

CZECHOSLOVAK ACADEMY OF SCIENCES
Institute of Organic Chemistry and Biochemistry

10th CONFERENCE ON ISOPRENOIDS
ABSTRACTS OF PAPERS



16th to 21st October, 1983

10th CONFERENCE ON ISOPRENOIDS

October 1983, Třebon', Czechoslovakia

The Conference is jointly organized by the Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences (Prague) and the Slovak Chemical Society (Bratislava)

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NEW DEVELOPMENTS IN THE SYNTHESIS OF GIBBERELLINS

G. Adam

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

Recent advances in the synthesis of gibberellin phytohormones and their analogs are presented. On the base of an X-ray study of the most important member gibberellin A₃ (GA₃) the structure and reactivity of these polyfunctionalized and highly strained molecule is discussed. Starting from GA₃ synthetic pathways to other structural types by chemical and photochemical transformations are described including the following main topics:

- Synthesis of rare native gibberellins, e.g. GA₅₅, GA₅₇, GA₆₀;
- Pathways to gibberellin analogs, e.g. amino and thio compounds;
- Synthesis of labelled gibberellins, especially tritiated in position 6 and 15.

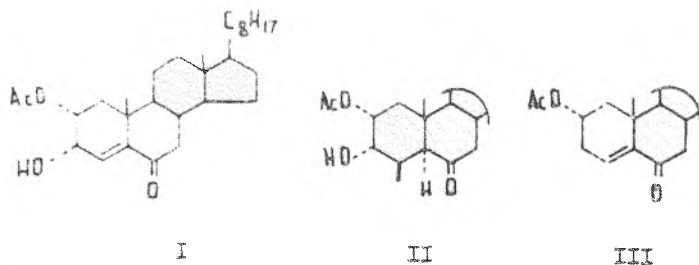
Many of the synthesized compounds open new possibilities for further biological studies, biosynthetic investigations and structure-activity relationships of this phytohormone class.

1,4-ADDITION OF GRIGNARD REAGENTS TO 2,3-DISUBSTITUTED
 Δ^4 -6-KETOSTEROIDS

A. Akhrem, P. Lakhvich, V. Khripach, N. Kovganko

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

The Cu^{+1} -catalysed 1,4-addition of Grignard reagents to Δ^4 -6-ketosteroids, bearing oxygen containing substituents (OH, OAc) in the 2 α ,3 α -positions, has been investigated. The two major products, the 4 β -methyl and 2-deoxycompounds II and III, respectively, were obtained from the reaction of methyl magnesium iodide with 2 α -acetoxy-3 α -hydroxy-4-cholesten-6-one. The structure and stereochemistry of the compounds II and III have been elucidated by PLR (360 MHz) and other spectroscopical and chemical methods.



ON THE STEREOCHEMISTRY OF CIS-HYDROXYLATION OF
2,4-DIENE-6-KETOSTEROIDS

A. Akhrem, F. Lakhvich, V. Khripach, N. Kovganko,
N. Galitskiy

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

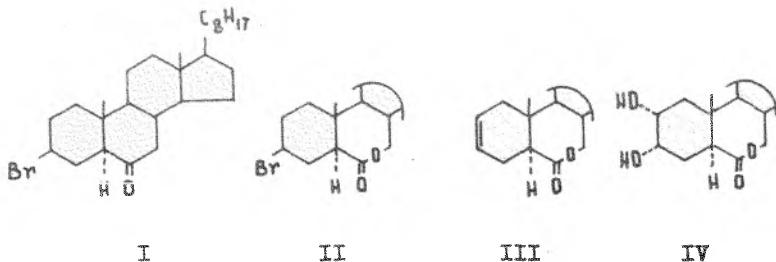
The cis-hydroxylation of Δ^2 -steroids is widely used for the preparation of 1,2-cis-diols such as ecdi- and brassinosteroids. The α - and β -cis-configurations of vicinal OH-groups are usually achieved by OsO_4 -hydroxylation and by Woodward addition ($\text{CH}_3\text{COOAg} + \text{I}_2 + \text{CH}_3\text{COOH} + \text{H}_2\text{O}$) to Δ^2 -bond, respectively. We established that the conjugation of Δ^2 -bond with Δ^4 -6-keto function leads to a reverse of the stereochemical direction of both reactions. This fact may be explained not only by changing of A-ring stereochemistry, but also by influence of electron factors. Some spectral and X-ray crystallographic data as well as possible reaction mechanisms will be discussed.

A NEW APPROACH TO THE SYNTHESIS OF 2 α ,3 α -DIHYDROXY-
B-HOMO-7-OKSA-6-KETOSTEROIDS

A. Akhrem, F. Lakhvich, V. Khripach, N. Kovganko,
V. Zhabinskiy

Institute of Bioorganic Chemistry, Byelorussian SSR
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A new approach to the synthesis of 2 α ,3 α -dihydroxy-B-homo-7-oksa-6-ketosteroids, such as brassinolide and its analogs, is discussed. Contrary to previously described methods, the formation of the B-ring lactone group was achieved at the first step of the synthesis. Application of this method is illustrated by the formation of 2 α ,3 α -dihydroxy-B-homo-7-oksa-5 α -cholestan-6-one IV resulting from Bayer-Villiger oxidation of the ketone I followed by dehydrobromination of the ketone II and α -cis-hydroxylation of the Δ^2 -steroid III.



- 2 -

NEW MODIFICATIONS OF THE STEROIDIC NUCLEUS BY OXIDATION
AND REDUCTION WITH OLD OXIDIZING AND REDUCING AGENTS.

M. Anastasia, A. Fiecchi, A. Scals, P. Allevi, P. Ciuffreda,
and M. Del Puppo.

Department of Chemistry and Biochemistry,
School of Medicine, University of Milan,
Via Saldini 50, 20133 Milano, Italia

Readily available steroids, essentially unfunctionalised, can be transformed into natural compounds, otherwise obtainable only with difficulty, by means of simple old oxidizing or reducing agents. Steroidic rings C and D can be functionalized through a sequence of epoxidations and rearrangements by oxidation of the $\Delta^{8,14}$ diene system of steroids with chromic acid.

The mechanisms involved were clarified.

The adductus, obtained from the reaction of steroidic enes or dienes with diethyl-azodicarboxylate or 4-phenyl-1,2,4-triazoline-3,5-dione, are transformed by reduction with ethylamine dissolved in lithium into natural compounds.

Key intermediates for the synthesis of steroids of biological interest are obtained in the same way.

The utility of these reactions in the synthesis will be discussed.

SESQUITERPENE LACTONES FROM ARTEMISIA UMBELLIFORMIS LAM.

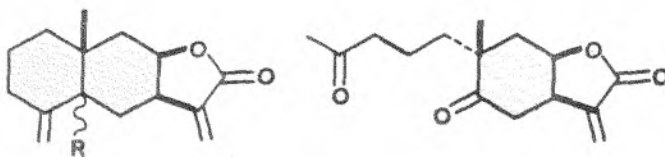
G. Appendino, P. Gariboldi¹ and G.M. Nano

Laboratorio RMN e Spettroscopie applicate alla Tossicologia,
Facoltà di Farmacia, Corso Raffaello 31, 10125 TORINO (Italy)

¹Laboratorio di Chimica Organica della Facoltà di Scienze,
Via Venezian 21, 20133 MILANO (Italy)

Investigation of the mountain plant Artemisia umbelliformis Lam. afforded, besides known compounds, the new hydroperoxyeudesmanolides 1 and 2, and a diketolactone having the hitherto unreported 4,5-secoeudesmane skeleton (3).

A conformational study of 2 and some transformation products showed that these cis-decalin type derivatives exist in solution at room temperature as single preferred rotamers, whose conformation



3

R

1 α OOH

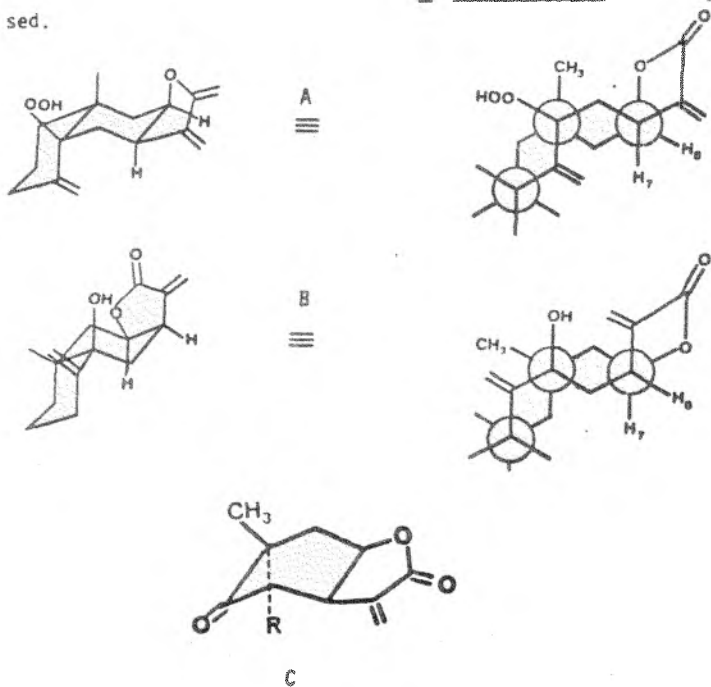
2 β OOH

4 β OH

depends on the substituent at C-5: these conformations are typified by the steroid-like conformation of 2 (A) and the non-steroid conformation of its corresponding alcohol (4, B).

3 adopts in solution at room temperature the $\theta = 60^\circ$ cyclohexanone boat conformation (C), and has an exomethylene γ -lactone group belonging to the pseudorotational P-type.

The CD curves of these compounds as well as their pyrazoline derivatives are presented. A possible biogenetic relationship among the sesquiterpene lactones of A. umbelliformis is discussed.



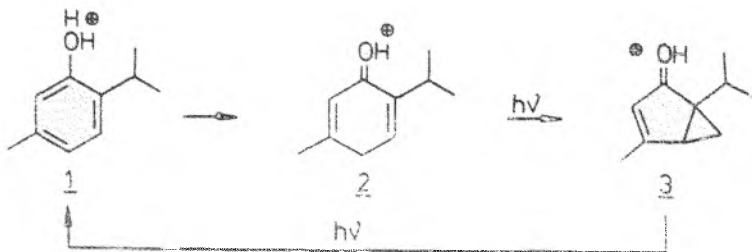
PHOTOCHEMICAL TRANSFORMATIONS OF PROTONATED PHENOLS. A ONE-STEP SYNTHESIS OF UMBELLULONE FROM THYMOL.

