

CZECHOSLOVAK ACADEMY OF SCIENCES
Institute of Organic Chemistry and Biochemistry

9th CONFERENCE ON ISOPRENOIDS
ABSTRACTS OF PAPERS

Prague, September 1981

O r g a n i z i n g C o m m i t t e e

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^aabstract available, see pages 1-11.

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NEIGHBORING GROUP PARTICIPATION IN ELECTROPHILIC ADDITIONS.
THEORETICAL ASPECTS AND EVALUATION IN SYNTHESIS AND
STRUCTURE ELUCIDATION OF ISOPRENOIDS

Pavel Kočovský

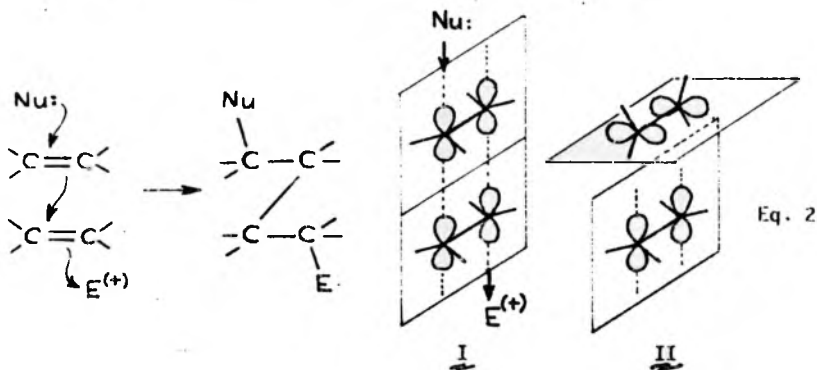
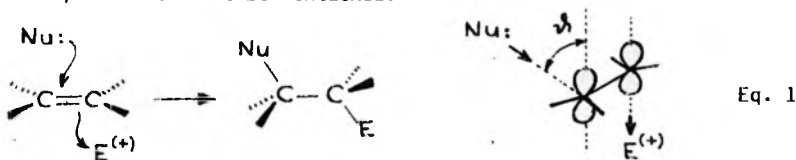
Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences, 166 10, Prague 6, Czechoslovakia

Our investigation of neighboring group participation in electrophilic additions to a series of unsaturated steroids leads to the following conclusions:

1. Ability of a neighboring group (OH, OCH₃, OAc) to participate decreases with increasing both the distance (2.5 → 3.0 Å) from the reaction center and the angle of approach ($\vartheta = 0^\circ \rightarrow 40^\circ$).

2. Participation of a second double bond (Eq. 2) is also influenced by stereoelectronic factors. In the case I in which π -orbitals are lying in the same plane, (C)^π participation proceeds readily under the formation of a new C-C bond. In contrast, similar process is not operative in a model II with perpendicularly oriented π -orbitals.

Stereoelectronic effects in additions in which C⁽⁺⁾ serves as an electrophile will also be mentioned.



ACID-CATALYSED CYCLISATION OF
p-METHOXYPHENYLETHYLTRIMETHYLCYCLOHEXANOLS

B.W. Axon, B.R. Davis, and P.D. Woodgate

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New Zealand

The acid-catalysed reactions of two p-methoxyphenylethyl-trimethylcyclohexanols, precursors to tricyclic diterpenoids, were investigated. Treatment with boron trifluoride - ether, or tin(IV) chloride, or methanesulphonic acid - phosphorus(V) oxide produces both a bicyclic alkene and a tricyclic molecule, with the former being converted to the latter in protic media. Conditions were established for the formation of the naturally occurring trans A/B ring stereochemistry and the mechanism of cyclisation explored with the aid of deuteriated substrates. Polyphosphoric acid-catalysed cyclisation produces a more complex mixture.

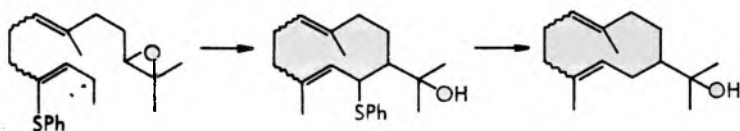
SYNTHESIS AND TRANSANNULAR REACTIONS OF GERMACADIENES

Shô Itô

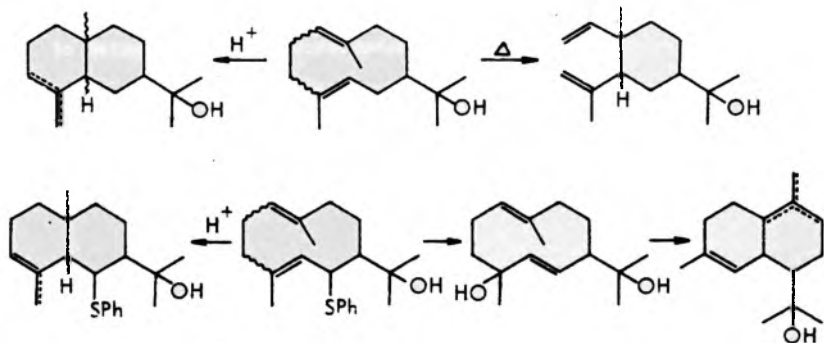
Department of Chemistry, Tohoku University

Sendai 980, Japan

Hedycaryl and its geometrical isomers were successfully synthesized utilizing anion-induced cyclization of the corresponding epoxyfarnesyl phenyl sulfides.



Stereochemistry of transannular reactions of hedycaryl isomers and their phenyl sulfides to eudesmols, elemols and cadinenols will be discussed.

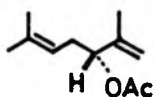


RECENT PROGRESS IN THE SYNTHESIS OF
BIOLOGICALLY ACTIVE ISOPRENOIDS

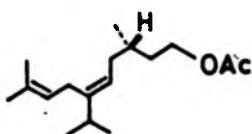
Kenji Mori

Department of Agricultural Chemistry, The University
of Tokyo, Bunkyo-ku, Tokyo 113, Japan

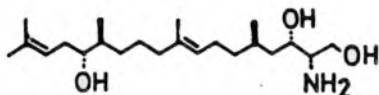
Syntheses of some of the recently discovered biologically active isoprenoids or their analogs will be discussed. The target molecules are the comstock mealybug pheromone 1, the yellow scale pheromone 2, aplidiasphingosine 3 (an antimicrobial and antitumor diterpene obtained from a marine tunicate), and brassinolide 4 (a new plant-growth regulator isolated from rape pollen).



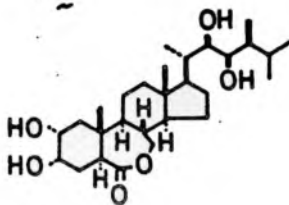
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CHEMISTRY OF SOME ANTI-FEEDANT DITERPENOIDS

B.S. Joshi¹, K. Nakanishi² and D. Rogers³

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² Columbia University, New York, N.Y. 10027, U.S.A.

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In recent years a variety of compounds have been found to display feeding inhibition against insects. One of the important groups of natural products which exhibits anti-feedant activity is the terpenoids. Investigations of Clerodendron inerme showed that the anti-feedant activity is due to 3-epicaryoptin. The chemistry and the absolute configuration of this and some related terpenoids will be discussed.

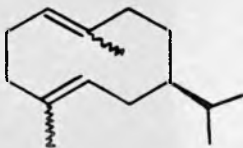
Recent Studies on Germacranolide Type Sesquiterpene Lactones
from Melampodium (Heliantheae, Compositae).

Nikolaus H. Fischer

Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803, U.S.A.

In memory of Zdenek Samek

The germacranolides (I) are cyclodecadiene-type sesquiterpene lactones and represent the major structural group of sesquiterpene lactones which are commonly found in the family Compositae. Our interest in configurational and conformational aspects of these medium-ring compounds has led to investigations related to detailed structural studies and chemical interconversions which provide insight into the possible biogenetic relationships between subgroups of germacranolides found in the genus Melampodium (Heliantheae, Compositae).



SESQUITERPENE LACTONES OF THE UMBELLIFERAE FAMILY

M. Holub

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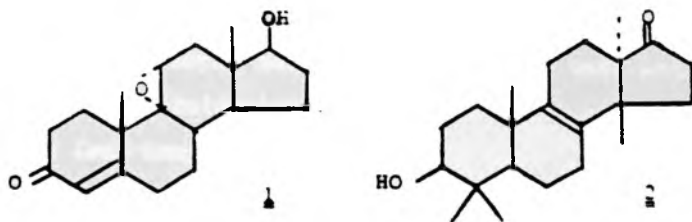
A short review is presented of sesquiterpene lactones which were isolated so far from the species of the Umbelliferae family and the structure of which has been at least partly described. New structural, especially stereostructural types of the native substances mentioned will be discussed in greater detail, especially of those which have been detected so far only in species of the given family.

SYNTHETIC ENDEAVOURS
TOWARDS EUPHOL AND TIRUCALLOL

Max Audouin and Jacques Levisalles

Laboratoire de Chimie Organique, Université Pierre
et Marie Curie, 75230 Paris Cedex 05, France

The backbone rearrangement of compound **1** affords products which can be transformed into ketol **2**, a degradation product of euphol.



Experiments, leading to the preparation of ketol **2**, both from compound **1** and from euphol, will be described.

PROGRESS IN THE CHEMISTRY OF BUXUS ALKALOIDS

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Although Buxus alkaloids have a long history, the structure of these bases has been an enigma, since all attempts to solve their constitution by classical chemical methods failed. The break-through started in the early sixties, when progressive physical methods were the proper tools enabling to elucidate their structure. Since then more than one hundred formulas have been ascribed to those alkaloids by scientists working on this project all over the world, while a good deal of other bases are still waiting for structural assignment.

As will be shown, one group of Buxus alkaloids is believed to be the decomposition products of naturally occurring bases decomposed during the isolation process.

In addition to substances basic in nature, neutral and acid ones have been separated from various species of the Buxaceae family. Surprisingly, biochemists and pharmacologists have not found this field exciting enough and therefore, not much information appeared in this field.

This paper offers an outline on what has been done in the chemistry of Buxus alkaloids in the last two decades.

RECENT PROGRESS IN THE GROUP OF VERATRUM AND FRITILLARIA
ALKALOIDS

J. TOMKO

DEPARTMENT OF PHARMACOGNOSY AND BOTANY FACULTY OF PHARMACY,
COMENIUS UNIVERSITY, BRATISLAVA

The alkaloids of *Veratrum* plants/*Veratrum album* subsp. *Lobelianum* /Bernh./ *Suessenguth*, *Veratrum nigrum* L./ belong to the steroid and C-nor-D-homo steroid compounds with 27 carbon atoms forming the skeleton. Also bases with 26 carbons have been isolated, especially from the above-ground part of the plants.

The nitrogen atom in the 27 carbons possessing compounds is embodied in a piperidine or quinolizidine rings, whilst in those of 26 carbons in a pyrroline ring in the side chain.

The alkaloids separated from *Fritillaria imperialis* L. are characterized by a C-nor-D-homo backbone. The principal alkaloid of this plant species, *imperialine*, has been obtained together with *verticine*, *verticinone* and *isobalmidine*, the latter being a new base.

Structural relation between the *Veratrum* and *Fritillaria* alkaloids is being discussed.

ISOLATION AND STRUCTURE OF A NEW SESQUITERPENE FROM
LACTARIUS CAMPHORATUS: 12-HYDROXYCARYOPHYLLENE-4,5-OXIDE

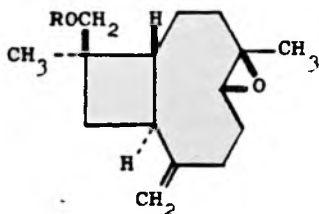
Włodzimierz M. Daniewski[†], Paul A. Grieco^λ, John C. Huffman^x
Apoloniusz Rymkiewicz[§] and Andrzej Wawrzun

[†]Institute of Organic Chemistry, Polish Academy of Sciences,
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From the ethanolic extract of *Lactarius camphoratus* (Basidiomycetes) a new sesquiterpene, 12-hydroxycaryophyllene-4,5-oxide I, has been isolated. The structure, stereochemistry and absolute configuration were determined by a combination of spectral data and single-crystal X-ray analysis of the p-bromobenzoate derivative 3.



- I R = H
2 R = Ac
3 R = p-BrC₆H₄CO

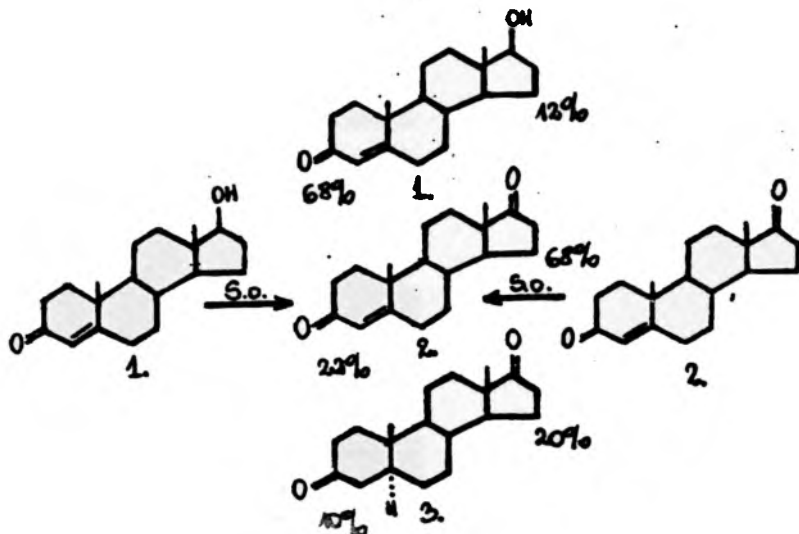
TRANSFORMATIONS OF SELECTED STEROIDS BY MEANS OF
SPIRODELA OLIGORRHIZA CULTURE

E. Tłomak, W. Czerwiński and A. Siewiński

Institute of Fundamental Chemistry, Academy of Agriculture,
Wrocław, Poland

The purpose of our work was to study the abilities of the enzymatic system of plant *Spirodela oligorrhiza* from the Lemnaceae family for biotransformation of some organic compounds.

The conditions of the course of transformation with water plants are similar to those of the microbiological reactions. In order to study the abilities of the mutual transformation ketone \rightleftharpoons alcohol testosterone (1) and androstenedione (2) have been used as the model compounds.



REVISION OF THE STRUCTURE OF 3-METHOXY-14 α -HYDROXY-
D-HOMO-1,3,5(10)-ESTRATRIEN-17 α -ONE

Ž. Procházka, M. Buděšínský and Huynh Kim Thoa

Institute of Organic Chemistry and Biochemistry, Cze-
choslovak Academy of Sciences, 166 10 Prague 6,
Czechoslovakia

Eignerová and Procházka have found for 3-methoxy-
-14 α -hydroxy-D-homo-1,3,5(10)estratrien-17 α -one the
value $\Delta\epsilon = -2.76$. According to Klyne the calculated
 $\Delta\epsilon$ value for this compound is substantially lower,
which led him to the hypothesis that the structure of
the measured substance was not correct and that it
probably had an epimeric structure, with the hydroxyl
group in the position 14 β . This hypothesis was investi-
gated by means of the measurement of the $^1\text{H-NMR}$ spectra
of the title substance and some synthetic models, using
TAI-acylation shifts of the angular methyl group in
 α -position to the tertiary hydroxyl. The measured values
indicated that the structure with the tertiary hydroxyl
group in position 14 β and not in 14 α should be assigned
to the mentioned compound.

