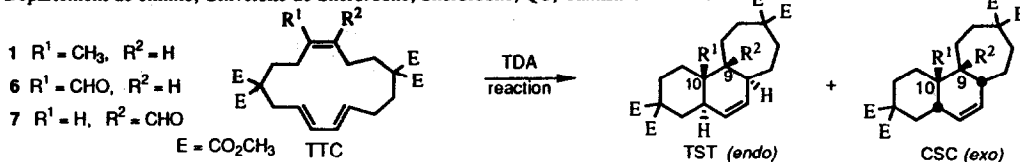
Département de chimie, Université de Sherbrooke, Sherbrooke, QC, Canada J1K 2R1.



TRANSANNULAR DIELS-ALDER REACTION OF TRANS-TRANS-CIS 15-MEMBERED MACROCYCLIC TRIENES. EVIDENCE FOR ASYNCHRONOUS TRANSITION STATE.

Dennis G. Hall, Renate Müller and Pierre Deslongchamps.

Département de chimie, Université de Sherbrooke, Sherbrooke, QC, Canada J1K 2R1.

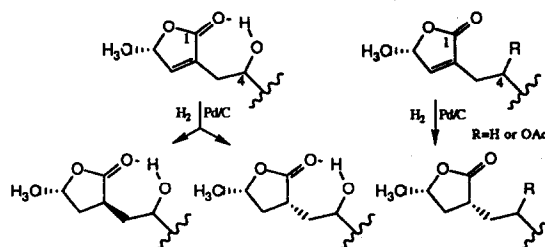


CATALYTIC HYDROGENATION OF ANNONACEOUS ACETOGENINS

Diego CORTES*, Saw H. MYINT, Jean C. HARMANGE, Sevser SAHPAZ and Bruno FIGADERE*

Laboratoire de Pharmacognosie, Faculté de Médecine et Pharmacie, Université de Rouen, 76800 Saint Étienne du Rouvray; and Laboratoire de Pharmacognosie, UA-CNRS, Faculté de Pharmacie, Université Paris-Sud, 92290 Châtenay-Malabry, France.

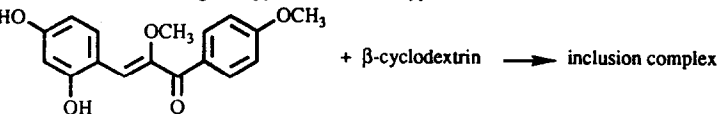
Catalytic hydrogenation of cytotoxic Annonaceous acetogenins afforded two or one diastereoisomers whenever the γ -lactone acetogenin possess or not an hydroxyl group at the 4-position.



Two very distinct types of anthocyanin complexation: copigmentation and inclusion

O. Dangles, C. Stoeckel, M. C. Wigand and R. Brouillard* Laboratoire de Chimie des Polyphénols associé au CNRS (URA31), Université Louis Pasteur, Faculté de Chimie, 1 rue Blaise Pascal, 67 Strasbourg, France

Abstract: Some natural and synthetic anthocyanic pigments are studied for their ability to give inclusion complexes into cyclodextrins. The effect of inclusion on colour (fading) is opposed to that of typical molecular interactions involving anthocyanins (copigmentation).

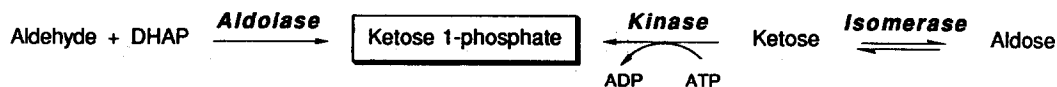


ENZYMATIC SYNTHESIS OF RARE KETOSE 1-PHOSPHATES.