P. Baeckström, U. Jacobsson, B. Koutek^x and T. Norin

Department of Organic Chemistry

Royal Institute of Technology, S-100 44 Stockholm, Sweden

Irradiation at 254 and 300 nm of the protonated cross-conjugated dienone 2, formed by dissolving thymol in trifluoromethanesulfonic acid, yields umbellulone (3), which is photochemically in equilibrium with the starting material. A slower photochemical dealkylation-alkylation process also occurs. Products of the latter reaction were isolated and characterized.



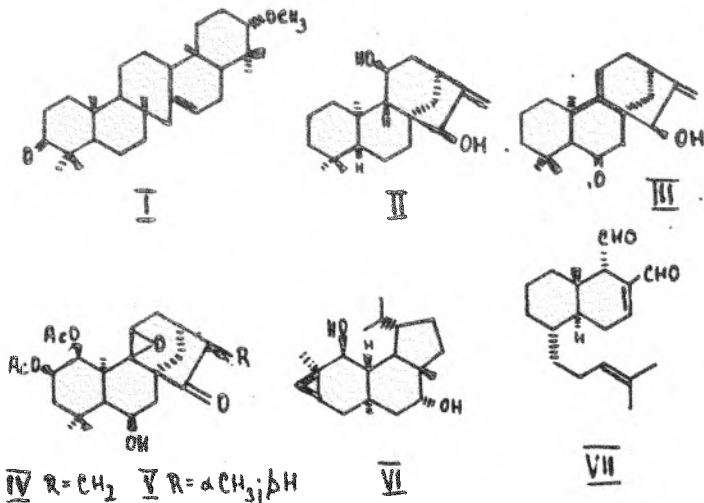
^x Visiting research scientist from Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Flemingovo nám. 2, 166 10 Prague, Czechoslovakia.

CONSTITUENTS FROM THE LIVERWORT *NARDIA SCALARIS*,
MYLIA ANOMALA AND *PELLIA ENDIVIIFOLIA*

I. Beneš, T. Macek, T. Vaněk and M. Buděšínský

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, CS-16610 Prague 6

From *N. scalaris* S. GRAY corr. TREV. (+)-3-oxo-2 α -methoxyerrat-14-ene I, nardiin(ent-15 α -hydroxy-9(11),16-kauradien-6-one) III, ent-kaur-16-en-11 α ,15 α -diol II, ent-1 α ,2 α -diacetoxy-6 α -hydroxy-9(11)-epoxy-kaur-16-en-15-one IV and ent-1 α ,2 α -diacetoxy-6 α -hydroxy-9(11)-epoxy-(16R)-kauran-15-one V were isolated and identified. The previously described¹ diterpenoid A from *Mylia anomala* HOOK. S. GRAY was identified as (-)-2 β ,9 α -dihydroxyverrucosane VI and the diterpenoid from *P. endiviifolia* DICKS. DUM. seems to be identical with saoculatal VII isolated from the same liverwort by Asakawa².



1. V. Benešová et al.: Coll. Czech. Chem. Commun. 40, 658 (1975).

2. Y. Asakawa, T. Takemoto: Phytochem. 17, 153 (1978).

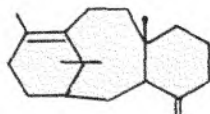
AN APPROACH TO THE SYNTHESIS OF TAXANE DERIVATIVES.

J.M. Bernassau, H. Cervantes, D. Do Khac Manh, M. Fétizon,

I. Hanna and C. Prevost.

Ecole Polytechnique, Laboratoire de Synthèse Organique,
91128 Palaiseau, France.

Several approaches of taxane derivatives will be reported, essentially based on inter or intramolecular $[2 + 2]$ photochemical cycloadditions. In particular, the rather unpredictable chemistry and conformational analysis of 9,9 dimethyl of bicyclo $[3,3,1]$ -nonane will be presented in detail.



taxane

INTRAMOLECULAR CYCLIZATION OF DIKETOALDEHYDE

Zbigniew Bończa-Tomaszewski

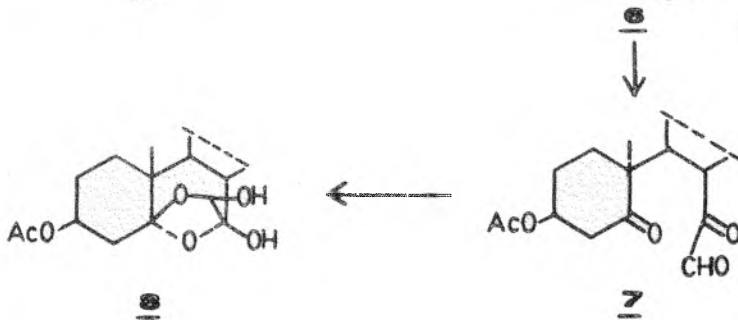
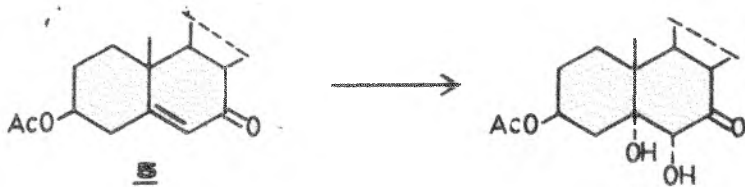
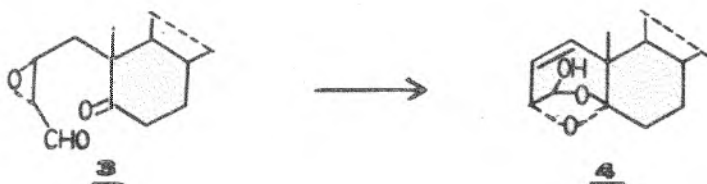
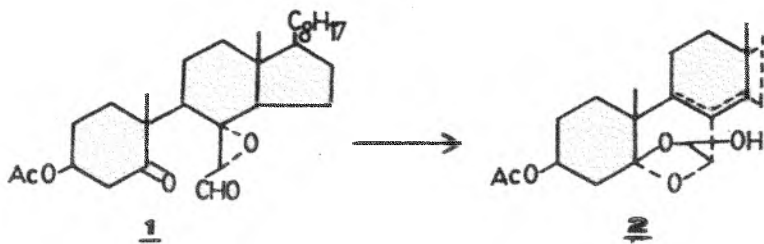
Department of Chemistry, Warsaw University

02093 Warszawa, Poland

Few years ago we discovered that epoxyketoaldehydes (1 and 3) have undergone the intramolecular cyclization into ketal-acetals 2 and 4, respectively.* It seems to be likely that such a reaction would have more general character. For that reason studies on behaviour of diketoaldehyde 7 under various conditions have been undertaken.

3 β -Acetoxycholestan-5-one-7 (5) was transformed into ketodiol 6 with potassium permanganate. Ketodiol 6 was converted into diketoaldehyde 7 with lead tetraacetate. It was found that diketoaldehyde 7 in acid medium underwent the intramolecular cyclization into ketal-acetal (8). The mechanism of the formation of 8 has been proposed.

*W. J. Rodewald, Zb. Bończa-Tomaszewski, Tetrahedron Letters, 3, 169 (1979).

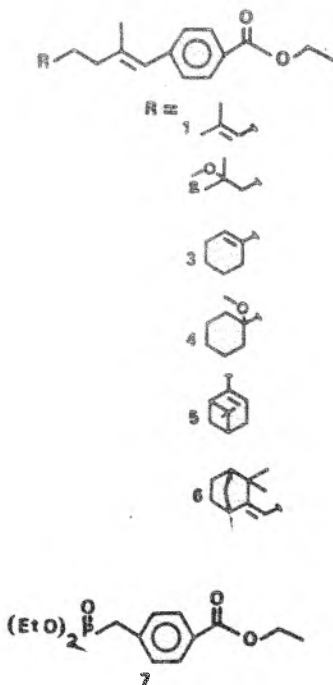


THE SYNTHESIS OF JUVENIDS WITH AROMATIC MOIETY

L. Borowiecki, A. Kazubski, E. Reca, W. Wódzki

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

Some novel potential juvenoids with p-substituted benzoate moiety in the molecule were obtained. Syntheses of all insect juvenile hormone analogs /e.g. 1-6/ were based on Wittig-Horner condensation of the phosphonate 7 with the appropriate methyl ketones.

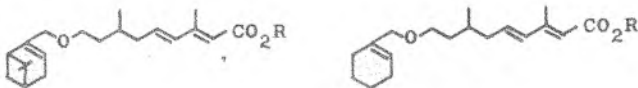


SYNTHESIS OF ETHERAL
INSECT JUVENILE HORMONE ANALOGS

L. Borowiecki, E. Reca

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

A synthesis of some 10-oxa-2,4-dienoic ester, potential insect juvenile hormone analogs, containing pinene and cyclohexene ring in the terminal position is presented.



R = Et, i-Pr

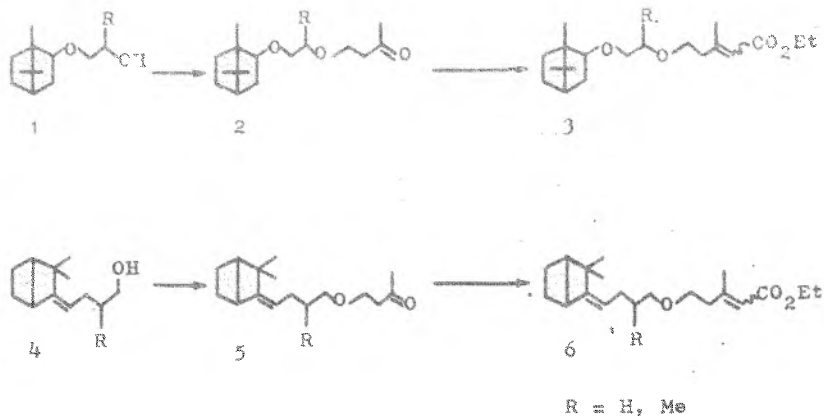
Myrtenol and cyclohexenylmethanol were the starting materials in these syntheses.

THE SYNTHESIS OF SOME OXA JUVENOIDS WITH BORNANE
AND CAMPHERE RINGS

L. Borowiecki, M. Weiniak, W. Wódzki

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

Novel oxa analogs of insect juvenile hormones with bornane /3/ and camphene /6/ rings in a terminal position were obtained according to the scheme:



The condensation of methyl vinyl ketone with the appropriate alcohols 1 and 4 produces oxa ketones 2 and 5 which are subsequently subjected to Wittig-Horner condensation with diethylphosphonoacetate.