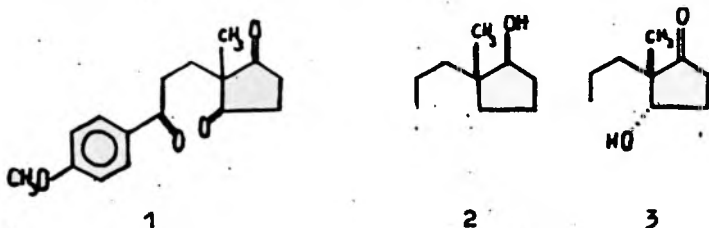
STEREOSPECIFIC REDUCTION OF TRIKETONES INTERMEDIATES IN STEROID SYNTHESIS BY MEAN OF SOME YEAST STRAINS

W. Buchowiecki, H. Zając

Institute of Organic Chemistry - Technical University
Łódź

J. Kiersanowski, L. Nowak, A. Siewiński - Institute of Fundamental Chemistry - Academy of Agriculture - Wrocław

/2R,3S/- and /2S,3S/-3-hydroxy-2-methyl-2-[3'-/p-methoxyphenyl/-3'-oxo]-propyl-1-cyclopentanones were prepared by stereospecific reduction of achiral 2-methyl-2-[3'-/p-methoxyphenyl/-3'-oxo]-propyl-1,3-cyclopentanedione by mean of yeast of the species *Saccharomyces cerevisiae* and *Candida utilis*. The microbiological reduction was carried out at a substrate concentration of 0.5-1.0g/dm³ nutrient. The hydroxydiketones 2 and 3 shown in the figure were obtained at a rate of 28% and 80% respectively and can be used as intermediates in steroid synthesis



TRANSFORMATION OF SOME KETONES BY MEANS
OF IMMOBILIZED RHODOTORULA MUCILAGINOSA CELLS

A.Mironowicz, A.Siewiński

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Academy of Agriculture, 50-375 Wrocław, Poland

Microbiological transformations of selected terpene ketones: /-/-menthone, R-+/-methyl- α -campholenone, /+/-carvone and eucarvone by means of *Rhodotorula mucilaginosa* cells immobilized in polyacrylamide gel were investigated.

A thermostated column with packed beds of immobilized cells is used for continuous transformations of substrates.

The course and yield of transformations by immobilized cells and submerged cultures are discussed.

MICROBIAL TRANSFORMATION OF RACEMIC

5-/2',2',3'- TRIMETHYL -3'- CYCLOPENTEN/-3 PENTEN-2- ONE

A.SLEWIŃSKI, J.DMOCHOWSKA-GLADYSZ and T.KOLEK

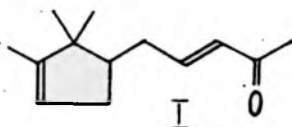
Academy of Agriculture, Wrocław, Poland

and

A.ZABŹA and K.DERDZIŃSKI

Technical University, Wrocław, Poland

Racemic ketone I was transformed by means of two strains: *Aphanocladium album* isolated from intestine of *Tenebrio molitor*, and the soil strain *Rhodotorula mucilaginosa*.



Optical active products: saturated ketones and alcohols were obtained.

Both mentioned strains reduced the conjugated double bond of both enantiomeric ketones. Each of these strains showed substrate selectivity in ketone reduction, but each of them to another enantiomer.

MICROBIOLOGICAL TRANSFORMATIONS OF SOME MONOTERPENIC
HYDROCARBONS BY MEANS OF *Armillariella mellea*

B. Draczyńska, Cz. Cagara, A. Siewiński, A. Zabża,
A. Rymkiewicz, A. Leufren

Institute of Fundamental Chemistry, Academy of Agriculture,
50-375 Wrocław, Poland

Abstract not available

+ PARTIAL CHARACTERIZATION OF PRODUCTS OF SPONTANEOUS
DEGRADATION OF γ -TARAXASTEROL

B. Wiłkomirski and Z. Kasprzyk

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02-089 Warsaw, Poland

Our previous works on enzymatic hydroxylation in position 16 of pentacyclic triterpene monools to triterpene diols in *Calendula officinalis* flowers suggested that free alcohols as well as their 3-esters were direct precursors of free diols and their 3-monoesters.

In present investigation, 3-³H- γ -taraxasterol / the main triterpene monool in *Calendula*/ was used as precursor in the process of hydroxylation *in vivo*. It was shown that this compound, besides enzymatic conversion into faradiol, degraded into few more polar products which located on TIC just on the level of free diol or between free monool and free diol. The total contents of degradation products was about 4%. In TLC the presence of three compounds, in GLC of five compounds was proved. None of them was faradiol, - the 16-hydroxy derivative of γ -taraxasterol. The structure of the main product was established by MS and chromatographical data as γ -taraxasterol epoxide, i.e. 20,21-epoxy, 3-hydroxyursane.

BIOSYNTHESIS OF STEROL ESTERS IN SINAPIS ALBA ROOTS

J.Zimowski and Z.A.Wojciechowski

Institute of Biochemistry, Warsaw University, 02-089
Warsaw, Poland

Sinapis alba L. /white mustard/ roots contain an acyltransferase catalyzing esterification of various natural and synthetic sterols with utilization of triglycerides as fatty acid sources. The enzyme is present in cell membranes but can be solubilized by acetone treatment and partially purified by gel filtration. Beta configuration of the -OH group at C-3 of sterol molecule is absolutely required for the action of acyltransferase. Moreover, a distinct preference to sterols with a planar ring system / A/B trans or double bond at C-5 / is observed. The rate of esterification depends also on the presence of double bonds in the ring system. For various C₂₇ sterols the following sequence is found: $\Delta^0 > \Delta^5 \gg \Delta^{3,7} > \Delta^7$. In contrast, the structure of the side chain at C-17 has little effect on the reaction rate. Purified acyltransferase can be used for microscale preparation of ¹⁴C or ³H sterol esters labelled both in sterol or fatty acid moiety.

BIOSYNTHESIS OF CUCURBITACINS

Gianni Balliano, Laura Delprino and Luigi Cattel

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The cucurbitacins constitute an important group of tetracyclic triterpenoids, originally found in Cucurbitaceae family, characterized by a wide range of biological activities. It had been suggested that the cucurbitacins were biosynthesized from squalene epoxide through the formation of a lanostane C-9 carbonium ion which could undergo different pathways. The intermediacy of lanosterol was excluded by Zander (1970) who considered either cycloartenol or parkeol as a possible intermediate.

We have now been able to illuminate some of these pathways by parallel incubations of [$2\text{-}^3\text{H}$]-cycloartenol, [$2\text{-}^3\text{H}$]-parkeol and [$2\text{-}^3\text{H}$]- 10α -cucurbita-5,24-dien- 3β -ol in Cucumis sativus seedlings. The incubation of [$2\text{-}^3\text{H}$]- 10α -cucurbita-5,24-dien- 3β -ol gave the labelled cucurbitacin C which was identified by crystallization to a constant specific radioactivity after HPLC purification. Under the same conditions [$2\text{-}^3\text{H}$]-parkeol was not converted into cucurbitacin C and [$2\text{-}^3\text{H}$]-cycloartenol afforded only the expected labelled phytosterols.

On the other hand the incubation of [$11\text{-}^3\text{H}$]-squalene-2,3-epoxide in microsomes of Cucurbita maxima seedlings yielded the radioactive 10α -cucurbita-5,24-dien- 3β -ol together with the expected labelled cycloartenol and 24-methylene-cycloartanol. By contrast, following incubation of both [$2\text{-}^3\text{H}$]- 11 -cheto-cycloartenol and [$2\text{-}^3\text{H}$]-24,25-dihydro-9,11-epoxy-parkeol under the same conditions, no rearranged products were detectable.

These results, by excluding the intermediacy of both cycloartenol and parkeol during the biosynthesis of cucurbitacins, suggested the presence in Cucurbitaceae of an enzyme very similar to SqO-cycloartenol synthetase, capable of converting the squalene-2,3-epoxide into the simplest tetracyclic triterpene with a cucurbitane skeleton.

IN VITRO - EXPERIMENTS ON THE BIOSYNTHESIS OF CANTHARIDIN

W.D. Woggon

Organisch-chemisches Institut der Universität Zürich

Abstract not available

6-FARNESYL-5,7-DIHYDROXY-4-METHYLPHthalIDE OXIDATION
MECHANISM IN MYCOPHENOLIC ACID BIOSYNTHESIS

C. Scolastico, L. Colombo, C. Gennari, D. Potenza,
F. Aragozzini

Institute of Organic Chemistry, University of Milan,
Italy

Abstract not available

THE LABELLING WITH ^{14}C OF AROMATIC RING OF MONOMETHYL-
TOCOLS IN PLANT

W. Janiszowska

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02-089 Warsaw, Poland

Previously we have shown the presence of α -, γ - and δ -tocopherols (α -, γ - and δ -T) in *Calendula officinalis* leaves. Theoretical consideration of tocopherol biosynthesis pathway suggests that plants can contain besides δ -T (8-methyltocol) both of its isomers: 5-MeT and 7-MeT (5- and 7-methyltocol). The purpose of this work was to check which of these isomers are present in the investigated plant. [$\text{U-}^{14}\text{C}$]Tyrosine was applied to *C. officinalis* shoots and the incorporation of radioactivity into tocopherols in 5 subcellular fractions was investigated. The synthesized monomethyltocols (condensation of phytol with toluquinol) were used as the carriers and standards. Tocopherols were separated by column, TL and r.ph. chromatography. The UV and visible spectra of free and nitroso derivatives were determined and radioactivity was counted.

It was shown that only two of radioactive monomethyltocols, i.e., 7-MeT in chloroplasts and 8-MeT in chloroplasts, mitochondria and microsomes are present. Any radioactivity in 5-MeT has been found.

SELECTION OF SOLANUM AVICULARE CALLUS AND SUSPENSION
CULTURES FOR GLYCOALKALOIDE PRODUCTION

T. Macek, T. Vaněk, M. Kamínek[‡], I. Beneš and L. Novotný

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About 80 caluses from sterile seedlings of *Solanum aviculare* were initiated. The cali were derived from various organs (leaves, stems, roots) of more plants of different origin. (The seeds were kindly supplied by botanical gardens in Kew, Gatteraleben and Bordeaux).

The cali were grown on several types of nutrient media differing in plant hormone content, and some of the selected clones were successfully grown in suspension cultures.

Samples (10 gram of fresh weight) collected from 50 well growing clones were homogenised and extracted with methanol, investigated compounds were concentrated by Sep-Pak C₁₈ cartridge. The glycoalkaloid content was determined by means of analytical HPLC.

The glycoalkaloids were identified by comparison of their retention times in HPLC with standards of glycoalkaloids and aglycones after hydrolysis, and by MS and NMR spectroscopy.

We were looking especially for glycoalkaloids containing solasodine aglycone. Five of the clones tested contained glycoalkaloids in quantities worth of further study. These were selected for optimisation of culture conditions for high production of glycoalkaloids.

STUDY OF $\Delta^{1,3,5(10)}$ -ESTRATRIENES-PROTEIN
INTERACTIONS BY FLUORESCENCE AND CD SPECTROSCOPY

T.N. Deshko, V.V. Egorova, T.I. Barkova, S.N. Ananchenko
Shemyakin Institute of Bioorganic Chemistry, USSR Academy of
Sciences, Moscow, USSR

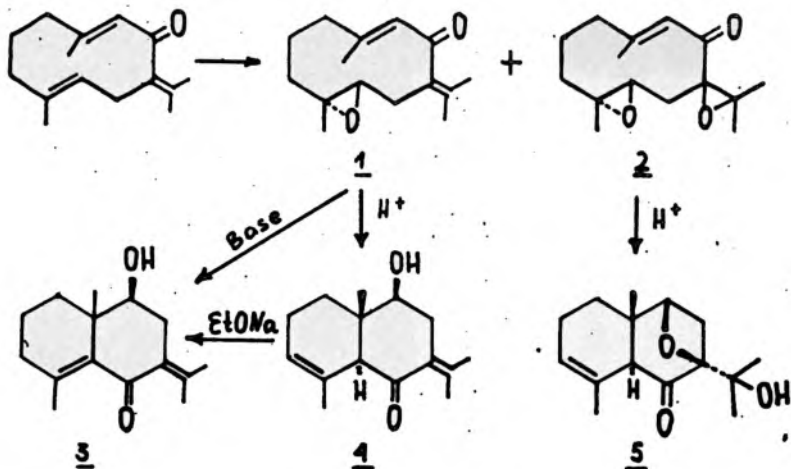
Formation constants of d-estradiol(I), d-estrone(II), d-3-deoxyestradiol(III), d-17-deoxyestrone (IV), d-3-deoxyestrone (V), d3,17-bisdeoxyestrone (VI), d,17 β -estradiol(VII), d,1-D-homoestrone (VIII), d,1-D-homoestradiol(IX) with bovine plasma albumin have been determined by fluorescence quenching titration. Influence of steroid polaricity on the formation constant of the steroid-albumin complex has been established. Interaction of estrogens (I-IX) with citosol fraction of receptors from rabbit's uterus results in some change of protein CD spectrum in 300 nm-190 nm region. On this case d-estradiol effect is more significant. The similar changes in the CD spectra are apparently connected with conformational changes of the estradiol's receptor upon its binding with estrogens.

STEREOSPECIFIC CYCLIZATION OF EPOXYISOGERMACRONES

E. Tsankova

Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

From a biogenetic point of view, acid- or base-catalyzed cyclization of epoxyisogermacrones 1 and 2 were carried out. In all cases, the stereospecific intramolecular cyclization took place to give the new selinan-type compounds 3, 4 and 5. Their structure and stereochemistry were determined on the basis of IR, H^1 - and ^{13}C -NMR and MS spectra. A possible mechanism of formation of the bicyclic products is discussed.



REARRANGEMENTS OF HUMULENE DERIVATIVES OF BIOGENETIC
SIGNIFICANCE

J.S. Roberts, I. Bryson, J.A. Mlotkiewicz

Department of Chemistry, University of Stirling,
Scotland, United Kingdom

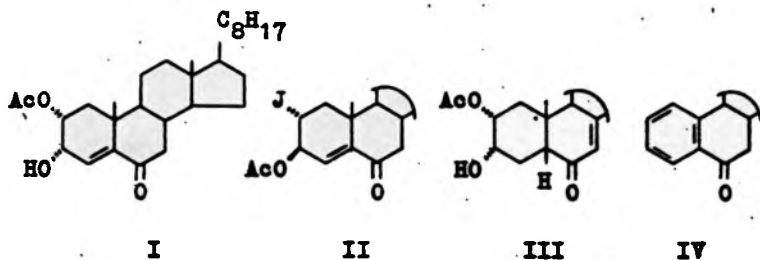
Abstract not available

**HYDROXYLATION OF STEROIDAL 2,4-DIENES
IN WOODWARD'S METHOD CONDITIONS**

A. Akhrem, F. Lakhvich, V. Khrinach and N. Kovganko

Institute of Bioorganic Chemistry, Byelorussian
SSR Academy of Sciences, 220600 Minsk, U.S.S.R.

The hydroxylation of cholesta-2,4-diene-6-one under Woodward's method conditions ($\text{CH}_3\text{COOAg} + \text{J}_2 + \text{CH}_3\text{COOH} + \text{H}_2\text{O}$) has been investigated, and unusually stereochemistry of this reaction has been established. The major addition product I had an α -configuration of substituents in 2- and 3-positions and was isolated in 70% yield. In some cases the minor compounds II, III and IV were obtained. The structures were proved by chemical transformations and spectral data. The possible mechanism of formation of the products is discussed.



THE PRINS REACTIONS OF OLEFINIC STEROIDS

B. Osipowicz, S. Mejer

Institute of Fundamentals of Chemistry, School of
Agriculture, 50-375 Wroclaw, Poland

Abstract not available

SOME RESULTS ON THE RING OPENING OF 5 α ,19-CYCLOSTEROIDS

G. Langbein, H.J. Siemann, I. Gruner, Chr. Müller

VEB-Jenapharm, Bereich Forschung, Jena, DDR

Abstract not available

SULFOLANE AS DEHYDRATION AGENT FOR SOME TERPENE ALCOHOLS

A. Matawowski

Institute of Chemistry, N. Copernicus University,
Toruń, Poland

Abstract not available

THE REACTION OF STEROIDAL α -EPOXYKETONES WITH BH_3

L. Tomaszewska, M. Zaidlewicz

Institute of Chemistry, University of M. Kopernik,
Toruń, Poland

Abstract not available

REACTION OF LITHIUM ALUMINUM HYDRIDE WITH
4,4-DIMETHYL-4 α ,5-EPOXY-A-HOMOCHOLESTANE DERIVATIVES

H. Velgoyá

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6,
Czechoslovakia

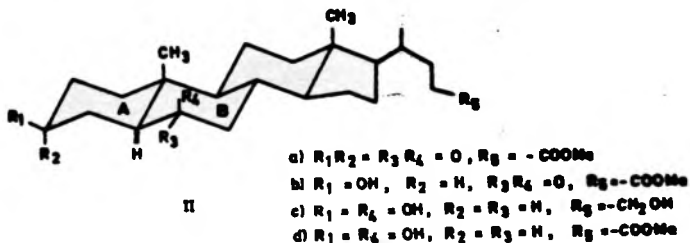
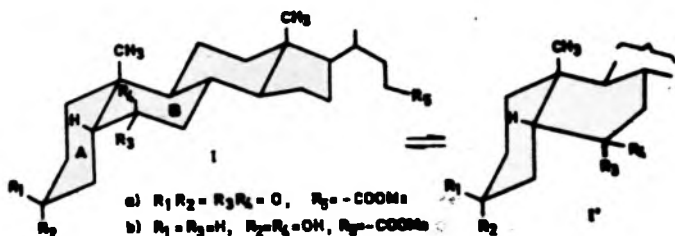
Reductive cleavage of stereoisomeric 4,4-dimethyl-4 α ,5-epoxy-A-homocholestane derivatives bearing an oxygen substituent (OH, OAc, OMe) in the position 3 by lithium aluminum hydride in refluxing dioxane was studied. It was found, that the 4 α ,5 α -epoxides are opened on the side of the least substituted carbon atom C_(4 α), whereas in the case of the 4 α β ,5 β -epoxides both attack on the C_(4 α) and C₍₅₎ carbon atoms occurred. The direction of the ring opening can be reversed by 5(O)^H participation of the neighbouring group. Effect of the character of the substituent in the position 3 on the ratio of the attack on the carbon atoms C_(4 α) and C₍₅₎ will be discussed.