Wolf-Dieter Fessner,* Josefa Badia, Oliver Eyrisch, Achim

Schneider, and Gudrun Sinerius. Department of Organic Chemistry and Biochemistry, University of Freiburg, W-7800 Freiburg i. Br., Germany

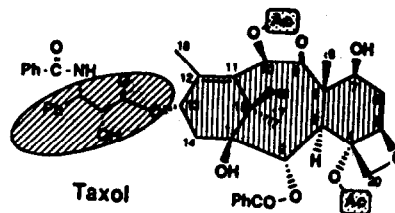
Ketose 1-phosphates are prepared from aldehydes by enzymatic aldol addition of dihydroxyacetone phosphate, and from aldoses (or ketoses) by isomerization and phosphorylation using overexpressed microbial enzymes.



Tetrahedron Lett. 1992, 33, 5235

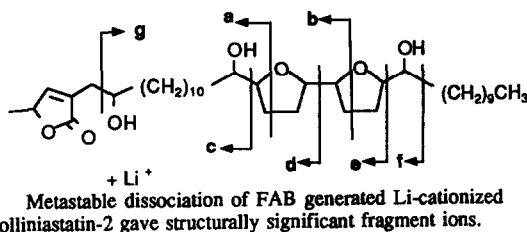
BIOSYNTHETIC BUILDING BLOCKS OF TAXUS CANADENSIS

TAXANES Lolita O. Zamir*, Maria E. Nodda*, and François X. Garneau*. *Centre de recherche en Microbiologie Appliquée, Université du Québec, Institut Armand Frappier, 531, boul. des Prairies, Laval, Québec, Canada, H7N 4Z3, *Université du Québec à Chicoutimi, 555 boul de l'Université, Chicoutimi, Québec, Canada G7H 2B1. Radiolabelling feeding experiments have confirmed that acetate, mevalonate and phenylalanine represent the biosynthetic building blocks of *Taxus canadensis* taxanes. The shadings emphasize the acetate (⊙) mevalonate (|||) and phenylalanine (///) building blocks.



Formation of Gas-Phase Lithium Complexes from Acetogenins and their Analysis by Fast Atom Bombardment Mass Spectrometry

Olivier Laprèvote, Christian Girard, Bhupesh C. Das Institut de Chimie des Substances Naturelles, C.N.R.S., av. de la Terrasse, 91198 Gif-sur-Yvette Cedex, France. Diego Cortes Facultad de Médecine et de Pharmacie, Université de Rouen, 76800 Saint-Etienne du Rouvray, France and André Cavé* Faculté de Pharmacie, U.A. C.N.R.S., rue J.-B. Clément, 92296 Châtenay-Malabry, France.



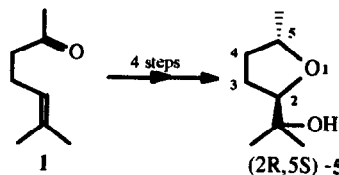
Tetrahedron Lett. 1992, 33, 5237

SYNTHESIS OF OPTICALLY PURE PITYOL - A PHEROMONE OF THE BARK BEETLE PITYOPHTHORUS PITYOGRAPHUS - USING A CHEMOENZYMATIC ROUTE.

A. ARCHELAS and R. FURSTOSS

Groupe de Chimie Organique et Bioorganique, associé au CNRS Faculté des Sciences de Luminy, case 901; 163, av. de Luminy F - 13288 Marseille Cedex 9

A four step synthesis of (2R,5S)-pityol 5, the pheromone of *Pityophthorus pityographus*, is described using in particular two highly stereoselective microbiologically mediated reactions

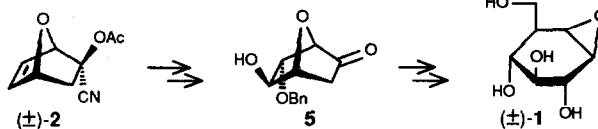


Tetrahedron Lett. 1992, 33, 5241

TOTAL SYNTHESIS OF CYCLOHELLITOL STARTING FROM FURAN

Viviane Moritz, Pierre Vogel*, Section de chimie de l'Université de Lausanne, 2, rue de la Barre, CH 1005 Lausanne, Switzerland.