SUBSTITUTION REACTIONS OF 5-FUNCTIONALIZED 6-OXO STEROIDS

Zdzisław Chilmonczyk and Wojciech J. Szczepek

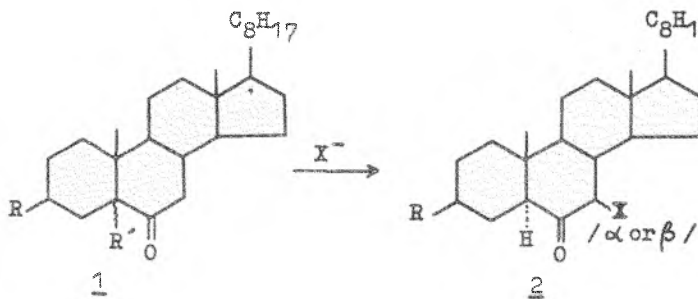
Department of Chemistry, Warsaw University

02093 Warszawa, Pasteura 1, Poland

The S_N2' reactions of 5-substituted 6-oxocholestanes have been investigated. We have found, that for all R' and X listed below, 1 \rightarrow 2 interconversions have appeared to be possible.

However, in the case of $R' = \alpha\text{-OH}$, $\alpha\text{-Cl}$ and $X = \text{Cl}$ the obtained results have not been in agreement with earlier observation of Shoppee. He stated that such interconversion could not be probable.

We have observed strong difference in reaction course for compounds with different R.



R = OAc, H

$R' = \alpha\text{-Cl}, \alpha\text{-Br}, \alpha\text{-OH}, \beta\text{-OH}, \alpha\text{-OMe}, \alpha\text{-OAc}$

X = Cl, Br

RECENT ADVANCES IN THE CHEMISTRY OF THE MELIACEAE

J.D. Connolly

Department of Chemistry, University of Glasgow, Scotland

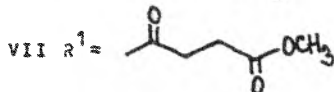
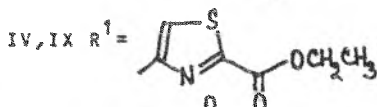
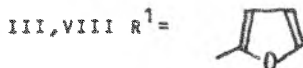
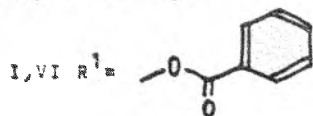
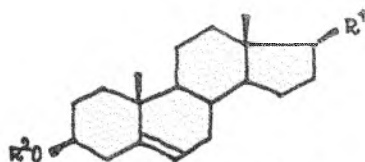
In biogenetic terms limonoids (tetranortriterpenoids) can be derived from simple C₃₀ tirucalol precursors by apo-rearrangement and loss of four carbon atoms from the side chain with formation of a furan ring. Subsequent ring cleavage processes and rearrangements lead to the wide range of known structural types. A brief overall picture of this group will be given, including discussion of representative structures and their chemistry. The structural elucidation of several new compounds, which arise by a novel ring cleavage, from Carapa procera and C. grandiflora will be detailed.

3 β -(β -D-GLUCOPYRANOSIDES) OF 17 β -FUNCTIONALIZED
5-ANDROSTEN-3 β -OL

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Institute of Organic Chemistry and Biochemistry,
Czech. Acad. Sci., 166 10 Prague 6, Czechoslovakia

In connection with biological activity testing we decided to prepare carbohydrate derivatives of 5-androsten-3 β -ol with various functions in 17 β -position. In view of the promising results with silver silicate in oligosaccharide synthesis¹ we decided to solve our problem by using this catalyst for steroid glycosylation. Using a two-fold excess of halogenose we prepared derivatives I-V (R^2 = tetra-O-acetyl- β -D-glc-) in 68, 78, 30, 43, and 76% yields, resp. On mild deacetylation with triethylamine in aqueous methanol² glucosides VI-X (R^2 = β -D-glc-) were obtained; in compound, II the lactone ring was destroyed.



1. H. Paulsen: *Angew. Chem.* **94**, 184 (1982).

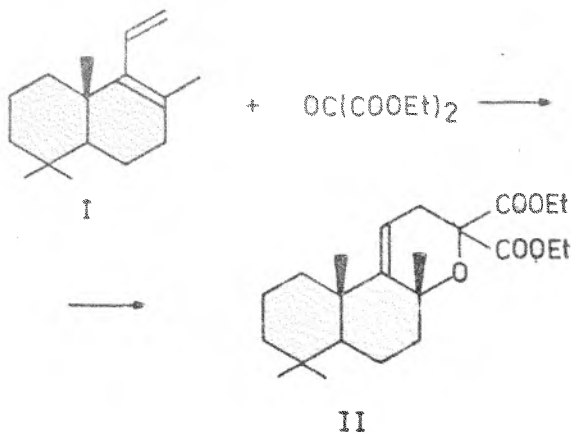
2. L. Brown, et al: *Arzneim.-Forsch.* **31**, 1059 (1981).

ATTEMPTED TOTAL SYNTHESIS OF AMBREINOLIDE

W.M. Daniewski, J. Jurczak and E. Kubak

Institute of Organic Chemistry, Polish Academy of
Sciences, 01-224 Warsaw, ul. Kasprzaka 44, Poland

The ambreinolide skeleton was prepared on multistage synthesis beginning from the 4-methyl-Wieland-Michler Ketone. The key step involved the reaction of the diene I with diethyl mesoxalate under very high pressure. The product of the reaction /II/ will be transformed into the title compound.



REGIOSELECTIVITY OF FURAN RING OXIDATION INDUCED
BY NEIGHBOURING HYDROXYL GROUPS

W.M. Daniewski, W. Kroszczyński and J. Krol

Institute of Organic Chemistry, Polish Academy of
Sciences, 01-224 Warsaw, ul. Kasprzaka 44, Poland

Oxidation of the furan ring of so called furandiol /known sesquiterpene isolated from the fungus *Lactarius necator*/ showed a profound effect of neighbouring hydroxyl groups on regioselectivity of this process. Protection of the secondary hydroxyl group by acetylation enabled to synthesize only one isomer. Preparation of lactarorufin A from furandiol confirmed its stereochemical structure as well as the hypothesis of formation of lactones from furans in biogenesis.

CHEMOTAXONOMIC STUDIES OF HIGHER FUNGI
MONOHYDROXY AND DIHYDROXY LACTONE CONTENTS
AS CHARACTERISTIC CHEMOTAXONOMIC FEATURES
OF LACTARIUS

W.M. Daniewski, W. Kroszczyński, A. Warzuń and
A. Rymkiewicz

Institute of Organic Chemistry, Polish Academy of
Sciences, 01-224 Warsaw, ul. Kasprzaka 44, Poland

Continuing our research we decided to elaborate a HPLC test for identification of Lactarius mushrooms. It was found that almost all Lactarius mushrooms contained monohydroxylactones of lactarane skeleton. The monohydroxylactones could be very easily isolated as a mixture from ethanolic extract of a particular mushroom and then analysed by HPLC. The identity of peaks could be confirmed by mass spectroscopy. It appeared that these monohydroxylactone contents were characteristic chemotaxonomic features of every species. It was very interesting to find out if the dihydroxylactone contents were also a characteristic feature of every species. The chromatograms of monohydroxylactone and dihydroxylactone mixtures of various mushrooms will be presented and conclusions on biogenesis of the sesquiterpenes will be drawn.

CIRCULAR DICHROISM STUDY OF STEREOCHEMISTRY OF STEROID
(16,17)- δ -LACTONES

T.N.Deshko[✉], A.V.Kamernitzky, I.G.Reshetova,
E.S.Chernoburova

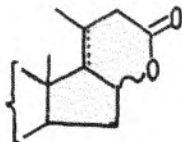
[✉]M.M.Shenyakin Institute of Bioorganic Chemistry, Academy
of Sciences, USSR

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

Physiologically active steroid (16,17)- δ -lactones
(1-8) were assigned to D⁻ and L⁻ series according to CD-
spectra analysis. Using this method it became possible to
establish the junction of D and E rings of the studied
compounds interpreting our data in terms of a lactone sec-
tor (rule (the molecule the bisectrix of the O-C-O angle;
the molecule is projected on to the plane of the lactone
ring). Judging from the positive sign of the Cotton effect
of the lactone chromophore n \rightarrow π^* transition we arrived to
the conclusion on trans junction of D and E rings in com-
pound (1 - 5) and cis-junction of these rings in com-
pounds (6 - 8), having the negative sign of the Cotton
effect the same transition.

D - 16 β H (1-5); L - 16 α H (6-8)
(1-2) Δ^5 -3-OAc; 5 α ,6 α -epoxy-3-OAc;
 $\Delta^{17(20)}$

(3-5) Δ^5 -3-OAc; 5 α H, 3-OAc; 5 α -OH, 6=O
(6) 5 α H, 3-OAc
(7) 3 α , 5 α -cyclo-6-OH
(8) 3-OAc, 5 α H, 6=O



IRIDOID GLYCOSIDES OF PENSTEMON DIFFUSUS

J. Diak and St. Kohl^{''}münzer

Institute of Pharmacology, Polish Academy of Sciences,
Department of Phytochemistry, Kraków, Poland

Previous investigations on the genus *Penstemon* /Scrophulariaceae/ resulted in the isolation of 15 cyclopentane monoterpenes of the iridoid class.

We have studied this group of compounds in the above ground parts of *Penstemon diffusus* Dougl.

The ethanolic extract after concentration to dryness was partitioned between CHCl_3 and H_2O . An aqueous phase was subjected to column chromatography. TLC-detection showed the presence of iridoid compounds in fractions eluted with 5,10% MeOH in CHCl_3 . Repeated column chromatography followed by preparative TLC led to the isolation of two compounds as amorphous solids which hydrolysed with β -glucosidase to glucose and aglycone moieties. On the base of spectral data one of them was identified as known iridoid - aucubin and the other is under investigation.

REDUCTION OF TESTOSTERONE AND ITS DERIVATIVES BY MEANS
OF THE APHANOCLADIUM ALBUM SPECIES *

J. Dmochowska-Gładysz, T. Kołek, A. Siewiński and A. Nespiak^a

Institute of Fundamental Chemistry, Agricultural University of Wrocław, Medical Academy of Wrocław^a, Poland

We found earlier that there are differences in stereochemistry of reduction of α, β -unsaturated ketones - synthons of juvenile hormones - carried out by means of *Rhodotorula mucilaginosa* and *Aphanocladium album*.