CONFORMATION-REACTIVITY RELATIONSHIP IN BILE ACIDS

D. Miljković, D. Medaković and J. Hranisavljević

Faculty of Sciences, Institute of Chemistry, University of Novi Sad, 21000 Novi Sad, Veljka Vlahovića 2, Yugoslavia

The sodium borohydride reduction and the catalytic hydrogenation of the derivatives Ia, IIa and IIb has been studied in details. Based upon the structures of the reduction products a conformation equilibrium ($I \rightleftharpoons I'$) has been assumed in the A/B - cis series. On contrary, the comparable sodium borohydride reduction rate of the C_{24} -ester group and the 6-oxo function in IIb excludes the flexibility of ring B in the A/B - trans case.

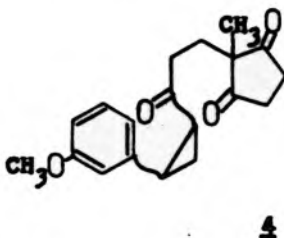
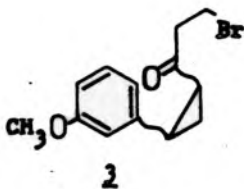
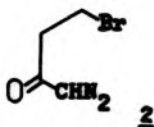
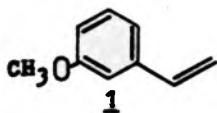


TOTAL SYNTHESIS OF EQUILENIN AND ESTRONE

A.R. Daniewski and T. Kowalczyk-Przewłoka

Institute of Organic Chemistry, Polish Academy of Sciences, 01-222 Warsaw, Poland.

The synthesis of an equilenin and Torgov-Ananchenko's 3-methoxyestra-1,3,5(10),8,14-pentaene-17-one is described. The starting materials, m-methoxystyrene (1) and 1-diazo-4-bromo-butanone-2 (2) were coupled affording cyclopropane derivative 3 using palladium or copper as a catalyst. The addition of 2-methyl-cyclopentadione-1,3 to compound 3 gave triketone 4, which was transformed into title compounds. The optically active cyclopropane derivative 3 was obtained and then transformed to optically active equilenin and estrapentaene using chiral catalyst.

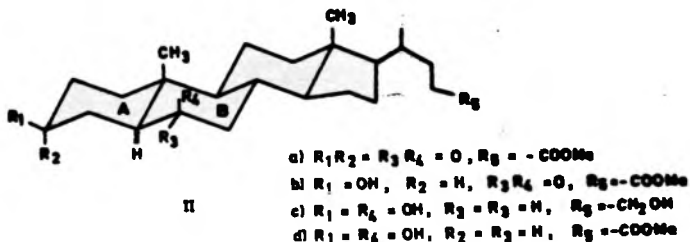
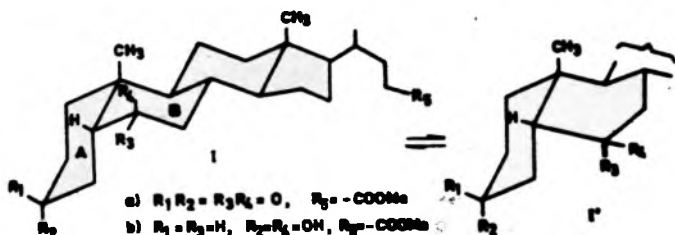


CONFORMATION-REACTIVITY RELATIONSHIP IN BILE ACIDS

D. Miljković, D. Medaković and J. Hranisavljević

Faculty of Sciences, Institute of Chemistry, University of Novi Sad, 21000 Novi Sad, Veljka Vlahovića 2, Yugoslavia

The sodium borohydride reduction and the catalytic hydrogenation of the derivatives Ia, IIa and IIb has been studied in details. Based upon the structures of the reduction products a conformation equilibrium ($I \rightleftharpoons I'$) has been assumed in the A/B - cis series. On contrary, the comparable sodium borohydride reduction rate of the C_{24} -ester group and the 6-oxo function in IIb excludes the flexibility of ring B in the A/B - trans case.



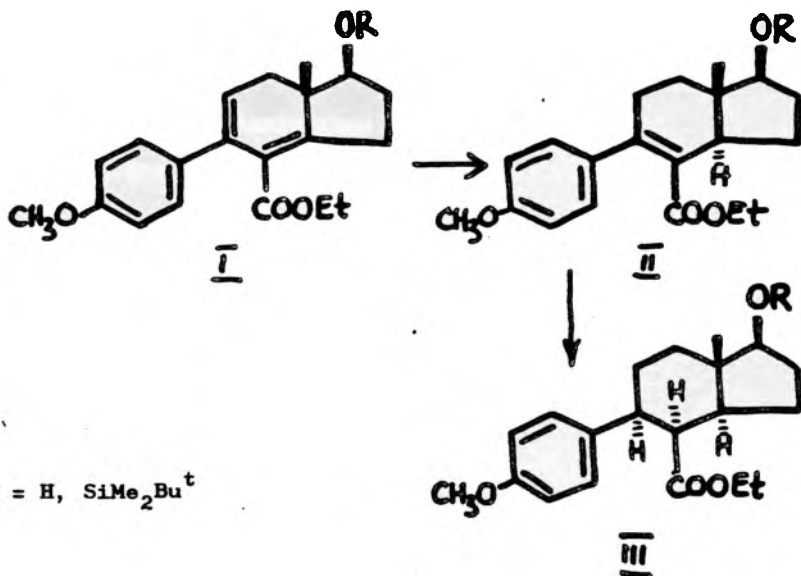
TOTAL SYNTHESIS OF STEROIDS

CATALYTIC REDUCTION OF SOME 8/14/9/11/-STEROID DIENES

W. Buchowiecki and H. Zajac

Institute of Organic Chemistry, Technical University,
90-924 Łódź, Poland

Catalytic reduction (Pd, H_2 , various solvents) of totally synthetic I has been investigated.



It was found that under certain conditions compounds II or III with C/D - trans ring junction can be obtained as major products. Spectroscopic arguments (NMR, MS, UV, IR) has been used to prove the structures of compounds II and III.

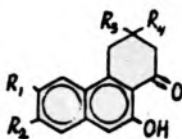
SIMPLE SYNTHESIS OF 3,4-DIHYDRO-10-HYDROXYPHENANTRENONES

F. Lakhvich, T. Khlebnicova and A. Akhrem

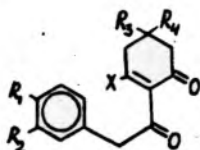
Institute of Bioorganic Chemistry, Byelorussian S.S.R.
Academy of Sciences, 220600 Minsk, U.S.S.R.

A new method for preparation of substituted phenantrenones I on the base of 2-arylacetylcyclohexane-1,3-diones has been proposed. The method involves conversion of triacylmethanes II into vinylogous acyl chlorides III by treating oxalic chloride followed by cyclization via an intramolecular ketovinylation in the presence of $AlCl_3$. Attempts to cyclize the vinylogous acids II directly into I failed.

Phenantrenones I are convenient intermediates for the synthesis of steroids and related polycyclic compounds.

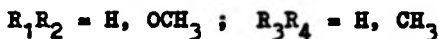


I



II, X = OH

III, X = Cl

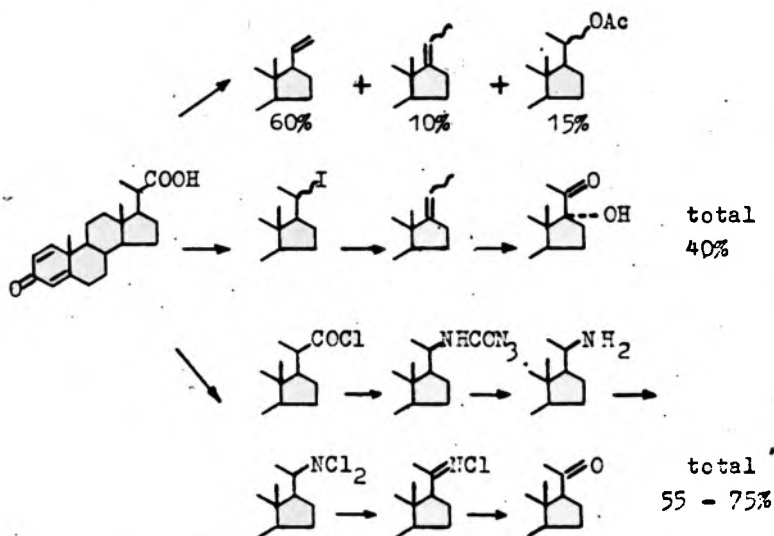


DEGRADATION OF BIS-NOR-CHOLA-1,4-DIEN-3-ONE-22-CARBOXYLIC ACID TO PREGNANE DERIVATIVES

K.Ponsold, M.Wunderwald, P.Neuland and G.Schubert

Academy of Sciences of the GDR, Research Centre of Molecular Biology and Medicine, Central Institute of Microbiology and Experimental Therapy, Jena

The degradation of the bis-nor-chola-1,4-dien-3-one-22-carboxylic acid, available from sterols by microbiological degradation [1], was examined: 1) by oxidative decarboxylation with $Pb(OAc)_4$ in the presence of catalytic amounts of cupric acetate, 2) by iododecarboxylation using a combination of $Pb(OAc)_4$ with I_2 and illumination, 3) by a modified CURTIUS reaction and then, in analogy to RUSCHIG, chlorination of the amine, dehydrochlorination and following hydrolysis.



[1] K. Schubert, K.-H. Böhme and C. Hörhold, WP (DDR) 132 271 (1976)

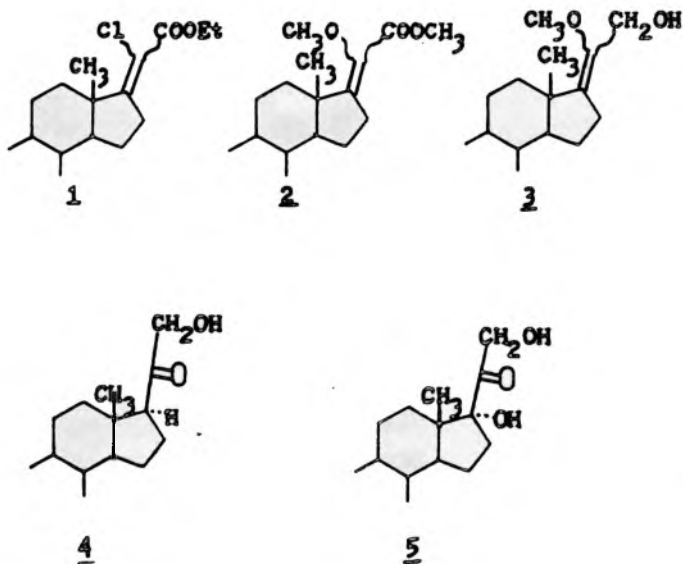
NEW SYNTHESIS OF TWO CARBON STEROID SIDE CHAIN

A.R. Daniewski and W. Wojciechowska

Institute of Organic Chemistry, Polish Academy of Sciences,

01-222 Warsaw, Poland

The androstan-17-one derivatives were transformed in one step into chloroester 1, which on heating with the methoxide in methanol solution yielded the methoxyester 2. The DIBAL reduction of 2 gave alcohol 3, which was easily transformed into desired compounds 4 and 5.

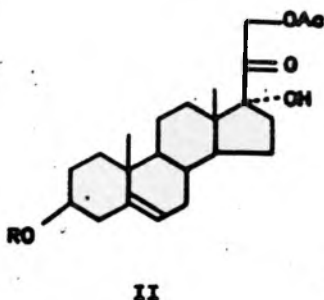
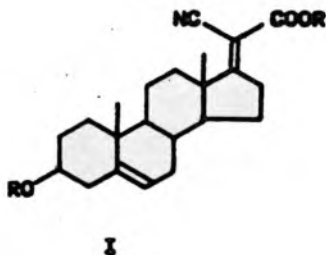


SYNTHESIS OF CORTICOSTEROIDS FROM 17-KETOSTEROIDS
VIA 20-CYANO-21-CARBOXYLATES

M. Gumułka, A. Kurek and J. Wicha

Institute of Organic Chemistry, Polish Academy of
Sciences, 01 224 Warsaw, Poland

Introduction of the dihydroxyacetone side chain at the position 17 of the steroidal skeleton via cyanocarbalcoxymethylidene derivatives (I) was developed. The compounds I were obtained by condensation of the corresponding 17-oxoandrostanes with ethyl cyanoacetate, carbalcoxy group in I was selectively reduced with diisobutylaluminum hydride to the alcohols, which were acetylated and oxidized with potassium permanganate to give II.

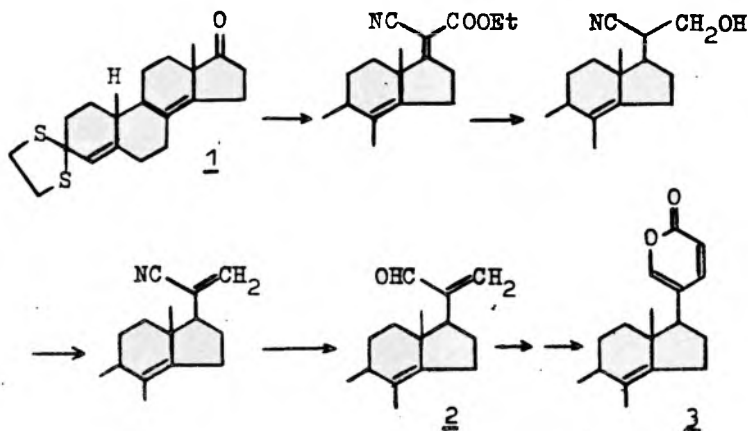


A SYNTHETIC APPROACH TO 19-NOR-BUFADIENOLIDES

B. Schönecker, G. Schubert, M. Wunderwald and K. Ponsold

Academy of Sciences of the GDR, Research Centre of Molecular Biology and Medicine, Central Institute of Microbiology and Experimental Therapy, Jena

Starting with the 17-ketone 1 a four-step synthesis of the unsaturated aldehyde 2 is described. Knoevenagel condensation with ethyl cyanoacetate, reduction with sodium borohydride, dehydration with diethyl azodicarboxylate/tri-n-butylphosphine and reduction with diisobutylaluminium hydride furnished 2 in a total yield up to 50 percent. The unsaturated aldehyde function in 2 is a suitable structural feature for the synthesis of the pentadienolide ring of 3.

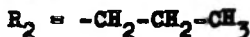
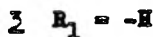
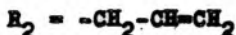
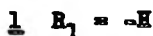
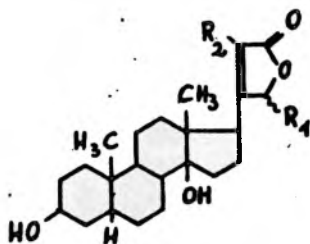


LACTONE RING-ALKYLATION OF CARDENOLIDES

Barbara Streckenbach, R.Hintsche, and Ingeborg Sünrich

Biomembrane Section, Central Institute of Molecular
Biology, Academy of Sciences, Berlin-Bush, GDR

Base-catalyzed alkylation of cardenolides with allyl
bromide, allyl chloride, and n-propyl bromide, resp.
results in the formation of 22-alkyl and 21^f,22-
dialkyl derivatives of digitoxigenin 1-4, digitoxin,
3^B,16^B-diacetyl gitoxigenin, and digoxigenin. The
structures were proved by spectroanalytical data.
The synthetic modifications are of special interest
with respect to the changes of conformational
flexibility and biological effectivity.