The Diels-Alder adduct (±)-2 of furan to 1-cyanovinyl acetate was converted into (±)-cyclohellitol ((±)-1) via ketone 5.



Tetrahedron Lett. 1992, 33, 5243

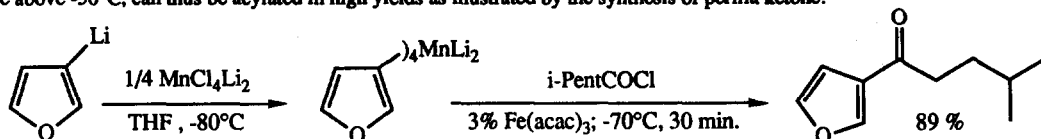
A New Simple Route to Furanic Ketones; Preparation of Elsholtzione, Naginata Ketone and Perilla Ketone.

G rard Cahiez*, Pierre-Yves Chavant and Eric Metals

Tetrahedron Lett. 1992, 33, 5245

Laboratoire de Chimie des Organoelements, tour 44-45; Universit  P. & M. Curie, 4 Place Jussieu F-75252 PARIS C dex 05

2- and 3-acylfurans are prepared in high yields by copper- or iron-catalyzed acylation of organomanganese reagents. Elsholtzione, naginata ketone and perilla ketone, three natural furanic ketones have been prepared according to this procedure. Interestingly, the iron catalysis allows to perform the acylation at low temperature. The 3-furyl manganese derivatives, which are not stable above -50 C, can thus be acylated in high yields as illustrated by the synthesis of perilla ketone:



Tetrahedron Lett. 1992, 33, 5249

SODIUM DI-POLYPRENYL PHOSPHATES FORM "PRIMITIVE" MEMBRANES

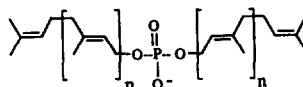
Niklas Plobeck, St phane Eifler, Alain Brisson^a, Yoichi Nakatani et Guy Ourisson*

Universit  Louis Pasteur, 5 rue Blaise Pascal, F - 67084 - Strasbourg

(a) -Laboratoire de G n tique Mol culaire des Eucaryotes, CNRS

11 rue Humann, F-67085 - Strasbourg

Sodium di-geranyl phosphate and higher homologues, synthesized via the phosphites, form in water closed vesicles, which may be models of "prebiotic" membranes.



Tetrahedron Lett. 1992, 33, 5253

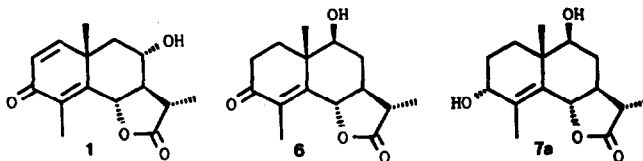
FUNCTIONALITY TRANSFER FROM C₈ TO C₉

IN SESQUITERPENES. SYNTHESIS OF THE NAMED HERBOLIDE E FROM ARTEMISIN.

Gonzalo Blay, Luz Cardona, Bego a Garc a and Jos  R. Pedro*

Departament de Qu mica Org nica, Facultat de Qu mica, Universitat de Val ncia, 46100-Burjassot (Valencia) Spain

The key intermediate **6** was obtained from artemisin (**1**). The spectroscopic characteristics of the synthetic product **7a** reveal that the proposed structure for the natural herbolide E must be revised.



Tetrahedron Lett. 1992, 33, 5257

9,10-Dihydrophenanthrene Metabolites from *Juncus effusus* L.