Continuing these investigations, we carried out reduction of steroid Δ^4 -5-ketones. The transformation of testosterone and androstenedione by means of *Aph. album* led to allylic alcohol; only alcohol $3\alpha/1/$ was formed. We did not find reduction of the 4,5-double bond which in the case of *Rh. mucilaginosa* preceded reduction of the carbonyl group. Presence of the chlorine atom at C-4 changed the direction of carbonyl reduction at C-3; allylic alcohol with the $3\beta/S/$ -configuration was formed.

Other substituents: at C-4 /Me/ and at C-17 /17 β -OAc, 17 α -Me and 17 β -COCH₃/ inhibited the transformation almost completely. Reduction of the carbonyl group at C-3 in 5- α and 5 β -dihydrotestosterone gave 3-hydroxy derivatives /3 α :3 β = 3:7 and 19:1, resp./.

* The strain isolated from intestines of insect *Tenebrio molitor*.

BIOTRANSFORMATION OF DIGITOXIN

BY STROPHANTHUS INTERMEDIUS TISSUE CULTURE

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Experiments of digitoxin biotransformation by *Strophanthus intermedius* Pax. /Apocynaceae/ callus strain and cell suspensions were performed in liquid Murashige-Scoog's medium, supplemented with 1mg/L 2,4-D, 0.3mg/L kinetin and 30g/L sucrose, under continuous light /1000 lux/. Digitoxin /40mg/L/ was added to a 10 day old culture. The experiments were carried out using two pH values /5.8, 7.2/. After 7-14 days of incubation, biotransformation products were analysed. The substratum did not cause any anatomical changes and only slightly restrained tissue mass increment when compared with control one /G.I.=3.0 and 3.5 resp./.

Phytochemical analyses revealed deacetyl lanatoside A /purpureglycoside A/ in experimental tissues and medium whereas control ones were devoid of cardenolide compounds. Moreover the traces of unmetabolized digitoxin were found in culture medium only. The biotransformation pattern was common to suspension and surface cultures independently from the pH level and the time of incubation. These results point out that the examined tissue strain is able to perform the glucosylation of the added digitoxin.

HYDROXYLATION OF SOME TERPENES BY MEANS OF THE
ARMILLARIELLA MELLEAE /HONEY FUNGUS/ SPECIES

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In the previous investigations we found that the *Ar. melleae* species oxidized α - and β -pinene. The reaction proceeded on at least two ways: alcohols with the retained pinyl skeleton and alcohols with the menthyl skeleton were formed.

Since diols /including trans-sobrerol/ with the menthyl skeleton were main products of pinene oxidation, we investigated more closely their formation. Among others we observed:

- transformation of \pm -pinene to trans-sobrerol proceeded enantiospecifically: \pm -trans-sobrerol was formed more rapidly from \pm -pinene,
- transformation of \pm - and \pm -limonene led to formation of corresponding enantiomeric \pm - and \pm -limonene-1,2-diols. The same reaction with dipentene was not enantiospecific; trans-Sobrerol was not found among the products of this reaction.
- \pm -menthene reacted similarly as limonene giving corresponding 1,2-diol.

- 2 -

Then /-/-aterpineol and /+/-cis-carveol were transformed. The first compound was oxidized to /+/-trans-sobrerol, and the second one did not undergo oxidation. Other compounds, including alcohols, were also formed but in smaller amounts.

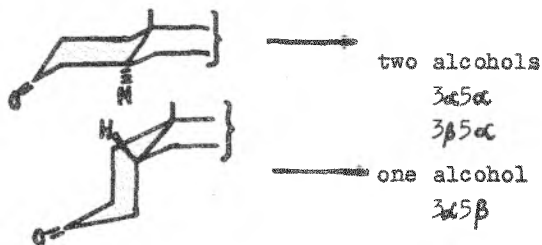
TRANSFORMATIONS OF 5α - AND 5β -DIHYDRO DERIVATIVES OF
TESTOSTERONE AND ANDROSTENEDIONE BY MEANS OF
RHODOTORULA MUCILAGINOSA

B.Draczynska, E.Tiomak, J.Dmochowska-Gładysz
and A.Siewiński

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In the series of preceding works we have studied
among others, an influence of substituents in the andro-
stane skeleton on transformations of Δ^4 -3-ketones[†].

In this paper we investigated an influence of the
junction of the A/B rings on reduction of ketone on C₂₀.
We found the lack of stereospecificity of this reduction
in the 5α -series, but compounds from the 5β -series
underwent stereospecific reduction to alcohol 3α .



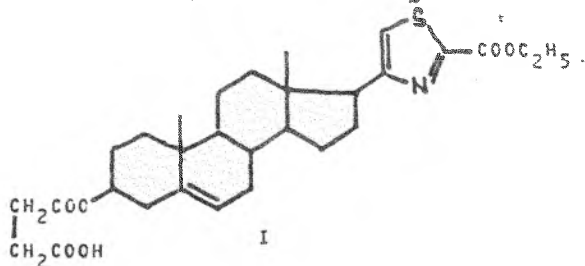
[†] The last paper from the series: Bull.Acad.Polen.Sci.,
Ser.sci.chim., 28, 1 /1980/.

SYNTHESIS OF 17 β -[4-(1,3-THIAZOLYL)]-5-ANDROSTEN-3 β -OL
3-HEMISUCCINATE

P. Drašar, V. Pouzar, I. Černý, and M. Havel
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In the continuation of the syntheses of biologically promising steroidal thiazoles¹ we have developed a new method of the synthesis of the title thiazole (I).

The key 21-hydroxy-20-ketone was prepared by the oxidation of 20,21-unsaturated 20-TMSO derivative by OsO₄-HMO. 21-Alcohol was transformed to bromide via the mesylate. 21-Bromo-20-ketone was coupled with ethyl thioxamate using the Hantzsch reaction to the thiazole. 3 β -Hydroxy-thiazole was transformed to the hemisuccinate by the new method², using the reaction pathway through 3 β -[4-(2,2,2-trichloroethoxy)-4-oxobutanoate].



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2. Drašar P., Pouzar V., Černý I., Havel M.: Czech. Pat. Appl. No. PV860-83 (1983) and PV1085-83 (1983).

ANALYSIS OF GIBBERELLINS BY MICROCOLUMN REVERSED-
-PHASE LIQUID CHROMATOGRAPHY WITH DOUBLE-WAVELENGTH
PHOTOMETRIC DETECTION

A.G.Druganov, G.I.Baram, V.A.Raldugin, M.A.Grachov
and V.A.Pentegova

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We elaborated a method of analysis of intact
gibberellins using microcolumn reversed-phase liquid
chromatography with detection by photometry at two
wavelengths, 210 and 240 nm. The instrument used for
the time-share dual-wavelength detection was the micro-
column liquid chromatograph "OB-4" designed in the
Siberian Division of the USSR Academy of Sciences.

Of crucial importance for the success of the analy-
sis was the use of 2 x 62 mm microcolumns. With such
small columns it was possible to increase the signal-
to-noise ratio and thus to employ gradient elution in
spite of the small absorbance of gibberellins and the
high, changing background absorbance of the eluent.
It is practically impossible to run similar separations
on the usual 5 ml, 250 mm long columns because of the
zero line drift. The limit of detection of gibberellin
A₃ by microcolumn liquid chromatography is some 3 ng.

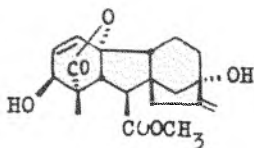
Gibberellins absorb at 210 nm, but exhibit no absorption at 240 nm. Hence, simultaneous detection at 210 and 240 nm allows to identify gibberellin peaks by excluding impurities absorbing at both 210 and 240 nm. The method was used to analyse the cultural liquor of Fusarium moniliforme which is an industrial strain used to produce gibberellin A₃. Gibberellin A₃ production wastes have been also analysed.

UNUSUAL CYCLIZATION OF GIBBERELLIN A₃ WHEN TREATED
WITH ZINC IN ACETIC ANHYDRIDE

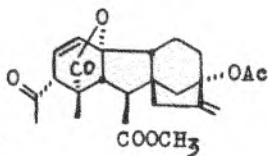
A.G.Druganov, V.A.Raldugin, V.A.Pentegova

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

In 1964 Jones, Grove and MacMillan have found that when treated with zinc in boiling acetic anhydride, methyl ester of gibberellin A₃ (I) undergoes an unusual transformation to compound II. We prepared the compound by the above procedure and analysed the data of IR-, ¹H- and ¹³C-NMR spectra. Since the analysis revealed some inconsistencies with the previous structure (II), we have carried out the X-ray analysis of the compound, which gave structure III. This compound is formed from compound I via an intermediate acid IV (R = H) and a

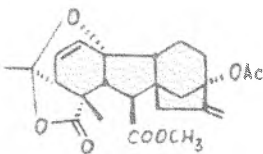


I

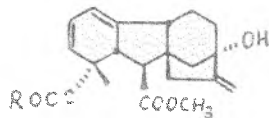


II

mixed anhydride IV ($R = \text{OCCH}_3$). The key step of the reaction appears to be an intramolecular Diels-Alder reaction between the conjugated diene fragment and the acetate carbonyl in the mixed anhydride IV ($R = \text{OCCH}_3$).



III



IV

PREFORMED ENOLATE IONS AND LITHIUM ALKYL CUPRATE REAGENTS
IN THE SYNTHESIS OF BIOLOGICALLY ACTIVE STEROIDS

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Québec, Québec, Canada G1K 7P4

Various syntheses of new steroidal products of biological interest, comprising in key reactions the use of preformed enolate ions, are reported.

In connection with certain syntheses, reactions of α -halogenated ketones with lithium alkyl cuprate reagents, leading to various α -substitution products of the ketonic starting materials, will be discussed. With the help of such reactions, α -alkylations, α -hydroxymethylations, and α -carboxylations of saturated ketones were performed. We shall show that alkylations of α -halogenated ketones with lithium alkyl cuprate reagents indeed proceed, as suggested by Dubois and Lion¹, by two different mechanisms, which may be operative simultaneously, one involving the intermediacy of an enolate and the other one representing, from a formal point of view, a "direct" replacement reaction of the halogen substituent. In contrast to alkylations with such reagents of chiral halides and tosylates not adjacent to carbonyl groups, which proceed essentially with inversion of configuration, the part of the reaction of α -halogenated ketones which does not involve the intermediacy of an enolate, proceeds stereoselectively with

retention of configuration. On the basis of various experiments with steroids, both with α -halogenated ketones and with halides lacking a carbonyl function adjacent to the halogenated carbon atom, the implications of the stereochemical results will be discussed.