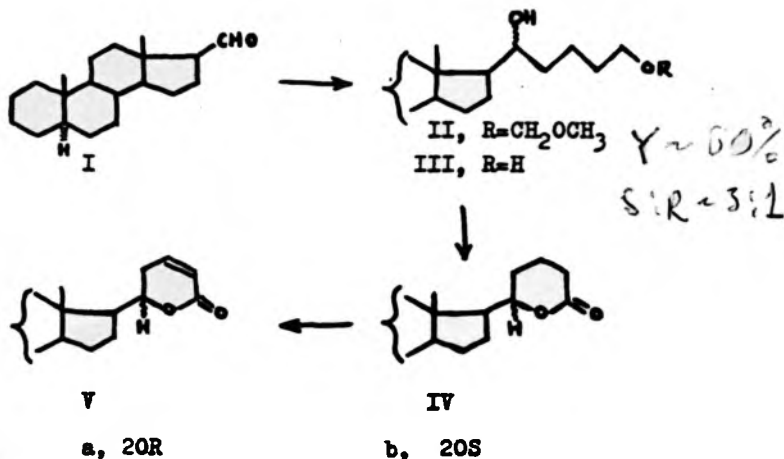


PREPARATION AND ABSOLUTE CONFIGURATION AT C₍₂₀₎ OF
21,26,27-TRINOR-5 α -CHOLESTAN-25 \rightarrow 20-OLIDE DERIVATIVES.

Vladimír POUZAR and Miroslav HAVEL

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague

Reaction of 17 β -formyl-5 α -androstane (I) with 4-methoxymethoxybutylmagnesium chloride gave two main products: protected diols IIa and IIb. Methoxymethyl group in the protected diol IIa was removed by treatment with hydrochloric acid in benzene-methanol mixture to give the diol IIIa. Oxidation of the diol IIIa by silver carbonate on celite yielded the lactone IVa. Analogously, the protected diol IIb gives the lactone IVb. Configuration at C₍₂₀₎ in protected diols IIa and IIb was established by chemical correlation with known derivatives of 21-nor-5 α -cholan-20-ol. For preparing the unsaturated lactones Va and Vb a procedure was applied using sulfenylation and dehydrosulfenylation of saturated lactones IVa and IVb.



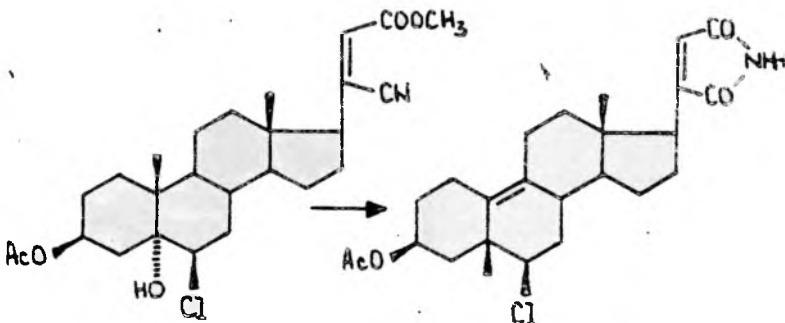
SYNTHESIS OF 17 β -(2-MALEIMIDO)-5-METHYL-19-NOR-5 β -ANDROST-9-ENES

Pavel DRAŠAR, Vladimír POUZAR, and Miroslav HAVEL
Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague

Recently, we have reported cyclization of steroid methyl cyanoacrylates to the corresponding maleimides. We have now applied this procedure to the preparation of Westphalen-type maleimides.

Both the cyclization and Westphalen rearrangement proceed under the influence of sulphuric acid, acetic acid and acetic anhydride mixture. We have found that the cyclization requires more vigorous conditions than the rearrangement. Cyclization of the rearranged derivative could not be achieved due to deep decomposition. However, the desired maleimides with the rearranged skeleton could be prepared by simultaneous cyclization and rearrangement in a one-flask procedure.

Thus (20Z)-3 β -acetoxy-5-hydroxy-6 β -chloro-20-cyano-21-methoxycarbonyl-5 α -pregn-20-ene provided 3 β -acetoxy-6 β -chloro-17 β -(2-maleimido)-5-methyl-19-nor-5 β -andro-
st-9-ene.



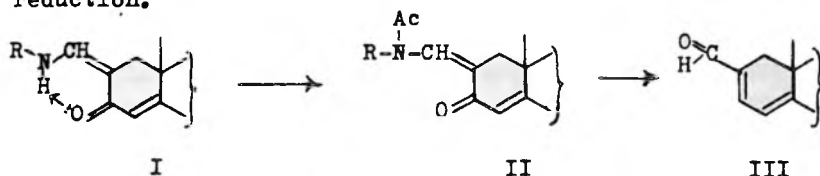
2-SUBSTITUTED ANDROSTENE DERIVATIVES

Cs. Somlai, I. Vincze and Gy. Schneider

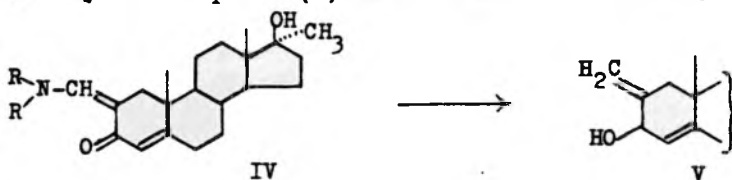
Institute of Organic Chemistry, Attila József University
H-6720 Szeged, Hungary

Reduction of 2-alkyl-aminomethylene- and aminomethyl testosterone derivatives was investigated.

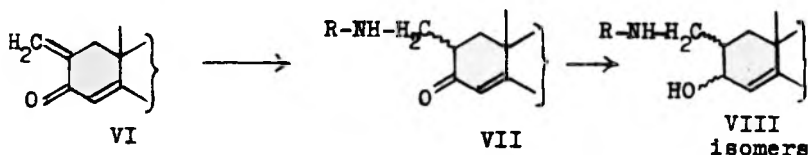
Enamines from primary amines (I) remained unaltered on treating them by sodium borohydride. Their N-acetyl derivatives (II) gave the diene aldehyde III during the reduction.



Enamines with tertiary amino group (IV) gave 2-methylene compound (V) under similar conditions.



Michael adducts (VII) afforded on reduction the expected amino alcohols (VIII).



The steric structure of each isomers has been established.

RING EXPANSION OF STEROID OXETHANS
INTO DIHYDROOXAZINES

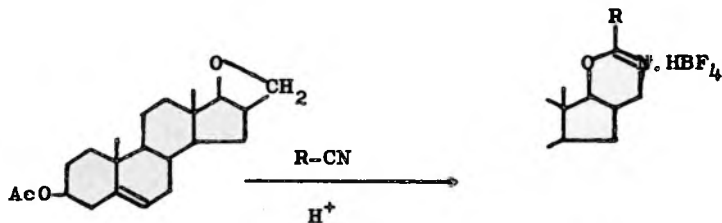
Gy. Schneider⁺, L. Hackler⁺ and P. Sohár⁺⁺

⁺Institute of Organic Chemistry, Attila József
University, Szeged

⁺⁺EGYT Pharmaceutical Chemical Works, Budapest,
Hungary

Epoxides and their substituted derivatives can be converted into derivatives of 1,2-hydroxycarboxamides with acid nitriles in the presence of acids under the conditions of the RITTER reaction.

In the case of oxethans condensed in an appropriate steric position to the sterane skeleton, the formation of six-membered dihydrooxazines has been observed almost quantitatively with aliphatic or aromatic acid nitriles in the presence of Lewis acids, involving thus ring expansion.



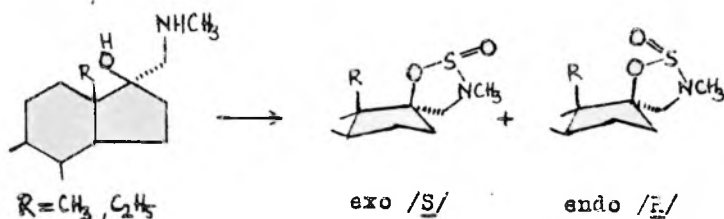
ASYMMETRIC INDUCTION IN FORMATION OF A NEW SPIRO-
STEROID SYSTEM: STEROID-17S-SPIRO-5'-/1',2',3'-
OXATHIAZOLIDIN/-2'-OXYDES

S. S6lyom and L. Toldy

Institute for Drug Research, Budapest, P.O. BOX 82
Hungary

Within the scope of different types of new spiro-steroid systems title compounds have been synthesized by reacting 17 α -methylaminomethyl-17 β -hydroxy-steroids with N-sulphinyl-amides and N,N'-sulphinyl-diamines. In the ring-forming reactions diastereomeric mixtures of exo/endo isomers of the title system resulted.

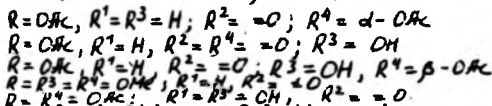
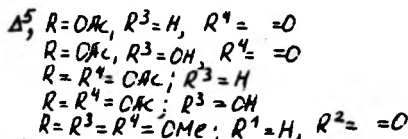
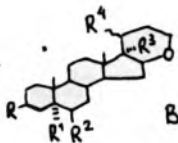
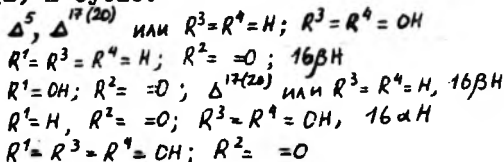
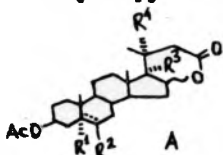
The effect of the ring-closing reagents on the ratio of the diastereomers, further the correlation between the structure of the steroid-aminoalcohol and the ring-closing reagents with the ratio of diastereomers were studied.



SYNTHESIS AND BIOLOGICAL ACTIVITY OF "SHIOGRA"- δ -LACTONES AND THEIR VINYLOGS

I.G. Reshetova, A.V. Kamernitzky, V.A. Kryvoruchko, V.G. Levy and E.I. Chernoburova
N.D. Zelinsky Institute of Organic Chemistry, the USSR Academy of Sciences, Moscow, USSR

Two types of 5,6-disubstituted steroids were synthesised: with the additional 1,2(A) and additional 1,4-tetrahydropyranone (B) E cycle.



5 α -Hydroxy-6-oxoderivatives of both series were prepared by the cleavage of 5,6 α -oxides with the following oxidation. 5 α -H-Ketones of A type were prepared from Δ^5 -23-carbethoxyderivatives via corresponding 3,5 α -cyclosteroids. 5 α -H-6-ketones of B type were obtained through hydroboration of Δ^5 -derivatives and following oxidation. A number of above compounds have shown an inhibitory effect against ecdysterone and Na,K-ATPase.

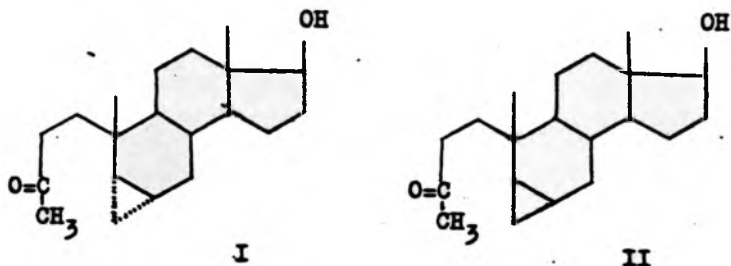
4,5-SECOANALOGUES OF DIHYDROTESTOSTERONE WITH
A CYCLOPROPANE RING IN POSITIONS 5 AND 6

Alexander Kasal and Ladislav Kohout

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6, Czechoslovakia

In an effort to obtain further information on the structural requirements of preparations with antiandrogenic effect we decided to prepare analogues of androgenic hormones which contained two structural peculiarities in the molecule: a cyclopropane ring and an opened ring between the carbon atoms 4 and 5.

Two such substances (I and II) were prepared from methyl 17 β -benzyloxy-A-nor-3,5-secoandrost-5-en-3-ate, which is easily accessible from testosterone. In preliminary biological tests it was observed that compound II is bound to the rat prostate cytosol receptor (competition with ^3H -dihydrotestosterone).

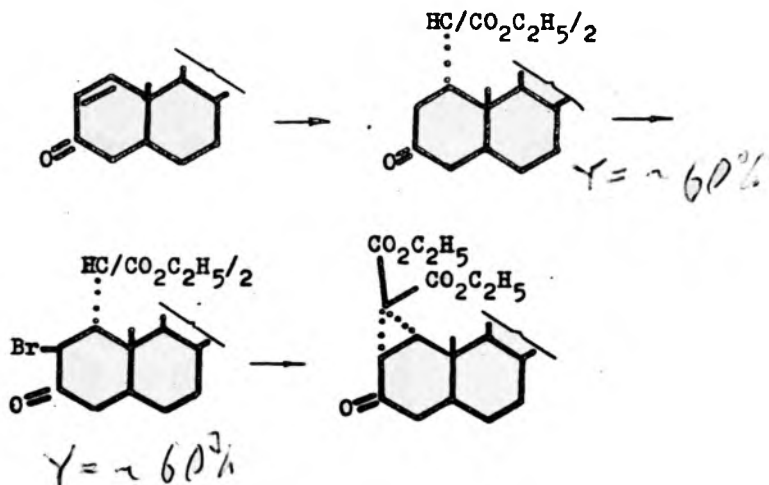


SYNTHESIS OF CYCLOPROPANE RING FUSED
WITH STEROID SYSTEM

W. Kroszczyński

Institute of Organic Chemistry, Polish Academy
of Sciences, 01 224 Warsaw, Poland

Treatment of steroidal 1-en-3-ones with diethyl malonate in the presence of tetramethylguanidine yielded ketones with dicarboethoxymethyl substituent in position 1. Bromination of adducts under standard conditions led to 2-bromoketones, which in the presence of tetramethylguanidine gave cyclopropane derivatives identical with earlier synthesized from 2-bromo-1-en-3-ones and diethyl malonate.

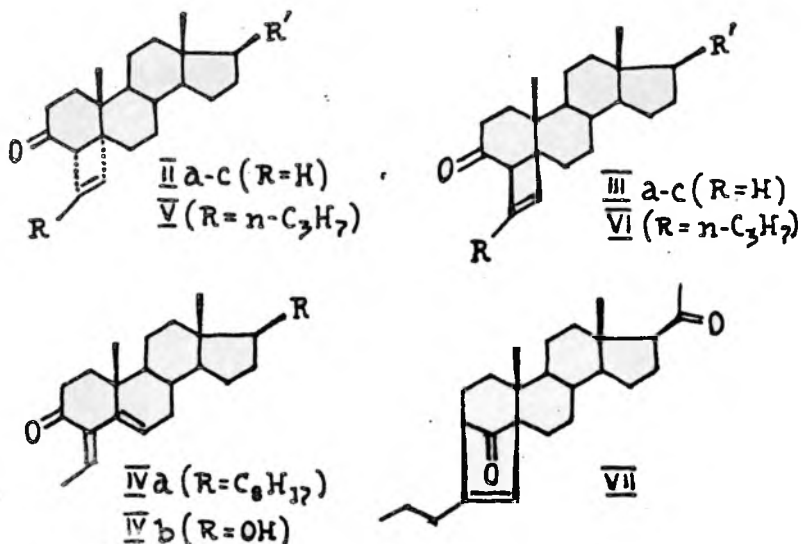


PHOTOCHEMICAL ADDITION OF STEROID
4-EN-3-ONES TO ACETYLENE AND 1-PENTYNE

E.P.Serebryakov, E.M.VoI'pin

(N.D.Zelinsky Institute of Organic Chemistry, the USSR
Academy of Sciences, Moscow 117913)

Photocycloaddition of 4-cholesten-3-one (Ia) and testosterone (Ib) to $\text{HC}\equiv\text{CH}$ gives a mixture of $4\alpha, 5\alpha$ -isomers (IIa,b) and $4\beta, 5\beta$ -isomers (IIIa,b) in a ratio ca. 5:1 with 4-ethylidene-5-en-3-ones (IVa,b) as side products. Progesterone (Ic) reacts with $\text{HC}\equiv\text{CH}$ to give (IIc) and (IIIc) in a ratio ca. 0.8:1. Although (IIc) and (IIIc) undergo photochemical interconversion, the slight predominance of $4\beta, 5\beta$ -isomer (IIIc) is due to a kinetic factor. The addition of (Ic) to 1-pentyne gives exclusively "head-to-head" cycloadducts (V) and (VI), again capable of photochemical interconversion. Acid-catalyzed rearrangement of (VI) produces $3\beta, 5\beta$ -etheno-4-oxo isomer (VII).