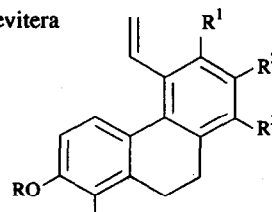
M.Della Greca, A.Fiorentino, L.Mangoni, A.Molinari, P.Monaco and L.Previtera

Dipartimento di Chimica Organica e Biologica, Universit  Federico II

via Mezzocanone 16, I-80134 Napoli, Italy.

Nine 9,10-dihydrophenanthrene metabolites variously substituted in the C ring have been isolated from *Juncus effusus* L. The structures have been defined on spectroscopic grounds.

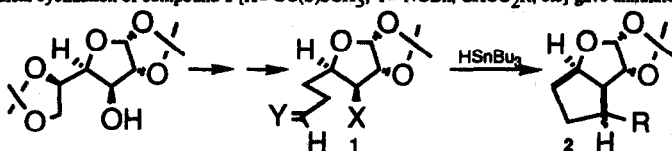
The most abundant compounds, tested for their antitumoural activity, were found to have a potential antileukemic activity.



A NEW SYNTHETIC ROUTE TO CHIRAL, MULTIPLY FUNCTIONALIZED CYCLOPENTANE RINGS.

José Marco-Contelles,* Pilar Ruiz, Belén Sánchez, and M.L. Jimeno.
 Instituto de Química Orgánica, CSIC; Juan de la Cierva, 3. 28006. Madrid. Spain.

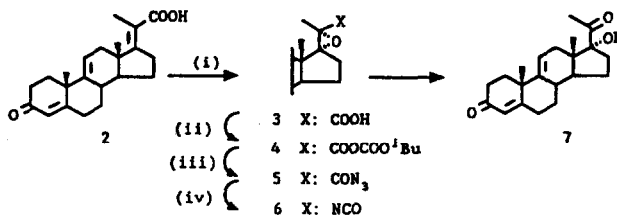
The free radical cyclization of compound 1 [X= OC(S)SCH₃; Y= NOBn, CHCO₂R, etc] gave annulated furanose 2.



Synthesis of 17 α -hydroxy-20-oxo-pregnanes from 17(20)-dehydro-23,24-dinorcholan-22-oic Acids

András Toró and Gábor Ambrus
 Institute for Drug Research
 Budapest, P.O.Box 82 H-1325 Hungary

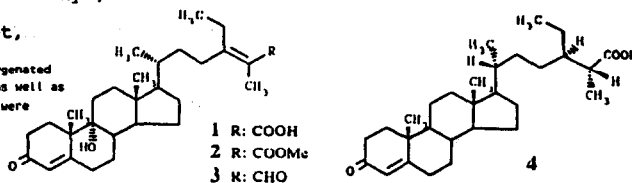
Microbial transformation product of natural sterols has been converted into precursors of antiinflammatory, antiandrogen and gestagen pharmaceuticals by a novel reaction sequence.



NOVEL INTERMEDIATES OF MICROBIAL SIDE CHAIN DEGRADATION OF SITOSTEROL

G. Ambrus, É. Ilkóy, Gy. Horváth, B. Podányi, Zs. Böcskei, S. Gyürky, A. Jekkel
 Institute for Drug Research, Budapest, P.O. Box 82, H-1325 Hungary.

Structures of side chains of three new 24(25)-dehydro-26-oxygenated microbial degradation products of sitosterol (1, 2 and 3), as well as of their precursor 25(R)-3-oxo-4-stigmaster-26-oic acid (4) were determined by NMR and X-ray studies.



New Diterpenes with a Valparane Skeleton

J.G. Urones*, P. Basabe, I. S. Marcos, C. Alonso, I. M. Oliva, N. M. Garrido, D. D. Martín and A. M. Lithgow
 Departamento de Química Orgánica. Universidad de Salamanca.
 Plaza de los Caídos 1-5, 37008 Salamanca, SPAIN

Nine new valparane diterpenoids have been isolated from *Halimium viscosum*, Valparaiso. Their structures were determined by spectroscopic methods and/or chemical correlations.