The investigations reported were carried out in collaboration with Dr. Chau Le Van, Dr. D. Mukherjee, Dr. Z. Bończa-Tomaszewski, Mrs. M. M. Lourdasamy, Mrs. J. Capitaine, Mr. I. H. Ibrahim, Mr. F. Baroan, Mr. D. Logbo, and Mr. N. Nguyen-Ba.

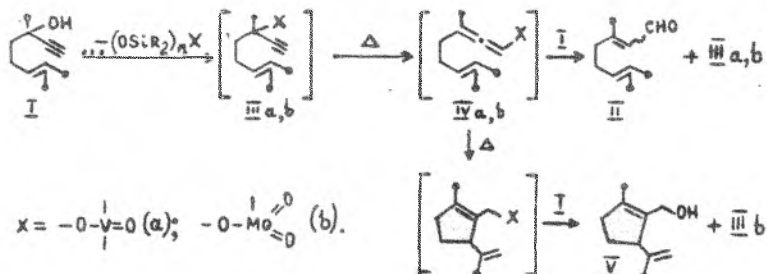
¹Tetrahedron, 31, 1227 (1975).

REARRANGEMENT OF DEHYDROLINALCOOL INTO CITRAL AND
THERMAL TRANSFORMATIONS OF ALLENE INTERMEDIATES

M.B. Erman, O.O. Volkova, G.V. Cherkaev, S.E. Gul'yi

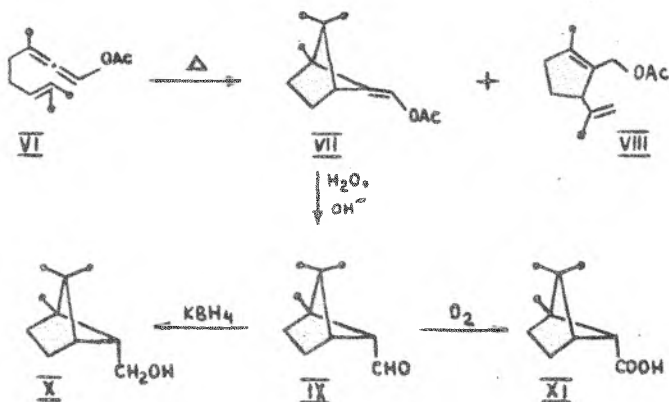
All-Union Research Institute of Synthetic and
Natural Fragrances, Moscow, USSR

Due to the shortage of citral-containing natural essential oils methods for synthesis of citral based on available chemicals are today intensively developed. Recently we have reported a method consisting in a rearrangement of dehydrolinalool (I) into citral (II) catalyzed by polymeric silylvanadates, the reaction proceeding via acetylene (IIIa) and allene (IVa) intermediates ¹/₁. Reaction conditions and co-catalysts to provide high yield of (II) (up to 98%) were found.



Replacement of silylvanadates by silylmolybdate catalysts resulted in reducing of citral yield due to the formation of alcohol (V) which may be considered as a product of thermal cyclization of allene intermediate (IV_b).

We have examined also thermal cyclization of allene acetate (VI) - an intermediate in "three-step rearrangement" of dehydrolinalool (I) into citral (II) (see /2/). When heated (130 - 180°C), acetate (VI) transformed exothermally into a mixture containing mainly two products: enol acetate (VII) and acetate (VIII) in a ratio of ~1.2 : 1.



Thermal transformations of (VI) afford in this way new possibilities for synthesis of terpenoids of 1,6,6-trimethylbicyclo/2.1.1/hexane group, for instance (IX-XI), as well as cyclopentanoid terpenes structurally related to iridomyrmecin (see/3/).

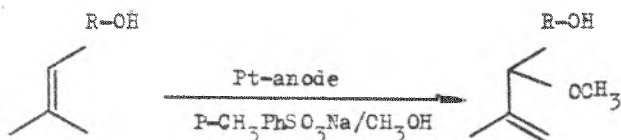
1. M.B.Erman, I.S.Aul'chenko, L.A.Kheifits, Zh. Org. Khim. 16, 23 (1980).
2. G.Saucy, R.Marbet, H.Lindlar, O.Isler, Helv. chim. acta, 42, 1945 (1959).
3. Cyclopentanoid Terpene Derivatives, ed. W.I.Tailor and A.R.Battersby, Marcel Dekker Inc., N.-Y., 1969.

ANODIC METHOXYLIATION OF UNSATURATED TERPENE
ALCOHOLS

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Institute of General Food Chemistry,
Technical University, Łódź

Synthesis of new odor compounds by anode
methoxylation of unsaturated terpene alcohols was
investigated.



R = alkyl, cycloalkyl

Methoxy derivatives of citronellol, elgenol,
linalool, dehydrolinalool and isopulegol were
obtained.

Some of them are gifted with interesting odor
properties.

SYNTHESIS OF EXO-HETEROCYCLIC STEROIDS

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József Attila University, Szeged, Hungary

The cardenolide glycosides, and bufadienolids have a 17β -oriented heterocyclic ring system. In attempts to modify the biological activity of natural cardenolides, we had synthesised N and O containing heterocyclic compounds in position C-17 on the steroidal skeleton.

5-Pregnenol-20-on-3-acetate was transformed to 21-hydroxymethyl-5-pregnene-3,20-diol by Claisen condensation, followed by reduction with sodium borohydride. The mixed acetate-urethane-toluene-p-sulphonate esters were made of this compound. With the 21-toluene-p-sulphonyloxymethyl-20-urethano compounds examined we observed a ring closure reaction to N-aryl-tetrahydro-1,3-oxazinones in the presence of base. With the 21-aminomethyl-20-toluene-p-sulphonate we observed also a ring closure reaction to azetidines in the same conditions.

Those two ring closure reactions are typical neighbouring group participations which could be characterised by the symbol (N-6) and (N-4), respectively.

REACTIONS AND BEHAVIOUR OF SOME SESQUITERPENE
 α -EXOMETHYLENE- γ -LACTONES AND THEIR AMINE ADDUCTS

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Structure elucidation of natural sesquiterpene α -exomethylene- γ -lactones by $^1\text{H-NMR}$ spectroscopy requires preparation of suitable derivatives providing additional spectroscopic information.¹ For this purpose, simple and efficient chemical transformations of small amounts of natural substances are highly desirable. This aim was achieved by development of a procedure involving protection of the exomethylene group by Michael additon of diethylamine followed by transformations of skeletal functional groups and by regeneration of the exomethylene double bond.²

Based on experience thus gained, these transformations were utilised not only for structural analysis but also for preparative operations in order to identify as well as isolate specifically α -exomethylene- γ -lactones from natural sources and also to synthesize structural analogues with potential biological activity, particularly the insect feeding deterrent activity.³

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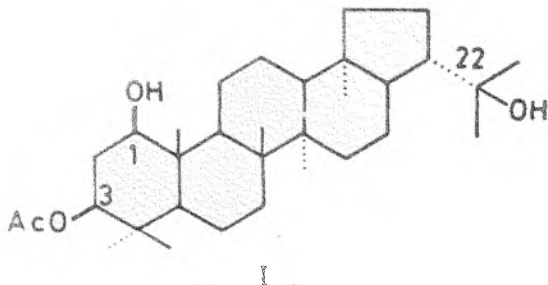
in the press

3 β -ACETOXYHOPAN-1 β ,22-DIOL, A NEW TRITERPENE
FROM SOUTH AMERICAN LICHENS

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 new triterpene 3 β -acetoxyhopan-1 β ,22-diol
(I) has been isolated from the South American
lichens Pseudoparmelia texana (Tuck.) Hale, Diri-
maria aegialita (Afz. in Ach.) Moore, D. applanata
(Fée) Awasthi and D. leopoldii (Stein) awasthi.
Its structure follows from NMR, ORD and mass
spectroscopic investigations.



STEREOCONTROL IN ORGANIC SYNTHESIS

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Chikusa, Nagoya 464, Japan

Some of the new methodologies for the synthesis of natural products have been developed for carbon-carbon bond formation accompanied by a highly stereoselection. New aspects of heteroconjugate addition using silicon and sulfur atoms will be discussed with special reference to the stereocontrol.

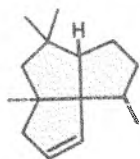
SYNTHESIS OF POLYQUINANE TERPENES

Shō Itō and Mitsuaki Kodama

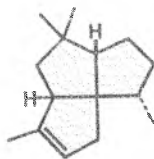
Department of Chemistry, Tohoku University

Sendai 980, Japan

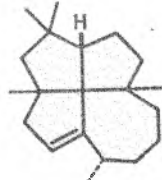
The polyquinanes are defined as a class of fused ring compounds containing only cyclopentane rings (L. Paquette). Since there has been isolation of many terpenoids containing or originated from such polyquinane carbon skeletons, we would classify them as polyquinane type. Attracted by their unique carbon frameworks, many syntheses of members of this group, such as isocomene, modhephene, hirsutane, have been accomplished. In this presentation, we describe our effort to synthesize sesquiterpenes, silphinene 1 and senoxydene 2, and a diterpene, laurenene 3, all of triquinane type, starting from dicyclopentadiene through common intermediates.



1



2



3

SYNTHESIS OF OLEANOLIC ACID GLUCURONIDES AND THEIR
ENZYMATIC DEESTRIFICATION

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Poland

A modified method of Meystre and Miescher was used for synthesis of oleanolic acid glucuronides. The reaction was continued for 2, 4 and 6 h. The best results were obtained after 6 h. yielding 4 products, i.e. unreacted oleanolic acid / I /, /1%/, and 6-methyl-2,3,4-triacetyl derivatives of: 3-glucuronide / II /, /24%/, 28-glucuronide / III /, /34%/, and 3,28-diglucuronide / IV /, /41%/.

After alkaline hydrolysis of the sum of reaction products with use of 15% NaOH only I, /54%/, and II, /36%/, were obtained.

After separation of glucuronide derivatives by TLC, each of them was subjected to an enzymatic deestrification using a crude enzyme preparations from sunflower seeds / supernatant 15000 x g/. Incubation was carried out for 15, 24 and 48 h. After enzymatic hydrolysis, products were obtained with best yield after 48 h. Compounds II, III and IV were deestrified in a yield of about 96, 90 and 85 % respectively.