OZONE OXIDATION OF SATURATED STEROIDS

J. Petrović, Dj. Čanadi and D. Miljković

Faculty of Sciences, Institute of Chemistry,
University of Novi Sad, 21000 Novi Sad, Veljka
Vlahovića 2, Yugoslavia

The action of ozone on 3 β -acetoxy-5 α -chloro-cholestone in methylene chloride at - 30°C has been investigated. Contrary to earlier observations regarding ozone oxidation of saturated hydrocarbons with the oxygen insertion into a C-H bond, in our case the oxygen insertion into a C-C bond has been noticed.

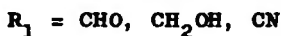
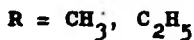
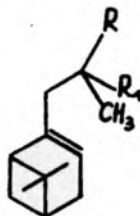
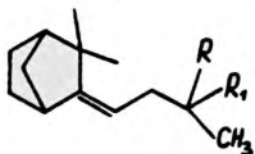
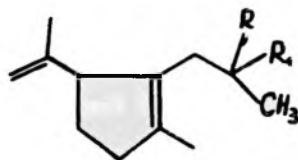
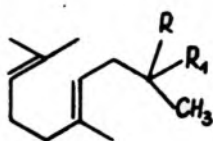
The structure of the main oxidation product, 24,25-ozonide of 3 β -acetoxy-5 α -chloro-cholest-24-ene, has been proved by spectroscopic data and by chemical transformations. The possible mechanism for the ozonide formation is proposed.

SIMPLE SYNTHESIS OF SESQUITERPENOIDS AND THEIR ANALOGUES

J. Góra, A. Monkiewicz, L. Markowicz, J. Gibka

Institute of General Food Chemistry, Technical University
90-924 Łódź, Poland

Some sesquiterpenoids and their analogues can be conveniently prepared from the corresponding acyclic 2-alkylaldehyde and the allyl terpene alcohol in the presence of the acidic catalyst.



The structures of the above compounds were confirmed by the ¹H-NMR, MS and IR data. Some relations between the structure and the odor are discussed.

RECENT RESULTS IN SYNTHESIS OF BISABOLONES

W. Kreiser, T. Müller, K. Zacher

Organische Chemie, Universität Dortmund, BRD

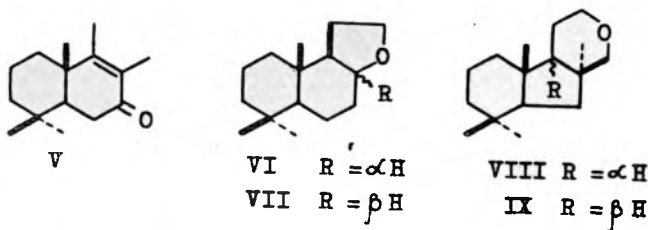
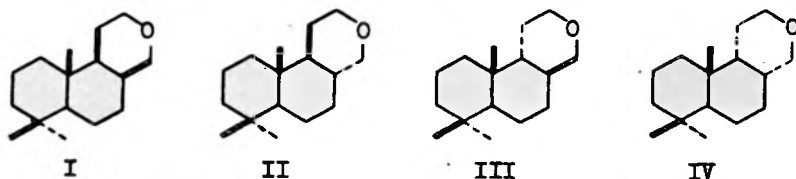
Abstract not available

**SYNTHESIS OF SOME BICYCLOHOMOFARNESANIC OXIDES
AND RELATED COMPOUNDS**

P.F.Vlad, N.D.Ungur, M.N.Koltza

Institute of Chemistry, Moldavian Academy of Sciences,
277028 Kishinev, USSR

The bicyclohomofarnesanic oxides (I) - (IV), ketone (V) and the related compounds (VI) - (IX) have been synthesized from the labdanic diterpenoids degradation products.



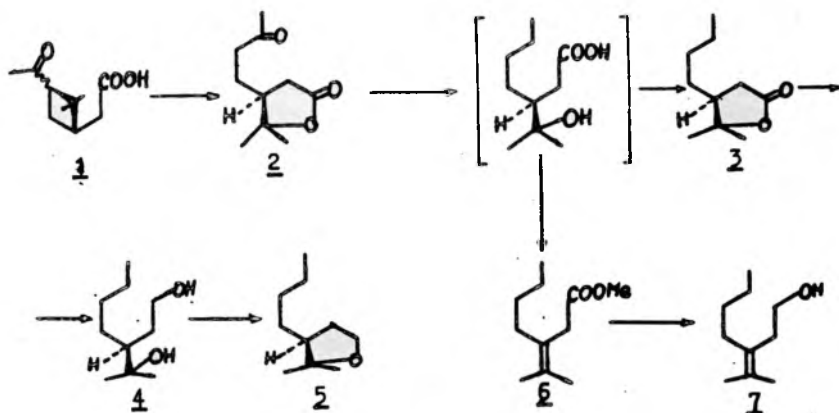
Although the compounds (I) - (V), (VIII) and (IX) are not in agreement with the known triaxial rule, they have ambergris odour.

THE CHEMICAL CHANGES OF THE (+)PINONIC ACID

J. Kula and J. Podlejski

Institute of Fundamental Food Chemistry, Technical University, 90-924 Łódź, Poland

As a result of ozonolysis of α -pinene (+)pinonic acid 1 was obtained (the mixture of cis, trans isomers), which was transferred to ketolactone 2¹⁾. The last compound has undertaken to the following reaction process:



The purity of received compounds were determined using gas chromatography analysis. The structure of compounds 3 - 7 were confirmed by means of spectral (IR and ¹H-NMR) methods.

References

1. A. Baeyer, Chem. Ber., 29, 326 (1896).

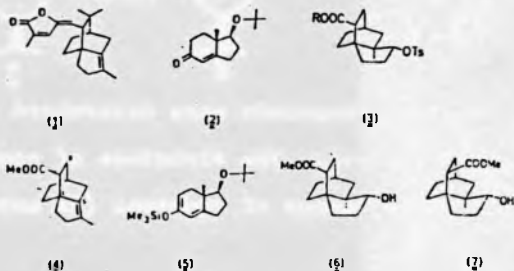
SYNTHESIS OF METHYL 4-METHYLTRICYCLO[5.2.2.0^{1,5}]UNDEC-4-ENE-9-CARBOXY-

LATE A POSSIBLE PRECURSOR OF ISOEREMOLACTONE

Wolfgang Kraus, Dietrich Spitzner, and Walter Weber

Department of Chemistry, University of Hohenheim, 7000 Stuttgart 70

Isoeremolactone (1), a diterpene from the crude oil of *Eremophila fraseri* and *E. freelingii*, possesses the unique tricyclo[5.2.2.0^{1,5}]undecene carbon framework as shown by X-ray analysis¹⁾. We report on the synthesis of this skeleton in the ester (4) by solvolytic rearrangement of the tosylate (3) starting with the racemic ketone (2) which has been used as the common CD-synthon in various steroid synthesis. The conversion of (4) into (1) by a few straight forward reactions is anticipated. A mixture of the alcohol (6) and its C-9 epimer (7) could also be obtained in a ration of 3:1 from trimethylsilylether (5) and methyl acrylate in a Diels-Alder reaction. The acid catalyzed rearrangement of (6) and (7) will be reported. All new compounds except of the labile silyl ether (5) gave satisfactory combustion analyses and/or high resolution MS data, and their structures were determined by IR, ¹H-NMR, and ¹³C-NMR spectra.



1) Y.-L. Oh and E.N. Maslen, *Tetrahedron Lett.* 1966, 3291.

SYNTHETIC ANALOGUES OF DITERPENOID FRAGRANCE COMPOUNDS

P.U. Naegeli, M. Wetli

**GIVAUDAN Research Company Ltd.
CH-8600 Duebendorf, Switzerland**

Abstract not available

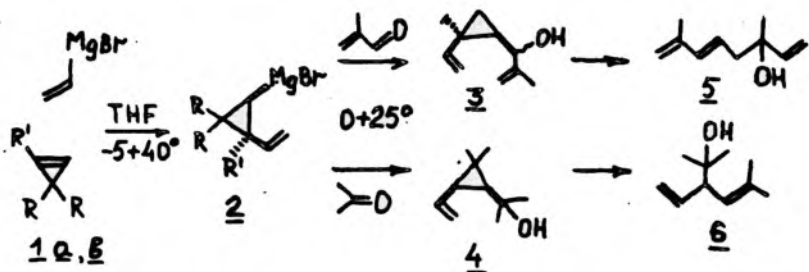


**SYNTHESIS OF (\pm)-HOTRIENOL AND (\pm)-SANTOLINA ALCOHOL
FROM CYCLOPROPENES**

**A.M.Moiseenkov, B.A.Czeskis, T.Yu.Rudashevskaya,
O.A.Nesmeyanova and A.V.Semenovsky[†]**

**N.D.Zelinsky Institute of Organic Chemistry, Academy
of Sciences, Moscow, U.S.S.R.**

cis-Addition of vinylmagnesium bromide to the cyclopropenes 1 gives rise to the Grignard reagents 2 in a moderate yield. Their quenching with an appropriate carbonyl compound affords the monoterpene cyclopropyl carbinols 3 (erythro/threo mixture) and 4. Their homoallylic rearrangement in the presence of catalytic amounts of 30% HClO₄ in THF solution gives smoothly the title monoterpenols 5 and 6, respectively. Structures of the compounds 3 - 6 were proven by spectral methods (IR, UV, PMR, MS).



R=H, R'=Me (a)

R=Me, R'=H (b)

CIS-C₅-HOMOLOGATION OF ISOPRENOIDS AS A ROUTE TO POLY-
PRENOOLS

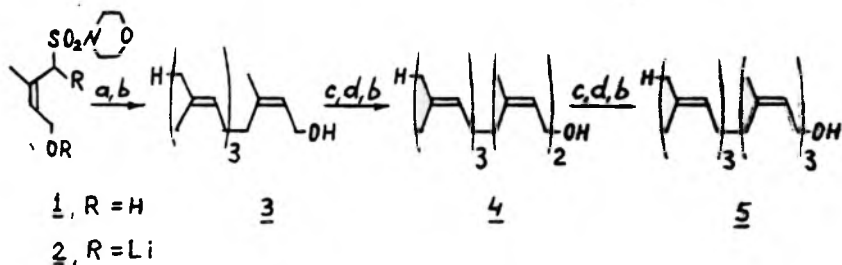
A.M.Moiseenkov, E.V.Polunin and A.V.Semenovsky[†]

N.D.Zelinsky Institute of Organic Chemistry, Academy
of Sciences, Moscow, U.S.S.R.

The extremely important role of polyprenols as carbohydrate carriers through cell membranes makes it necessary to synthesize these substances. One of the possible approaches to this problem requires the development of a stereospecific method of cis-C₅-homologation of isoprenoids. The synthon 1 was employed for this purpose; as an illustration, the synthesis of triterpenol 5 (betulaprenol-6) is represented (Scheme).

Successive prenylation of the Li salt 2 with E,E-farnesyl bromide and its Z mono- and, then, with Z,Z diprenenolgs yields the related sulfonamides, their Birch reduction catalyzed by dibenzo-18-crown-6 (DB18C6) affords the di- 3, sester- 4, and triterpenol 5, respectively.

The potentials of the approach considered for the stereospecific polyprenol synthesis will be discussed. Scheme



Reagents: E,E-FarBr, THF, -40° (a); Na/NH₃, 10 mol% of DB18C6, -40° (b); PBr₃/Et₂O (c); (2), THF, -40° (d).

NEW PREPARATION OF $\alpha,\beta\text{-}\gamma,\delta$ -UNSATURATED
KETONES

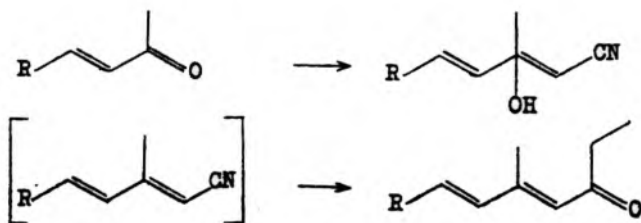
L. Streinz, M. Romaňuk

Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences, Prague

The synthesis of $\alpha,\beta\text{-}\gamma,\delta$ -unsaturated ketones have been elaborated using β -hydroxy- γ,δ -unsaturated nitriles treated with the excess of an alkyl magnesium bromide. The reaction proceeds via $\alpha,\beta\text{-}\gamma,\delta$ -unsaturated nitriles. The unsaturated nitriles in question can be prepared by the reaction of α,β -unsaturated ketones with the α -lithium acetonitrile.

Some of the $\alpha,\beta\text{-}\gamma,\delta$ -unsaturated ketones prepared by this method constitute very potent hormone analogues (juvenoids).

Reaction scheme (R = alkyl):



SYNTHESIS AND APPLICATION OF WATER SOLUBLE
JUVENOGEN COMPOUNDS

Z. Wimmer¹, M. Romaňuk¹, O. Melichar¹ and K. Sláma²

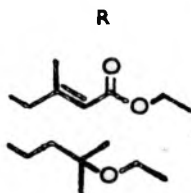
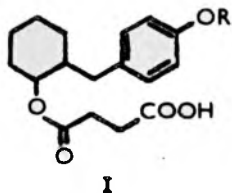
Institute of Organic Chemistry and Biochemistry¹
and Institute of Entomology²,

Czechoslovak Academy of Sciences, 166 10 Prague 6

Juvenogens are a new class of compounds liberating their biologically active components /Juvenile hormone analogues, Juvenoids/ under the influence of biotic factors within the insect organism.

During our search for new types of juvenoids, a special attention has been paid to the hydroxy derivatives capable of serving as the biologically active components of the juvenogens. Consequently, we have prepared the monohydrogen succinate derivatives I of some juvenoid alcohols. The compounds of the general formula I belong to the water soluble juvenogen compounds.

Possibilities of their application as non-traditional pesticides have been investigated.



A SYNTHESIS OF ETHERAL GERANYLIC AND CYTRONELLYLIC
JUVENILE HORMONE ANALOGUES WITH BICYCLIC TERPENE RINGS

L. Borowiecki, W. Wódzki, D. Zawacka

Department of Organic Chemistry, Institute of Chemistry,
N. Copernicus University, Toruń, Poland

The geranylic and cytronellylic ethers of 8-hydroxycamphene, borneol and mirtenol were obtained and then, transformed to corresponding epoxy- and methoxy derivatives. The biologic activity of the resulted compounds was estimated.

SYNTHESIS OF ETHERAL
INSECT JUVENILE HORMONE ANALOGS

L. Borowiecki, A. Kazubski, E. Reca

Department of Organic Chemistry, Institute of Chemistry
N. Copernicus University, Toruń, Poland

A synthesis of etheral, potential juvenile hormone analogs, containing pinene and cyclohexene rings systems in the terminal position is described.

REGIOSELECTIVE SYNTHESIS OF INTERNALLY BRANCHED
1,5,9-TRIMETHYLBALKANES OF SEX PHERMONES OF
TOBACCO HORNWORM (MANDUCA SEXTA)

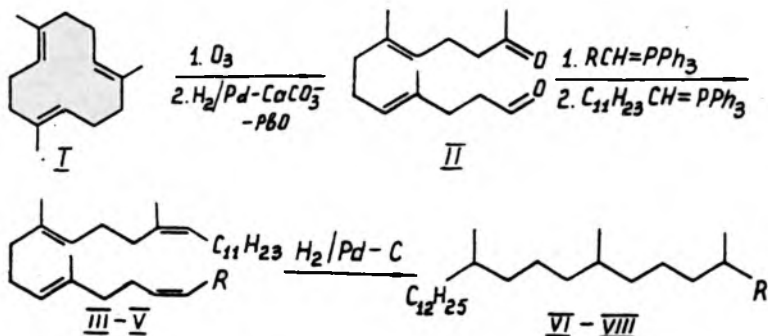
V.N.Odinokov, G.A.Tolstikov, V.R.Akhmetova

Institute of Chemistry of the Bashkirian Branch
of the Academy of Sciences, Ufa, USSR

A.M.Moiseenkov

N.D.Zelinsky Institute of Organic Chemistry
of the Academy of Sciences, Moscow, USSR

A new path to synthesis of 13,17,21- trimethyl-
tri-(VI), -penta-(VII) and -hepta-(VIII) triacona-
tanes which are sex phermones of tobacco hornworm
(Manduca Sexta), based on partial ozonolysis of
cyclootrimer of isoprene (I) and two stages selec-
tive olefination of ketoaldehyde (II) followed by
hydrogenation of tetraenes (III-V).



R=C₈H₁₇(III), C₁₀H₂₁(IV), C₁₂H₂₅(V, VI), C₁₄H₂₉(VII), C₁₆H₃₃(VIII)

SYNTHESIS OF PHEROMONE COMPONENTS OF THE IPS-SPECIES

P. Bäckström, F. Björkling, H.E. Högberg, T. Norin

Department of Organic Chemistry, Royal Institute of Technology, S-10044 Stockholm, Sweden

Abstract not available

STERESELECTIVE ALKYLATIONS OF DIANIONS IN THE SYNTHESIS
OF NATURAL PRODUCTS

G. Fráter

Socar Ag., Dübendorf, Switzerland

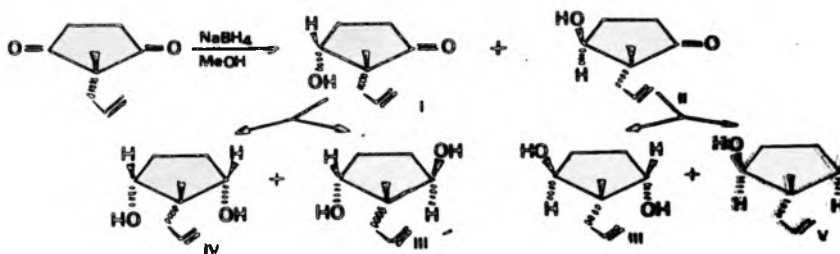
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REDUCTION OF 2-METHYL-2-ALLYLCYCLOPENTADIONE-1,3
WITH $\text{NaBH}_4/\text{NaOH}$ -RATIONALIZATION OF THE PRODUCTS RATIO

B. Nawrot and H. Zajac

Institute of Organic Chemistry,
Technical University, Łódź, Poland

Reduction of 2-Methyl-2-Allylcyclopentadione-1,3 with $\text{NaBH}_4/\text{MeOH}$ has been investigated. At $0-5^\circ\text{C}$ in methanol 72% of I and 28% of II were obtained. When I was reduced 50% of III and 50% of IV were obtained whereas reduction of II under the same conditions gave 64% of V and 36% of III. Conformational analysis of possible factors concerning the reduction course indicates that the approach, as presented by W. Todd Wipke and P. Gund⁽¹⁾ is the most fruitful. It is claimed that in both cases (I and II) it is the envelope conformation (A) that is responsible for the products ratio.



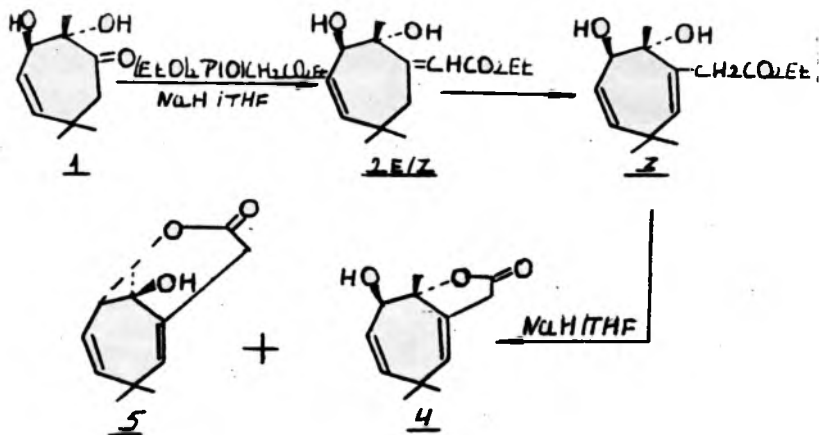
1) W. Todd Wipke and P. Gund: J. Am. Chem. Soc. 98, 8107 (1976).

SYNTHESIS OF γ - AND δ -LACTONES IN 1,1,4-TRIMETHYL
CYCLOHEPTANE SERIES VIA WITTIG-HORNER REACTION

H. Orszańska and F. Ruško

Department of Organic Chemistry, Institute of
Chemistry and Physics, School of Medicine,
50 137 Wrocław, Poland

The reaction of t-2,3-dihydroxy-2,6,6-trimethyl-4-
-cycloheptene-1-one /1/ with triethyl phosphonoacetate
afforded directly two lactones, i. e. 4 and 5.



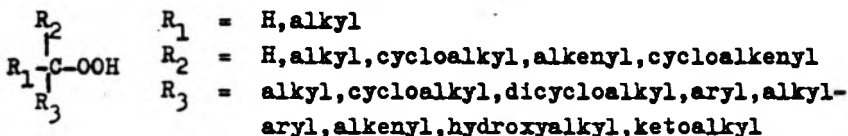
Explanation for that unexpected result was proposed.
Structures of both new lactones were proved on the basis
of spectral data / ^1H NMR and ^{13}C NMR mainly/ and on the
grounds of chemical transformations.

THE ELECTROCHEMICAL REDUCTION OF TERPENE HYDROPEROXIDES
TO ALCOHOLS

J. Górg, K. Śmigielski, A. Zachara, A. Socha

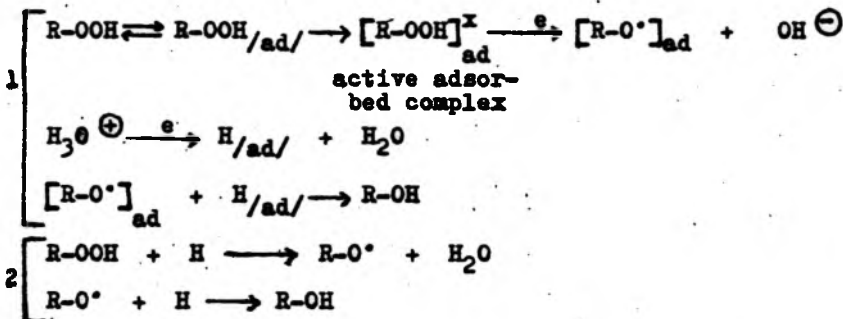
Institute of General Food Chemistry, Technical University,
90-924 Łódź, Poland

The novel electrochemical method of reduction of under-mentioned alkylhydroperoxides to alcohols was worked out.



Experiments were carried out in the standard electrochemical cell with diaphragm in aqueous-polar organic solutions on Ag, Ni, Zn, Fe, Hg or graphite cathodes. It was proved the adsorption of ROOH on the electrode surface.

Possible mechanisms of the reduction were discussed.



We have applied statistic methods of experiment planning to complete describe of the electrochemical reduction process.

We have obtained among other cis and trans pinanol, hydroxycitronellol, pinocarveol from suitable hydroperoxides with high yield.

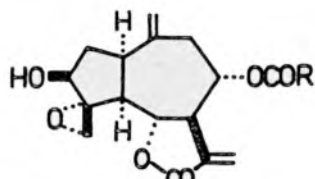
SESQUITERPENIC LACTONES FROM *Centaurea bella* TRAUTV.
 REVISION OF THE STRUCTURE OF ACROPTILIN, REPIN AND
 RELATED LACTONES

M. Holub^a, M. Buděšínský^a, + Z. Samek^a, B. Geppert^b and
 B. Droždž^b

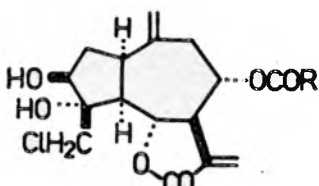
^aInstitute of Organic Chemistry and Biochemistry,
 Czechoslovak Academy of Sciences, 166 10 Prague 6

^bDepartment of Medicinal Plants, Institute of Drugs,
 Medical Academy, Poznań, Poland

From the aerial parts of *Centaurea bella* TRAUTV. repin (I), acroptilin (II) and janerin (III) were isolated. On the basis of a detailed study of the ¹H-NMR spectra of the isolated lactones and on the basis of the data described earlier, especially of some chemical correlations and X-ray analysis of centaurepensin (IV), revised or completed stereostructural formulas are proposed for repin (I), acroptilin (II), janerin (III), chlorohyssopifolin B (V), chlorohyssopifolin D (VI), chlorohyssopifolin E (VII), linichlorin A (VIII) (very probably identical with elegin) and chlorojanerin (IX).



- I R = C(CH₃)=CH₂
 II R = C(OH)(CH₃).CH₃Cl
 III R = C(CH₂OH)=CH₂



- IV R = C(OH)(CH₃)CH₂.Cl
 V R = H
 VI R = C(CH₃)(O.C₂H₅).CH₂OH
 VII R = C(OH)(CH₃).CH₂OH
 VIII R = C(CH₃)=CH₂
 IX R = C(CH₂OH)=CH₂

DIETHYLAMINE ADDITION TO NATURAL SESQUITERPENE
 α -METHYLENE- γ -LACTONES AND ITS USE FOR CHEMICAL
TRANSFORMATION OF THESE COMPOUNDS

J. Hermatha and †Z. Samek

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague,
Czechoslovakia

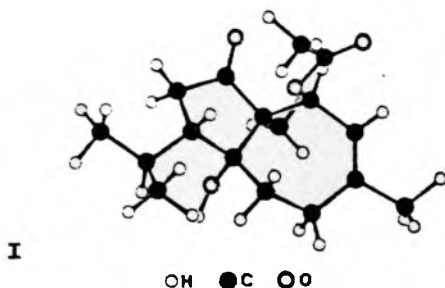
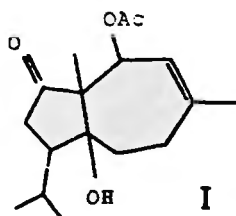
The addition of diethylamine to the exomethylene double bond in natural sesquiterpene α -methylene- γ -lactones is discussed. The advantage of the use of diethylamine in comparison with other currently used amines is stressed. It is shown that in some cases the solvolysis of the ester-group takes place simultaneously with the diethylamine addition. This is successfully used for a selective deacylation, avoiding thus the usual side-reactions such as relactonisation, cyclisation, irreversible addition, etc., occurring in the usual hydrolytic way. On the other hand, the possibility of this solvolysis complicates the potential utilisation of the amine adducts for the isolation of α -methylene- γ -lactones directly from the crude extract of the native source.

THE STRUCTURE OF SIOLACETATE

C.G. Casinovi⁺, G. Fardella⁺⁺, S. Cerrini[≡], O. Motl^{≡≡},
 W. Fedeli^o, E. Gavuzo[≡], D. Lamba[≡]

- ⁺ Istituto Superiore di Sanità, 00161 Roma, Italy
- ⁺⁺ Istituto di Chimica delle Sostanze Naturali, Università Perugia, Italy,
- [≡] Istituto di Strutturistica Chimica CNR, 00016 Montecitorio Stazione, Roma, Italy,
- ^{≡≡} Institute of Organic Chemistry and Biochemistry, 166 10 Praha, Czechoslovakia,
- ^o Istituto di Chimica Farmaceutica, Università Bologna, Italy

The molecular structure of siolacetate (I) $C_{17}H_{26}O_4$ (from fruits of *Sium latifolium*-Umbelliferae) was inferred from the examination of its NMR (1H , ^{13}C), IR and MS spectra. Further the structure and the relative stereochemistry was confirmed by an X-ray crystallographic study (crystal data - orthorhombic, space group $P2_1^2 2_1^2$, $a = 30.470$ (17), $b = 7.687$ (3), $c = 7.023$ (4) Å, $D_c = 1.19$ g . cm⁻³, for $Z = 4$, $\mu(\text{MokA}) = .9$ cm⁻¹) which will be discussed in detail. Siolacetate has the same relative configuration as carotol.



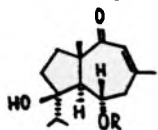
SESQUITERPENIC ESTERS OF CAROTANE TYPE
FROM FERULA LAPIDOSA AND FERULA PALLIDA.

A.I.Saidkhodjaev, L.A.Golovina, V.M.Malikov.
Institute of the Chemistry of Plant Substances,
Academy of Sciences of the Uzbek SSR, Tashkent,
USSR.

Eight esters of five new sesquiterpenic alcohols of carotane type with aromatic and aliphatic acids have been isolated from the *Ferula lapidosa* Eug. Kor. and *Ferula pallida* Eug. Kor. (Umbelliferae).

The structures and stereochemistry of substances have been proved on the basis of chemical transformations and spectral data.

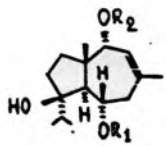
The absolute configurations have been established for three alcohols.



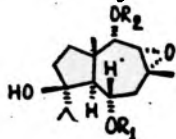
1. Lapidine, R=angeloyl.

2. Palliferine, R=trimethoxybenzoyl.

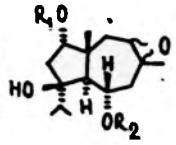
3. Palliferinine, R=3-methoxy,4,5-methylenedioxybenzoyl.



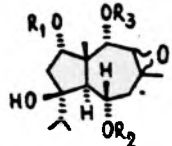
4. Pallinine, R₁=R₂=angeloyl.



5. Lapiferine, R₁=angeloyl, R₂=acetyl.



6. Lapiferinine, R₁=acetyl, R₂=veratroyl.



7. Lapidoline, R₁=R₃=acetyl, R₂=angeloyl.

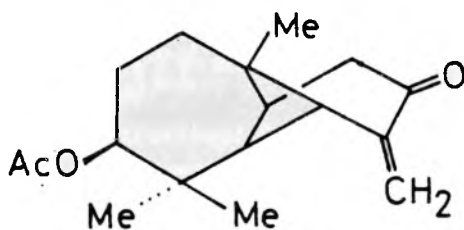
8. Lapidoline, R₁=R₃=acetyl, R₂=veratroyl.

(-)-12 α -ACETOXYLONGIPIN-2(10)-EN-3-ONE,
A NEW ENT-LONGIPINANE DERIVATIVE FROM
THE LIVERWORT MARSUPELLA AQUATICA

S. Huneck

Institute of Plant Biochemistry, Research Centre for
Molecular Biology and Medicine of the Academy of
Sciences of the GDR, DDR-401 Halle/Saale, Weinberg
German Democratic Republic

The structure and absolute configuration of a
new ent-longipinane type sesquiterpenoid, (-)-12 α -
acetoxylongipin-2(10)-en-3-one (I), from the
liverwort Marsupella aquatica have been elucidated
by spectroscopical and chemical methods.



I

EPOXYDATION OF ISOCEMBROL (THUNBERGOL)

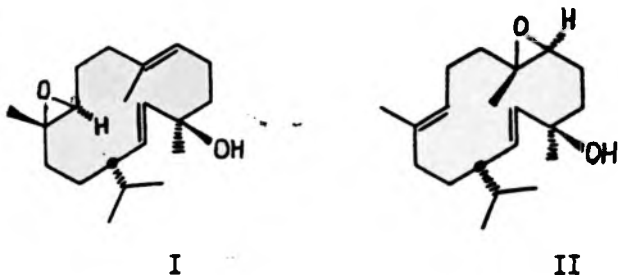
V.A.Kaldugin, N.I.Yaroshenko, V.A.Pentegova

Institute of Organic Chemistry, Siberian Division
of the Academy of Sciences, Novosibirsk 90, USSR

Epoxydation of isocembrol (thunbergol) by peracetic acid (1,5 eq.) in methylene chloride leads to two main epoxydes (I and II, yields - 50% and 20% respectively). Structures and stereochemistry of these compounds were determined by its conversion to known epoxycebrenes.

Spectral data of epoxyde I coincide with those of trocheliophorol, isolated by Groweiss /1/ from soft coral.

Conformation of isocembrol is discussed in relation to stereochemistry of epoxydes I and II.