STEROL ESTER DEGRADATION BY PLANT ENZYMES

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02-089 Warsaw , Poland

During white mustard / Sinapis alba L. / seed germination there is a progressive fall in the concentration of sterol esters with a concomitant increase in free sterols. This is accompanied by increased activity of sterol ester hydrolase.

The above enzyme is located in cell membrane structures but can be solubilized with 0.1 Triton X-100 and purified by ion-exchange chromatography on DEAE-cellulose and gel filtration on Sepharose 6B.

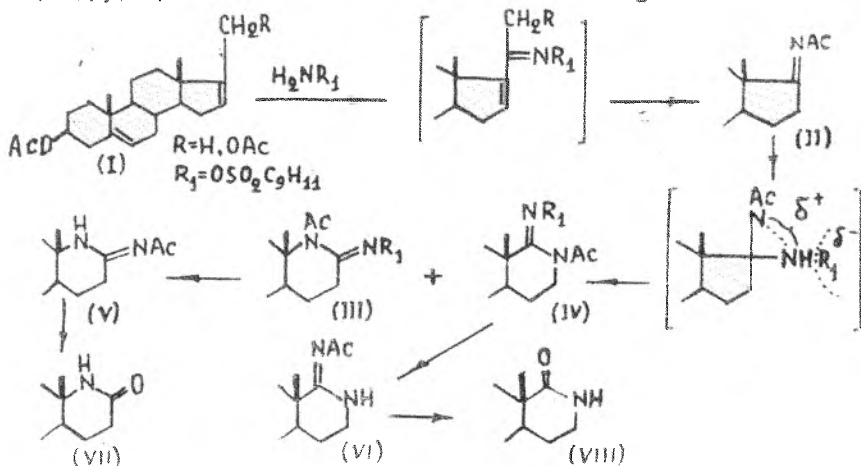
Sterol ester hydrolase exhibits a marked specificity with respect to the length of the acyl chain bound to sterol. Sterol esters containing C₁₄-C₁₈ fatty acids are hydrolyzed at the highest rate while sterol acetate, butyrate or behenate are poor substrates. The rate of sterol ester hydrolysis is not affected by large excess of acylglycerols or esters of long-chain primary alcohols suggesting a considerable specificity of sterol ester hydrolase present in white mustard plants towards esters of sterols.

A NEW REARRANGEMENT OF Δ^{16} -20-OXOSTEROIDS INTO
17a- AND 17-AZA-D-HOMOANDROSTANES.

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Zelinsky Institute of Organic Chemistry USSR Academy of
Sciences, Moscow, USSR.

A new one-pot rearrangement of 20-oxosteroids (I) into novel class of steroidal compounds-acylamidines(V),(VI) has been discovered. The reaction proceeds in the presence of *O*-mesitylenesulfonylhydroxylamine through an 1,2-attack of reagent at 20-oxogroup followed by Beckmann rearrangement to enamide (II), which then undergoes novel rearrangement, apparently, via electron-deficient nitrogen, to produce amidines (III),(IV). The latter under base treatment give rise to ami-



dines (V),(VI). The reaction is regioselective, the predominant amidine (III) is the one resulting from migration of the more substituted C¹³ atom. The chemistry of amidines and physico-chemical properties obtained compounds have been investigated.

[5,6-³H]-17 β -HYDROXY-4,5-SECOANDROSTAN-3-ONE

Alexander Kasal^a, Ladislav Kohout^a and Jiří Filip^b

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

^bInstitute for Research, Production and Application of
Radioisotopes, 102 27 Prague 10

Since 4,5-secodihydrotestosterone¹ was found to be active as an antiandrogen², the preparation of its suitably labelled derivative was desirable for further studies of the effect of the antihormone. The preparation of the title compound was carried out via 17 β -benzoyloxy-5-oxo-4,5-secoandrost-3-yne and 17 β -benzoyloxy-4,5-secoandrost-5-en-3-yne.

References:

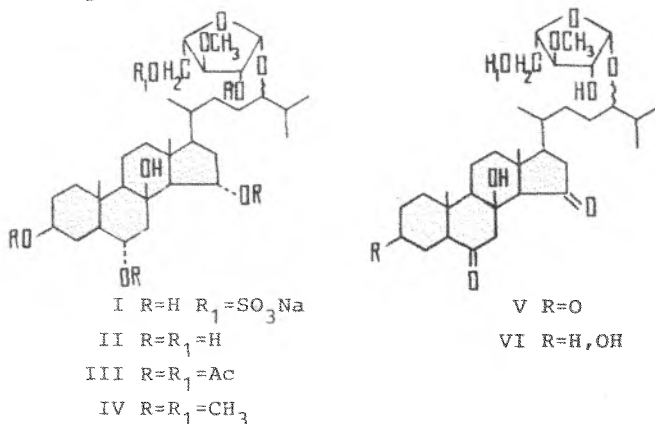
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ASTEROSAPONIN P₁ FROM THE STARFISH PATIRIA PECTINI-FERA

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Pacific Institute of Bioorganic Chemistry,
Academy of Sciences of the USSR, Vladivostok

We report the isolation of a hitherto unknown steroidal glycoside, asterosaponin P₁. The structure of the asterosaponin P₁ was established as 5'-O-sulfate 24-(α -3-O-methyl-L-arabinofuranosyl)-3 β ,6 α ,8 β ,15 α ,24 ξ -pentaoxy-5 α -cholestane, mp 191-192°C, $[\alpha]_D^{20} = +3.0^\circ$ (C=0.6, MeOH) (I).



On acid hydrolysis I gave 3-O-methyl-L-arabinose, while the aglycone was degraded to intractable material. The comparison ¹³C NMR spectra and ¹H NMR spectra of desulfated derivative II, pentaacetate III, hexa-O-methyl derivative IV, triketone V and diketone VI using spin-decoupling techniques established the location of the hydroxyl groups and sulfate group at C-5' of monosaccharide. A cholestane structure of the aglycone was determined by high-temperature catalytic reduction over the Pd/CaCO₃ catalyst.

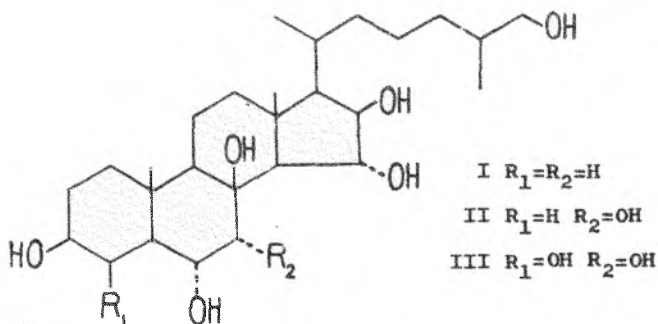
POLYHYDROXYLATED STEROLS FROM THE STARFISH
PATIRIA PECTINIFERA

Kicha A.A., Levina E.V., Stonik V.A.

Pacific Institute of Bioorganic Chemistry,
Academy of Sciences of the USSR, Vladivostok

Although starfish contain a number of polyhydroxy-sterols as aglycone constituents of saponins, free hydroxylated sterols have never been encountered before in this class of marine animals. We wish to report now the isolation of the steroidal hexol, heptol and octol from the pyloric caecum and cardiac stomach of the starfish *Patiria pectinifera*.

Polyhydroxylated sterols have been shown by spectral data and chemical transformation to be 5 α -cholestane-3 β , 6 α , 8 β , 15 α , 16 β , 27-hexol (I), m.p. 263-268°C, $[\alpha]_D^{20} = +33.1^\circ$ (c=0.83; MeOH); 5 α -cholestane-3 β , 6 α , 7 α , 8 β , 15 α , 16 β , 27-heptol (II), m.p. 261-263°C, $[\alpha]_D^{20} = +29.7^\circ$ (c=2.3; MeOH); 5 α -cholestane-3 β , 4 β , 6 α , 7 α , 8 β , 15 α , 16 β , 27-octol (III), m.p. 283-285°C, $[\alpha]_D^{20} = +22.5^\circ$ (c=0.5; MeOH).



SESQUITERPENE LACTONE GLYCOSIDES FROM CREPIS

CAPILLARIS

W. Kisiel

Institute of Pharmacology, Polish Academy of Sciences,
Department of Phytochemistry, Kraków, Poland

Chromatographic separation of the ethanol extract from the roots of *Crepis capillaris* /L./ Wallr. /Compositae/ led to the isolation of three closely related sesquiterpene lactone glycosides A, B and C.

That the sesquiterpene portions of the three lactones were identical was confirmed chemically by conversion of all lactones to the common intermediates: 11,13-methanol adduct of 8-epidesacylcynaropicrin and its 3- β -D-glucoside.

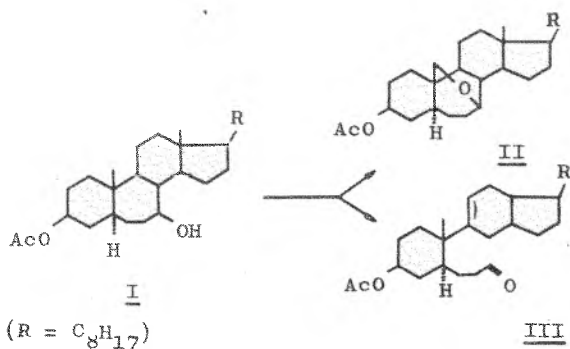
Enzymatic hydrolysis / β -glucosidase/ afforded 8-epidesacylcynaropicrin from A and two noncrystalline lactone esters $C_{21}H_{26}O_7$ and $C_{20}H_{24}O_7$ from B and C, respectively. Spectral parameters of the esters indicated that the structural differences between the two compounds were situated in the ester parts at C-8 and suggested that the ester side chains in B and C were $C_6H_{10}O_3$ and $C_5H_8O_3$, respectively.

On the basis of the above data the structure of A was deduced as 8-epidesacylcynaropicrin-3- β -D-glucoside. Lactones B and C were established to be the C-8 esters of A differing in the nature of the ester groups.

OXIDATION OF 3β -ACETOXY-B-HOMO- 5α -CHOLESTAN- $7\alpha\beta$ -OL WITH
LEAD TETRAACETATE

Ladislav Kohout and Jaroslav Zajíček
Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences, Prague

In one of our papers¹ on B-homosteroids we have studied the formation of cyclic oxides derived from B-homo- 5α -cholestanols. We have found that on oxidation with lead tetraacetate the $7\alpha\beta$ -alcohol I afforded the $7\alpha\beta,19$ -oxide II. However, this oxide is only the minor product of oxidation (4 %). The main product of oxidation of $7\alpha\beta$ -alcohol I is the seco-derivative III, the structure of which was established on the basis of chemical and spectroscopic data.