1. A.Groweiss, Y.Kasman, D.J.Vanderah, B.Tursch,
P.Cornet, J.C.Braekman, D.Dalose, Bull.Soc.Chim.Belg.,
87, 277 (1978).

NEW SESQUITERPENES FROM *Meriandra benghalensis*

G. Savona, M. Bruno, F. Piozzi, E. Rodriguez

Institute of Organic Chemistry, Palermo, Italy

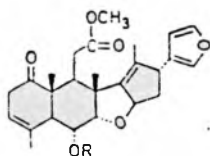
Abstract not available

PENTANORTRITERPENOIDS FROM AZADIRACHTA INDICA A. JUSS (MELIACEAE)

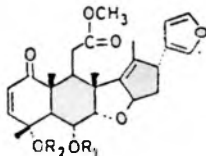
Wolfgang Kraus and Rudolf Cramer

Department of Chemistry, University of Hohenheim, 7000 Stuttgart 70

Pentanortriterpenoids have been isolated for the first time from seed oil, leaves, and bark of *Azadirachta indica*. Nimbinen (1a), 6-deacetylnimbinen (1b), nimbandiol (2a), and 6-acetylnimbandiol (2b) have been found in the seed oil, 1a, 1b, and 2a in the leaves, 1a and 1b in the bark. The structure determination by NMR will be reported.



(1a) R = Ac
(1b) R = H



(2a) R₁ = R₂ = H
(2b) R₁ = Ac R₂ = H

- 19 -

SESQUITERPENOIDS OF OLEORESINS CONIFERS FROM
PINACEAE

G.V. Dubovenko, V.A. Khan, V.A. Pentegova

Institute of Organic Chemistry, Siberian Division of the
Academy of Sciences, Novosibirsk 90, USSR

Abstract not available

NEW CHROMENES FROM LACTARIUS FULIGINOSUS FRIES

E. Conca^a, M. DeBernardi^a, G. Fronza^b, M. Girometta^a, G. Mellerio^a,
G. Vidari^a and P. Vita-Finzi^a

^aIstituto di Chimica Organica dell'Università degli Studi -
Via Taramelli 10 - 27100 Pavia (Italy)

^bCentro del CNR delle Sostanze Organiche Naturali del Politecnico
Piazza Leonardo da Vinci 32 - Milano (Italy)

In the last years many studies on the Russulaceae metabolites led to isolate sesquiterpenes with different skeleton: lactarane, seco-lactarane, marasmane, guaiane and drimane. The first three kinds of sesquiterpenes are biogenetically correlated and are widespread in most of the until now studied Russulaceae species. Drimanes and guaianes seem to be peculiar of the species belonging to the morphologically related groups named "uvidi" and "dapetes" respectively.

Here we report the results of a preliminary investigation on the metabolites of Lactarius fuliginosus Fries which belongs to the group named "fuliginosi".

From this mushroom no sesquiterpenes have been isolated but 6-methoxy-2,2-dimethylchromene along with some other new 6-methoxy-8-substituted-2,2-dimethylchromenes. To our knowledge this is the first finding of chromenes in Basidiomycetes. These compounds seem to be present also in Lactarius picinus Fries (fuliginosi).

Structures and spectroscopic data of these new natural products containing an isoprenoid moiety will be discussed.

ESSENCE OF POLYGONUM ODORATUM (POLYGONACEAE).
A CONTRACEPTIVE SUBSTANCE

Nguyen Gia Chan, Tam (Nguyen Thi)

Faculty of Pharmacy, 13 Le Thanh Tong, Hanoi, R.S.Viet-nam

Abstract not available

FURTHER INVESTIGATIONS IN CARBOCATIONIC
REARRANGEMENTS OF LANOSTANE DERIVATIVES

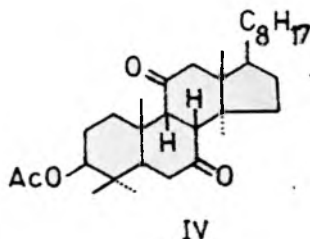
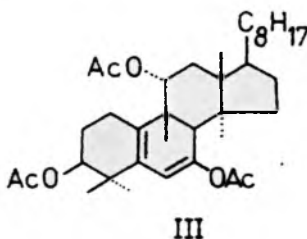
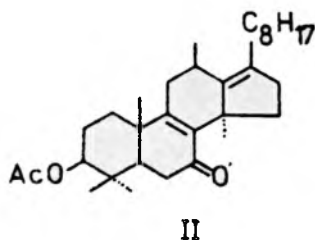
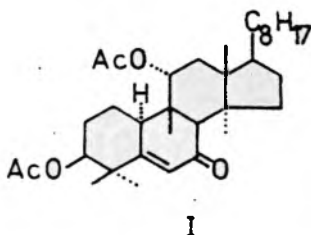
Z. Peryzek and R. Wydra

Institute of Chemistry, Adam Mickiewicz University,
Poznań, Poland

Little is known about structural and stereochemical features of the molecule which affect the direction and extent of rearrangement of carbocation generated in the central part of the steroidal skeleton.

The continuation of our studies on carbocationic rearrangements of epoxides, derivatives of lanostane, led to new observations.

Acid-catalysed reaction of 3 β -acetoxy-9 α ,11 α -epoxy-lanostan-7-one resulted in formation of four products, I - IV. Structure of the above-compounds was assigned on the basis of spectral data and chemical correlations. The mechanism of the rearrangement will also be discussed.



NEW ROUTE TO LANOST-9(11)-EN-7-ONES

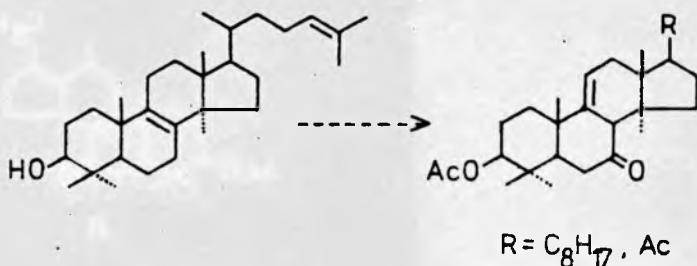
R. Wydra and Z. Paryzek

Institute of Chemistry, Adam Mickiewicz University,
Poznań, Poland

Derivatives of lanostane containing $\Delta^{9(11)}$ -7-keto grouping were found important intermediates in synthetic approaches to 19(10 \rightarrow 9)abeo-lanostane.

The previously described synthesis of 3β -acetoxy- 8β -lanost-9(11)-en-7-one proceeds with low and variable yield.

New efficient method of preparation of the title compound and its derivatives from lanosterol was elaborated and will be discussed.



THE HOMOGENEOUS HYDROGENATION AND DEUTERATION
IN TRITERPENOID CHEMISTRY

J. Protiva

Department of Organic Chemistry. Charles University,
Prague

Abstract not available

SOLVENT EFFECT IN THE STRUCTURAL STUDIES
OF ISOPRENOID KETONES BY CIRCULAR DICHROISM

J. Gawroński and K. Gawrońska

Institute of Chemistry, A. Mickiewicz
University, 60-780 Poznań, Poland

Circular dichroism spectra of several saturated and α,β -unsaturated isoprenoid ketones were recorded in 1,1,1,3,3,3-hexafluoro-2-propanol. The magnitudes of the $n-\pi^*$ Cotton effects reveal striking changes compared to the spectra taken in nonpolar solvents or ordinary alcohols.

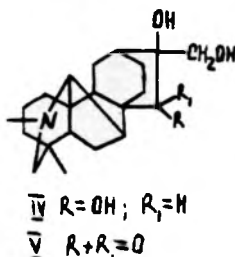
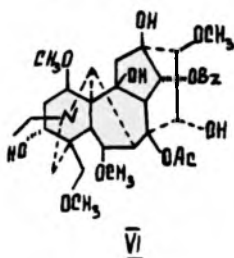
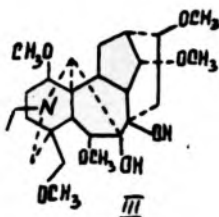
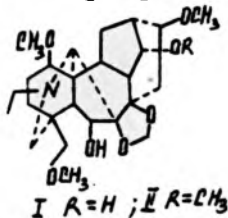
A possible relation of the solvent effect to the structural features and its application is discussed.

NEW DITERPENOID ALKALOIDS FROM SOME ACONITUM
AND DELPHINIUM SPECIES

M.S.Yunusov, B.T.Salimov, M.N.Sultankhodjaev,
M.G.Zhamierashvili, V.A.Telnov

Institute of the Chemistry of Plant Substances Ac.Sci.
UzSSR, Tashkent, USSR

From *Aconitum karakolikum*, *Delphinium iliense* and *Delphinium dictyocarpum* new alkaloids delcoridine, aconiphine, dictisine and dehydrodictisine have been isolated. The structures of all the new alkaloids have been elucidated on the basis of spectral data and chemical transformations. The correlation between delcoridine(I), delcorine(II) and delphatine(III) was carried out. The alkaloids dictisine(IV) and dehydrodictisine(V) possess the skeleton of denudatine, their structures finally being clarified by the help of the X-Ray analysis. Aconiphine(VI) is a diterpene alkaloid with the largest number of the functional groups.

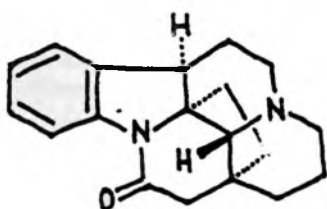


ABSOLUTE CONFIGURATION OF (-)-STREMPELIOPINE

Josef HÁJÍČEK and Jan TROJÁNEK

Research Institute of Pharmacy and Biochemistry,
19404 Prague 9, Czechoslovakia

(-)-Strempelepine (I), the parent base of schizozygine group of aspidospermane alkaloids, was isolated from the plant *Strempelepopsis strempeleoides* (Apocynaceae) of Cuba origin¹. Recently, we have finished² the total synthesis of (\pm)-I starting from 18-methylenevincadifformine (II)³.



(I)



(II)

Here, we report that the absolute configuration of natural (-)-base is as depicted in I. This assignment rests on its stereospecific synthesis from (+)-18-methylenevincadifformine (II), the absolute configuration of which follows from CD comparative measurements.

1) Laguna A.: Ph.D. thesis, Prague 1980

2) Hájíček J., Trojáněk J.: Paper presented at the Meeting on Stereochemistry, April 27-29, 1981, Liblice, Czechoslovakia

Hájíček J., Trojáněk J.: *Tetrahedron Lett.*, in press

CORRELATION BETWEEN CRYSTAL STRUCTURE AND PHOTOREACTIVITY
OF THREE 3-DEHYDROGIBBERELLIN A₃ DERIVATIVES

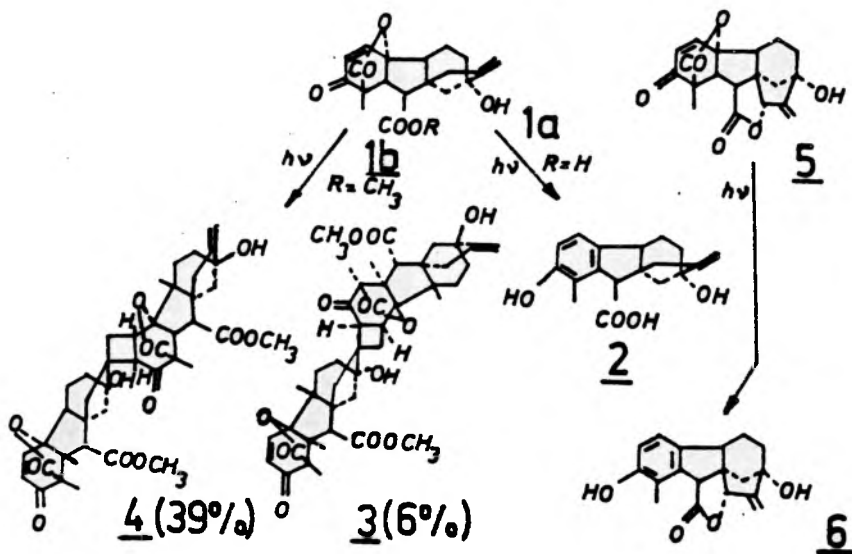
L. Kutschabsky and G. Reck

Central Institute of Molecular Biology of the Academy of Sciences of the GDR, Berlin-Buch, GDR

B. Voigt and G. Adam

Institute for Plant Biochemistry of the Academy of Sciences of the GDR, Halle (Saale), GDR

For 3-dehydrogibberellin A₃ type 1 a high photoreactivity in the crystalline state and a striking dependence of the photochemical reaction pathway on the kind of the substituent R have been observed. Whereas the free enone acid 1a undergoes intramolecular decarboxylation to the phenolic acid 2 upon $n \rightarrow \pi^*$ excitation, the corresponding methylate 1b gives two dimers 3 and 4 both arising from an intermolecular [2+2] photocycloaddition of the excited Δ enone double bond to the terminal olefine function of an adjacent second molecule. Unexpectedly, irradiation of the internal ester 5 in the solid state leads to a photoaromatization of ring A 6 instead of a photocycloaddition, although 5 is closely related to 1b. X-ray analysis showed that these differences in the solid-state behaviour are due to profound differences in molecular packing arrangements of these three compounds.

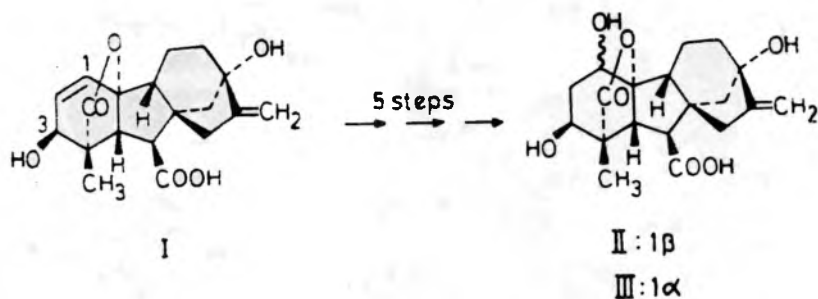


PARTIAL SYNTHESIS OF GIBBERELLIN A₅₅ AND A₅₇ FROM
GIBBERELLIN A₃

E. Voigt and G. Adam

Institute for Plant Biochemistry, Academy of Sciences of
the GDR, 4010 Halle/Saale, German Democratic Republic

A reaction sequence for the partial synthesis of the
gibberellins A₅₅ (II) and A₅₇ (III) from GA₃ (I) has been
carried out. Key reaction was the nucleophilic addition of
hydrazoic acid to the Δ^1 double bond of 3-dehydro GA₃
followed by NaBH₄ reduction of the resulting 1-epimeric
azido ketones. Photochemical excitation of the azido
chromophore in the obtained 1-azido 3-alcohols led under
loss of N₂ to imines which were smoothly hydrolysed to
the 1-oxo compounds. NaBH₄ reduction gave the desired
gibberellins A₅₅ (II) and A₅₇ (III) besides the corres-
ponding 3 α -epimers. Reaction pathways for the trans-
formation of I to 1 α - and 1 β -hydroxy GA₅ as well as the
corresponding GA₂₀ derivatives are also described.

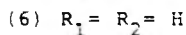
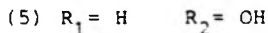
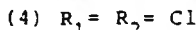
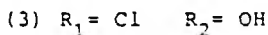
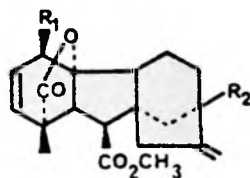
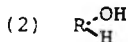
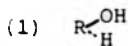
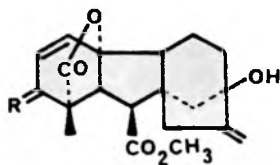


A PREPARATION OF GIBBERELLIN A₅ METHYL ESTER FROM
METHYL GIBBERELLATE

Z.J. Duri, B.M. Fraga and J.R. Hanson

School of Molecular Sciences, University of Sussex,
Brighton, BN1 9QJ, United Kingdom.

The reaction of methyl gibberellate (1) and 3-epi-gibberellate (2) with Ph₃P:CCl₄ in acetone and in pyridine has been examined. The major products, the 1 β -chloro and 1 β ,13-dichloro- Δ^2 -compounds (3) and (4), respectively, were reduced with tri-n-butyl tin hydride to GA₅ methyl ester (5) and the corresponding 2,3-dehydrogibberellin A₉ methyl ester (6). Deuteration studies showed that the reduction proceeded with predominant retention of configuration.