1. Kohout L.: Coll. Czech. Chem. Commun. 37, 2227 (1972).

THE ROLE OF ESTER GROUP AS CONTROL ELEMENT IN HYPOBROMOUS
ACID ADDITION TO SOME STEROID OLEFINS

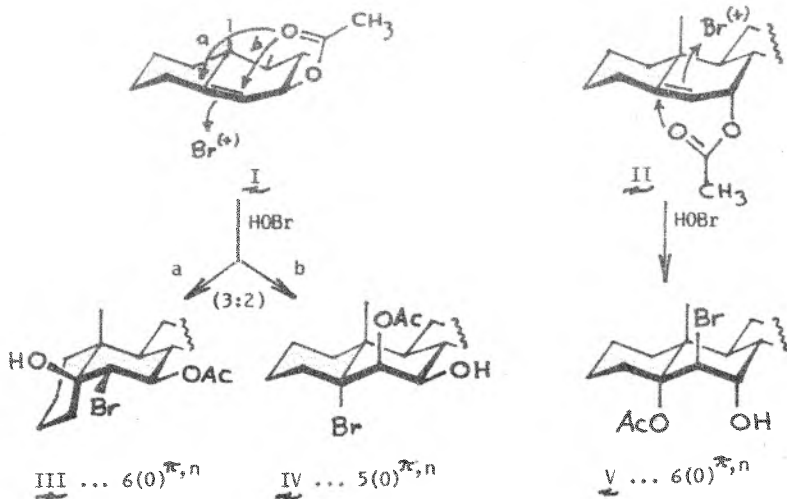
P. Kočovský, I. Starý, J. Zajíček, S. Vašíčková

Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences, 16610 Prague 6, ČSSR

Hypobromous acid action upon I proceeds via the 5 α ,6 α -bromonium ion and yields a mixture of the isomeric bromohydrins III and IV. The former arises by $6(0)^{\pi,n}$ participation of the 7β -acetoxy group whereas the latter is formed by $5(0)^{\pi,n}$ process.

Inversion of configuration of the participating group results in a change of stereoselectivity of the addition: The 7 α -epimeric derivative II reacts via the 5 β ,6 β -bromonium ion which is selectively cleaved with $6(0)^{\pi,n}$ participation to give V.

The role of Markovnikov and Fürst-Plattner rules in neighboring group participation will be discussed as well as the regio- and stereoselectivity changes imposed by intervention of neighboring group as an control element. Also discussed will be the choice of participating atom in ambident group and an attempt at formulation of selection rules in these processes will be presented.



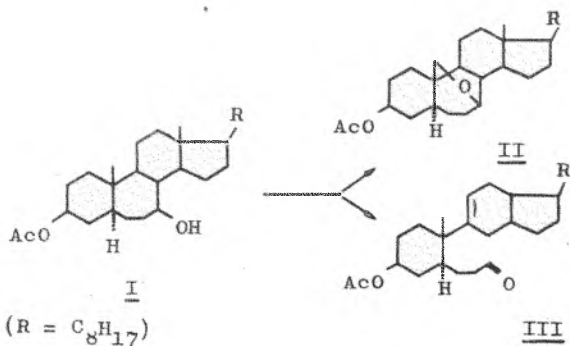
OXIDATION OF 3β -ACETOXY-B-HOMO- 5α -CHOLESTAN- $7\alpha\beta$ -OL WITH
LEAD TETRAACETATE

Ladislav Kohout and Jaroslav Zajíček

Institute of Organic Chemistry and Biochemistry

Czechoslovak Academy of Sciences, Prague

In one of our papers¹ on B-homosteroids we have studied the formation of cyclic oxides derived from B-homo- 5α -cholestanols. We have found that on oxidation with lead tetraacetate the $7\alpha\beta$ -alcohol I afforded the $7\alpha\beta,19$ -oxide II. However, this oxide is only the minor product of oxidation (4 %). The main product of oxidation of $7\alpha\beta$ -alcohol I is the seco-derivative III, the structure of which was established on the basis of chemical and spectroscopic data.



1. Kohout L.: Coll. Czech. Chem. Commun. 37, 2227 (1972).

BIOLOGICALLY ACTIVE COMPOUNDS FROM MELIACEAE

W. Kraus

Department of Chemistry, University of Hohenheim
D-7000 Stuttgart 70

Extracts of several melia plants such as *Azadirachta indica*, *Melia azedarach*, *Toona ciliata*, and *Toona sureni* show strong insect antifeedant activity. From these extracts we have isolated a series of novel biologically active tetranortriterpenoids and pentanortriterpenoids. The structure determination and the biological tests of these compounds will be reported. Preparative aspects will also be discussed.

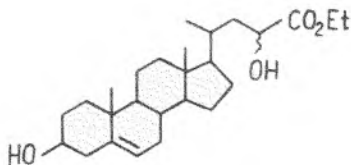
PREPARATION OF /23R and 23S/- 3 β ,23-DIHYDROXY-
-5-CHOLEN-24-OIC ACID ETHYL ESTERS

A. Kutner, A. Samborska and R. Jaworska
Institute of Pharmaceutical Industry, Rydygiera 8,
01-793 Warszawa, Poland

Title compounds /1a and 1b/ were obtained by the previously described /1/ molybdenum peroxide oxidation of lithium enolate of completely protected 3 β -hydroxy-5-cholesten-24-oic acid.

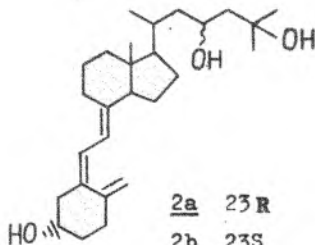
Configurational assignment of 23-hydroxyl by optical methods will be reported.

Compounds 1a and 1b are useful intermediates in synthesis of 23R,25- and 23S,25-dihydroxyvitamins D₃ /2a and 2b/.



1a 23R

1b 23S



2a 23R

2b 23S

1. A. Kutner and R. Jaworska, *Steroids*, 40,11 /1982/.

SYNTHESIS OF 15,16-CYCLOHEXENOANDROSTANES AND -ESTRANES

I.S.Levina, T.N.Galakhova, A.V.Kamernitzky

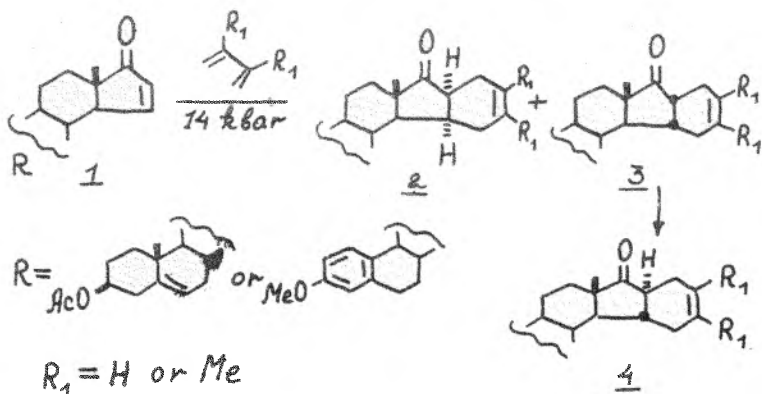
N.D.Zelinsky Institute of Organic Chemistry,

USSR Academy of Sciences, Moscow, U.S.S.R.

High pressure induced Diels-Alder reaction of steroidal 15-dehydro-17-ketones 1 with butadienes gave easily separable diastereomeric mixture of cycloaddition products 2 and 3. Lewis acid catalysed interaction of the same components at 1 kbar was found to produce 15 β ,16 β -isomer 2 only. Epimerization of 3 into 15 α ,16 β -cyclohexenosteroids 4 in the presence of strong bases was achieved.

The structure of compounds 2 - 4 was confirmed by spectral data (IR, CD, ^1H and ^{13}C NMR). X-Ray data were employed for the description of molecular conformations of 1 - 3.

Some considerations concerning steric course of the above steroidal dienophile - butadiene interaction will be discussed.

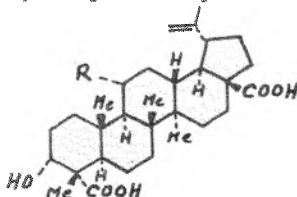


ISOLATION AND STRUCTURE OF SOME NEW TRITERPENES FROM
THE VIETNAMESE PLANT SCHEFFLERA OCTOPHYLLA

M. Lischewski¹⁾, H.V. Phiet²⁾, Ph. D. Ty²⁾, T.v. Sung²⁾,
J. Schmidt¹⁾, A. Preiss¹⁾, G. Adam¹⁾

- 1) Institute for Plant Biochemistry of the Academy of
Sciences of the GDR, 4010 Halle, German Democratic
Republic
- 2) Institute of Chemistry, National Research of the SRV,
Hanoi, Vietnam

Continuing a programm of studies on Vietnamese plants
of medical and biological interest, we have examined the
species Schefflera octophylla (Araliaceae) which is used
in Vietnamese folk medicine as a tonic drug, antirheuma-
ticum and for liver diseases. We now report the isola-
tion of the new pentacyclic triterpenes 3 α -hydroxy-lup-
20(29)-ene-23,28-dioic acid (1) and 3 α ,11 α -dihydroxy-
lup-20(29)-ene-23,28-dioic acid (2) from dried leaves
in 7 and 1.6 % yield, respectively.



1: R = H

2: R = OH

The structures of 1 and 2 were established by spectroscopic data (IR, MS, ¹H-NMR, ¹³C-NMR) and chemical transformations. In the biological test, 1 shows an antibiotic and cytotoxic activity.

NEW TRITERPENE GLYCOSIDES FROM THALICTRUM MINUS L.

V.I.Lutsky, A.S.Gromova and A.A.Semenov

Institute of Organic Chemistry, Siberian Division of
the USSR Academy of Sciences, 664033 Irkutsk, USSR

Saponins of the *Thalictrum* genus have not been studied until time. The saponin fraction isolated from *Thalictrum minus L.* growing in East Siberia contains 5 saponins, two of which, thalicosides A and B being predominant (0.5 and 0.1%, respectively). Thalicoside A genin named thalicogenin is a new tetracyclic triterpenoid - 3 β ,16 β ,22(S),29-tetrahydroxy-9,19-cycloleanost-20(S)-24-ene. Thalicoside A was assigned a structure 3-O- β -D-galactopyranoside, 29-O- β -D-glucopyranoside thalicogenin.