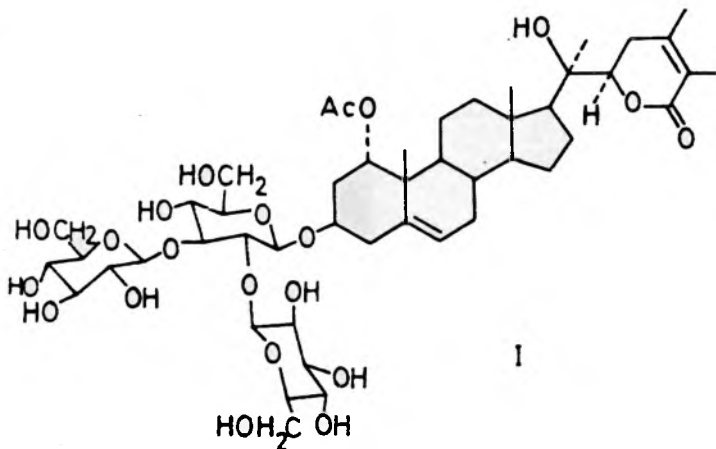
* Postal address: Institute of Organic Natural Products, CSIC, University of La Laguna, Tenerife, SPAIN.

DUNAWITHANINE A AND B - THE FIRST NATURALLY OCCURRING
WITHANOLIDE GLYCOSIDES, ISOLATED FROM DUNALIA AUSTRALIS

G. Adam, N. Q. Chien and N. H. Khoi

Institute for Plant Biochemistry, Academy of Sciences of
the GDR, 4010 Halle/Saale, German Democratic Republic

From dried leaves of *Dunalia australis* (Griseb.) Sleum.
(Solanaceae) the two withanolide glycosides dunawithanine
A and B have been isolated and their structures elucidated
as (2OR:22R)-O(3)- β -(1',3'-di-O-(β -D-glucopyranosyl)- β -
D-glucopyranosyl)-3 β ,20-dihydroxy-1 α -acetoxy-witha-5,24-
dienolide (I) and the corresponding O(3)- β -D-glucopyra-
nosyl-(1' \rightarrow x)- β -D-glucopyranosyl compound by spectro-
analytical and chemical data. Both compounds are the
first withanolide glycosides to be found in the plant
kingdom.



TENTATIVE CONFIGURATIONAL ASSIGNMENT OF NATURAL
3 α ,7 α ,23 α -TRIHYDROXY-5 β -CHOLAN-24-OIC ACID

A. Kutner and R. Jaworska

Institute of Pharmaceutical Industry, Rydygiera 8,
01-793 Warszawa, Poland

The absolute configuration of C-23 hydroxyl in 3 α ,7 α ,23-trihydroxy-5 β -cholan-24-oic acid isolated from seal bile /1/ has been determined. This involved the synthesis, as standard substances, of both C-23 hydroxyl epimers of the compound examined.

As could be expected the spectroscopic and mass spectrometric data for both synthetic compounds and the natural product were almost identical.

Molecular rotations of both synthetic compounds have been measured and their differences from that of the corresponding 3 α ,7 α -dihydroxy compound calculated. A comparison has been made of the values thus obtained with the molecular rotation differences reported elsewhere for methyl esters of 23 α - and 23 β -hydroxy-5 β -cholan-24-oic acids as related to methyl ester of 5 β -cholan-24-oic acid /2/.

The physicochemical data and chromatographic properties of natural 3 α ,7 α ,23-trihydroxy-5 β -cholan-24-oic acid are indicative of an α orientation of its 23-hydroxyl.

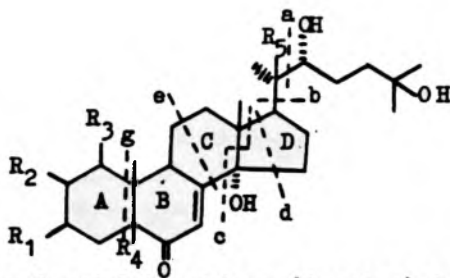
1. A. Kutner, R. Jaworska, W. Kutner, A. Grzeszkiewicz, in *Advances in Steroid Analysis*, Ed. S. Görög, Akadémiai Kiadó, Budapest, 1981, in press.
2. Y. Yanuka, R. Katz, S. Sarel, *Tetrahedron Letters*, 5229 /1970/.

THE NEW ELECTRON IMPACT FRAGMENTATION MODES OF ECDYSTEROIDS

Ya.V.Rashkes, N.K.Abubakirov

Institute of the Chemistry of Plant Substances,
Academy of Sciences of the Uzbek SSR, Tashkent, USSR

Mass spectrometry has been used in structure determining of the new ecdysteroids isolated from the middleasian plants. Their spectra were compared with that of the known samples of ecdysterone and α -ecdysone series. The relations between the number and position of hydroxyls and peak abundances of the main fragments a, b, c have been studied^{/1/}. The analytically important bond rupture processes of the steroid skeleton and the side chain C20-C27 have been detected by means of the high resolution technique.



The ring C and D breakdown (d and e) increases when $R_2-R_5=H$, whereas $R_2-R_4=OH$ leads to the ring A decomposition (g mode), other fragmentation patterns being simultaneously suppressed. The C22-C23, C23-C24, C24-C25 proved to be typical of both natural ecdysteroids and their acetates. The high sensibility and selectivity of the metastable defocusing technique was used with a view to observe the breakdown processes of the unstable ions, in particular, of the molecular ones. The step-like manner of the a, b, c fragments formation has also been ascertained with the aid of this method.

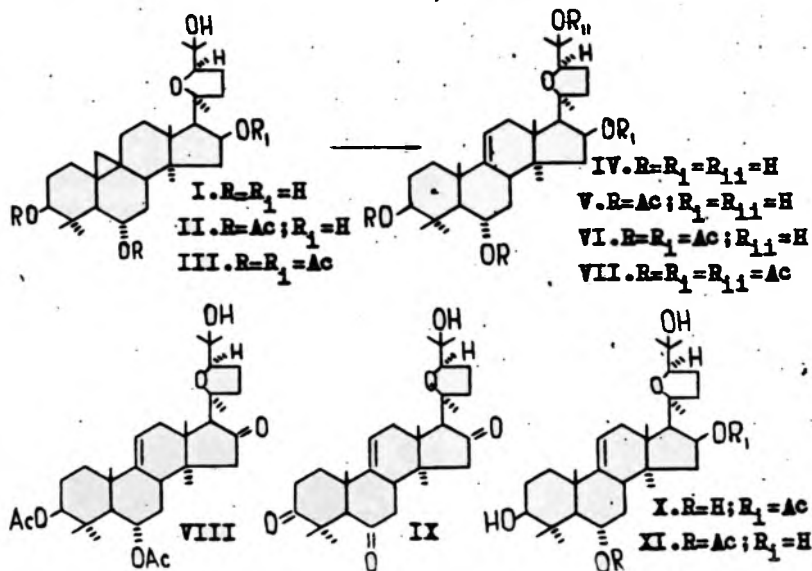
/1/ Ya.V.Rashkes, N.K.Abubakirov, Khimiya prirodnykh soedinenij, n.4, 518 (1980).

**CYCLOSIVERSIGENIN - A NEW ISOPRENOID FROM
ASTRAGALUS SIEVERSIANUS**

A.M.Svechnikova, R.U.Dmarova, M.B.Gorevits, K.L.Sel-
tanidi, Ya.V.Rashkes, M.R.Yagudaev, N.K.Abubakirov

Institute of the Chemistry of Plant Substances,
Academy of Sciences of the Uzbek SSR, Tashkent, USSR

A new isoprenoid - cyclosiversigenin (I), $C_{30}H_{50}O_5$ - has been isolated from the roots of the middleasian plant *Astragalus sieversianus* Pall. When heating with 3,5 % H_2SO_4 cyclosiversigenin (I) isomerizes into Δ^9 (II) - methylsteroid - siversigenin (IV). This transformation as well as some spectral data made it possible to refer the substance to the cycloartane series. Basing on the investigation results of the chemical properties and spectral features of the genin I and that of its derivatives II - XI cyclosiversigenin has been shown to be 20(S),24(R)-epoxycycloartane-3 β ,6 α ,16 β ,25-tetraol.

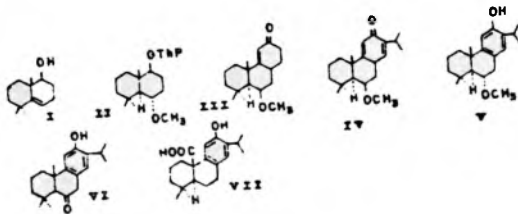


Synthetic Studies on Pisiferic Acid—a Diterpene
with Antimicrobial Activity.

Ajoy K. Banerjee and Sulbarán M. Carrasco

(Centro de Química, I.V.I.C., Apartado 1827, Caracas 1010A
Venezuela)

In connection with our studies on diterpene, attempt was made to synthesize VI, a potential intermediate for Pisiferic acid VII, isolated from *Chamaecyparis pisifera* Endle. For the synthesis of VI, the olefin I was chosen as reference material. Hydroboration of the tetrahydropyranyl derivative of I followed by treatment with MeI and NaH afforded II in 56% yield. Acid treatment of II, oxidation with Jones reagent and then Robinson annelation with 1-diethylaminobutanone-3-methiodide successively furnished III. The condensation of the zinc enolate of III with acetaldehyde, dehydration with TsOH, addition of Me_2CuLi and phenylselenenylation followed by elimination gave the enone IV. Acid catalysed hydrolysis furnished the phenol V which on demethylation and then oxidation afforded VI. Attempted conversion of VI to Pisiferic acid VII will be discussed.

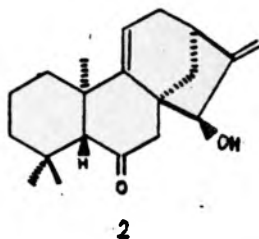
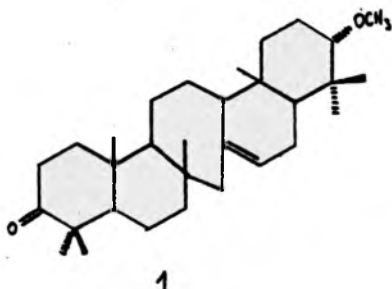


COMPONENTS OF THE LIVERWORT NARDIA SCALARIS

I. Beneš, T. Vaněk, T. Macek and V. Herout

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Flemingovo nám. 2, 166 10 Prague, Czechoslovakia

A homologous series of n-alkanes containing 17-35 carbon atoms, with an equal content of even and odd isomers was isolated from the liverwort *Nardia scalaris* S. GRAY corr. TREV. The major component was n-C₂₀H₄₂. In addition to this glycerides containing the C-16:0, 16:1, 18:0, 18:2 and 18:3 acids were isolated as the acid component, as well as a homologous series of n-alcohols C₂₄-C₃₄ with predominating even homologues. The major component is alcohol C₂₈. Of the terpenoid components we isolated (+)-3-oxo-21d-methoxyserrat-14-ene (1), and nardiine, ent-15α-hydroxy-9(11),16-kauradien-6-one (2).

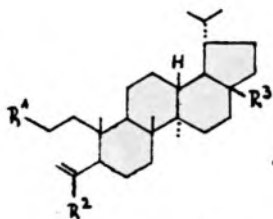


SYNTHESIS OF 3,4-SECODERIVATIVES OF BETULINIC ACID

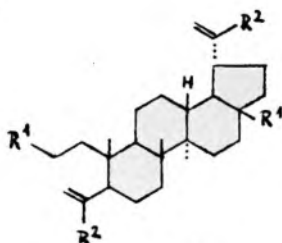
I. Valterová, J. Klinot, A. Vystrčil

Department of Organic Chemistry, Charles University,
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In relation to the study of the biological activity of some triterpenoid acids, a series of mono-, di-, tri- and tetracoic acids derived from the lupane skeleton /general formula I, II/ has been prepared using betulinic acid as a starting material. Methods for the partial esterification of these acids have been developed. The structure of the partially esterified derivatives has been confirmed by the mass spectrometry. The antibacterial activity of the synthesised compounds will be discussed.



I



II

R^1 : CN, COOH, COOCH₃

R^2 : ClC, CH=NOH, CN, COOH, COOCH₃, CH₂OH, CH₂OCOCH₃

R^3 : COOH, COOCH₃

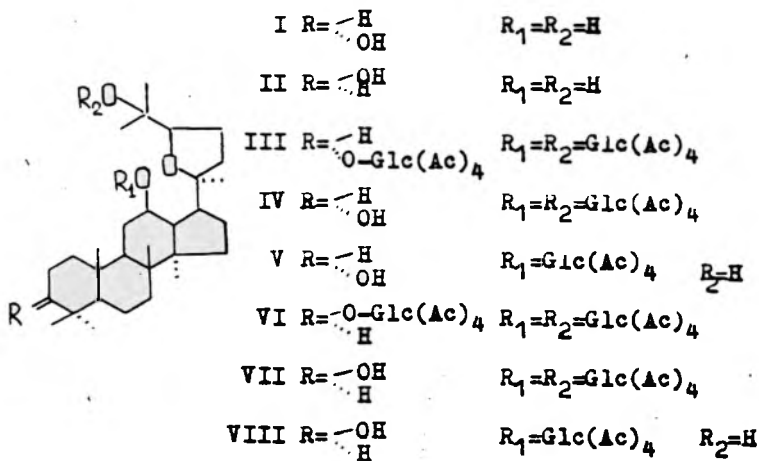
DAMMARANE TRITERPENES IN O-GLYCOSIDE SYNTHESIS

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In connection with glycosilation studies on damma-
rane type triterpenes glycosides III-VIII of triol I
and its 3-epimer II were obtained by using 2,3,4,6-tet-
ra-O-acetyl- α -D-glucopyranosyl bromide and mercury (II)
cyanide as catalyst. Glycosilation of I and II with equi-
molar amounts of acetobromoglucose and mercury (II) cya-
nide was regioselective yielding 12-O-glucosides V and
VIII. The structure of glycosides has been established
on the basis of IR, ^1H and ^{13}C -NMR spectroscopy data.

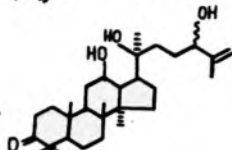
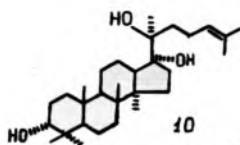
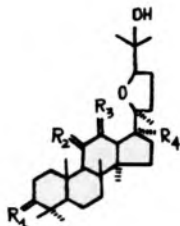


STRUCTURES OF NEW TRITERPENOIDS FROM LEAVES OF
 FAR EAST SPECIES OF BETULA GENUS

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Eleven new triterpenes of dammarane type have been
 isolated from unsaponifiable fraction of ether extract
 of the Far East species of Betula genus leaves. The
 structure of the compounds has been established on the
 basis of spectral data and chemical transformations.



- | | | | |
|--|---|--|-------------------|
| 1. $R_1 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_2 = \text{H}_2$ | $R_3 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_4 = \text{OH}$ |
| 2. $R_1 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_2 = \begin{array}{c} \diagup \text{OAc} \\ \diagdown \text{H} \end{array}$ | $R_3 = \text{H}_2$ | $R_4 = \text{H}$ |
| 3. $R_1 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_2 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_3 = \text{H}_2$ | $R_4 = \text{H}$ |
| 4. $R_1 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_2 = \begin{array}{c} \diagup \text{OAc} \\ \diagdown \text{H} \end{array}$ | $R_3 = \text{H}_2$ | $R_4 = \text{H}$ |
| 5. $R_1 = \begin{array}{c} \diagup \text{OAc} \\ \diagdown \text{H} \end{array}$ | $R_2 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_3 = \text{H}_2$ | $R_4 = \text{H}$ |
| 6. $R_1 = \text{O}$ | $R_2 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_3 = \text{H}_2$ | $R_4 = \text{H}$ |
| 7. $R_1 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_2 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_3 = \text{H}_2$ | $R_4 = \text{H}$ |
| 8. $R_1 = \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{H} \end{array}$ | $R_2 = \text{H}_2$ | $R_3 = \text{H}_2$ | $R_4 = \text{OH}$ |
| 9. $R_1 = \text{O}$ | $R_2 = \text{H}_2$ | $R_3 = \text{H}_2$ | $R_4 = \text{OH}$ |

USE OF ^{13}C NMR SPECTROSCOPY FOR CONFORMATIONAL ANALYSIS
OF SIDE CHAIN OF DAMMAZANE TYPE TRITERPENOIDS

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Abstract not available

SEPARATION AND STRUCTURAL EXAMINATION
OF FOUR GEOMETRIC BIS-OXIME ISOMERS

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Abstract not available

REACTIONS OF PHOSPHOROUS PENTACHLORIDE WITH SOME TRICYCLIC
TERPENE KETONES

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Abstract not available

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