The present communication deals with establishing the structure of thalicoside B (1). 1 contains an ester group (1740 cm^{-1}). The acid hydrolysis of this compound leads to genin containing a free carboxy group (1700 cm^{-1}), as well as to rhamnose, arabinose and glucose in a ratio of 1:1:2 (GLC of aldononitril acetates). The intense fragments in the mass spectrum of genin acetate methyl ether with m/z 262 and 190 indicate a retro Diels-Alder fragmentation of a compound of the oleanen series. Because physico-chemical characteristics the genin studied was identified as oleanolic acid.

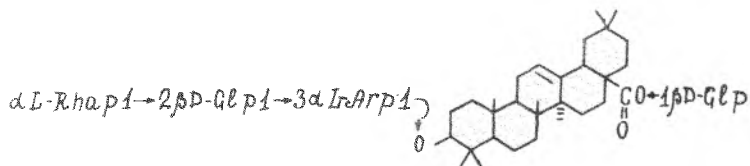
The 10 ppm downfield shift of the C-3 signal in the ^{13}C NMR spectrum of 1 as compared with the spectrum of

genin shows the C-3 glycosylation. A partial hydrolysis of I gives three progenins with the following carbohydrate signals of anomeric carbon atoms in the ^{13}C NMR spectrum: progenin 1-Ar, 106.0 ppm; progenin 2-Ar, Gl, 106.9 and 106.5 ppm; progenin 3-Ar, Gl, Rha, 106.5, 104.4, 101.7 ppm.

The alkaline hydrolysis of I lead to progenin 3. Consequently, one of the two glucose molecules is attached to carboxy group C-28. This is supported by the 95.6 ppm signal in the ^{13}C NMR spectrum of I, absent in the spectrum of progenin 3.

Methylation, methanolysis followed by acetylation have allowed methyl-2,3,4,6-tetramethylglucopyranose, methyl-2,3,4-trimethylramnopyranose, methyl-2,4-dimethyl-3-acetylarabinopyranose and methyl-3,4,6-trimethyl-2-acetylglucopyranose to be identified by GLC-MS. The configuration of glycoside bonds is determined from ^1H and ^{13}C NMR spectra and confirmed by calculations using Klein's method.

Thus, thalicoside B is of the following structure:



The authors are very grateful to Yu.N.El'kin for his interpretation of GLC-MS spectra and to R.B.Valeev for the NMR spectra registration.

STUDIES OF THE QUATERNARY SALTS OF SOME AMINOANDROSTANES
BY MASS SPECTROMETRY

M. Mák¹, J. Tamás¹ and Z. Tuba²

¹ Central Research Institute for Chemistry, Hungarian
Academy of Sciences, H-1525 Budapest, P.O. Box 17.

² Chemical Works of Gedeon Richter Ltd., Budapest.

The mono- and bis-quaternary salts produced by alkylation of 2- and/or 16-(4'-methyl-1'-piperazino) androsterane derivatives with different alkyl halides were analysed by mass spectrometric methods.

As the quaternary salts do not evaporate in the electron impact source of the mass spectrometer, it is only the products of their thermal decomposition ("in situ" dealkylation) that can be observed. The advantage of this method is that from the analysis of the mass spectra of the compounds - amines and alkyl halides - resulted in these dealkylation processes, the position(s) of alkylation can be established. Our results showed that the alkylation of the studied aminoandrosteranes by various alkyl halides (e.g. CD_3X , nC_3H_7X , $CH_2=CH-CH_2X$) took place specifically at the 4'-nitrogen atom(s) of the piperazino group(s).

The ion current - time curves of the appropriately selected characteristic ions proved to be suitable to establish the relative amount of the decomposition products and hence to determine the number of the alkylated centres in the aminosteroid molecules.

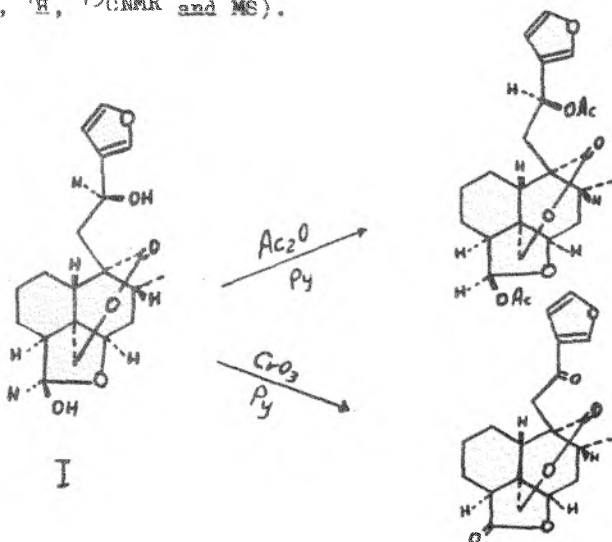
TEUCHAMEDRIN C, A NEW NEO-CLERODANE DITERPENOID
FROM TEUCRIUM CHMAEDRYS L.

F.Malakov and G.Papanov

Plovdiv University, Department of Organic
Chemistry, 24 "Tsar Assen" Street 4000 Plovdiv
Bulgaria

From the aerial parts of *Teucrium chamaedrys* a new
neo-clerodane diterpenoid Teuchamedrin C (I) has been
isolated, besides the previously known diterpenoids di-
hydroteugin and 6- α -hydroxyteuscerdin.

The structure and stereochemistry of teuchamedrin C
was established by chemical and spectroscopic means
(IR, ^1H , ^{13}C NMR and MS).



HYDROLYSIS OF \pm -MENTHYL ACETATE BY MEANS OF TISSUE CULTURES OF EPIDENDRUM OCHRACEUM AND CYMBIDIUM SAINT PIERRE, PLANTS FROM THE ORCHIDACEAE /THE ORCHIDS/ FAMILY

A.Mironowicz^a, A.Siewiński^a and K.Kukulczanka^b

Institute of Fundamental Chemistry, Agricultural University of Wrocław^a, Botanical Garden, University of Wrocław, Poland

In the fragrances of some species of the Orchidaceae family, some number of monoterpenes, and among them hydrocarbons, ketones, alcohols, and their esters, were found^{3*}.

We carried out a screening of two species of Epidendrum ochraceum and Cymbidium Saint Pierre with several monoterpenes and steroids. Most of these substrates were transformed by the tissue cultures of above species. We investigated more closely the course of hydrolysis of \pm -menthyl acetate and found the formation of \pm -menthol in slight predominance. Dependence of the course of hydrolysis on reaction time, quantity of biomass, substrate concentration, and age and adaptation of the culture to the reaction was also studied.

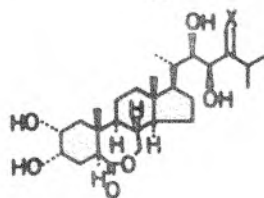
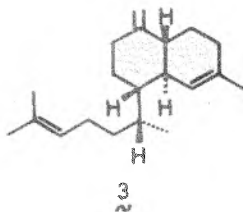
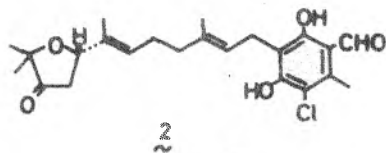
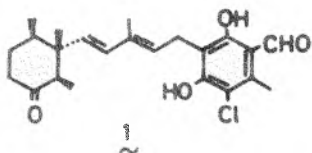
^{3*} C.L.Withner, in: The Orchids. Scientific studies. New York 1974, p.147.

RECENT PROGRESS IN THE SYNTHESIS OF
BIOLOGICALLY ACTIVE ISOPRENOIDS

Kenji Mori

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

Synthesis of some of the recently discovered biologically active isoprenoids will be discussed. The target molecules are : (1) (\pm)-ascochlorin **1** and (\pm)-ascofuranone **2**, the antiviral antibiotics, (2) (1R, 6S, 7S, 11R)-(+)-biflora-4,10 (19), 15-triene **3**, a new diterpene from a termite soldier, and (3) brassinolide **4**, dolicholide **5** and homodolicholide **6**, the phytosterols with plant growth promoting activity.



4 X = α -H, β -Me

5 X = CH₂

6 X = C $\begin{matrix} \text{H} \\ \diagup \\ \text{Me} \end{matrix}$

A NOVEL METHOD OF SYNTHESIS OF 25-HYDROXYVITAMIN D₂

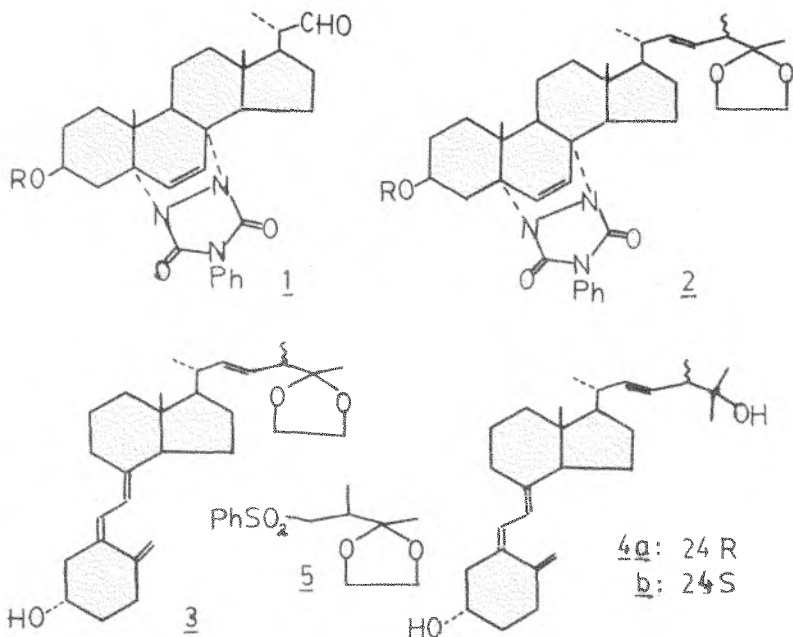
Jacek W. Morzycki^{*}, Heinrich K. Schnoes^{**} and Hector F. DeLuca^{**}

^{*} Department of Chemistry, University of Warsaw, Poland

^{**} Department of Biochemistry, University of Wisconsin, Madison, USA

Studies on metabolism of vitamin D₂ (ergocalciferol) have shown that it undergoes both 25-hydroxylation and 1 α -hydroxylation during its conversion to the active calcium mobilizing hormone. This activation pathway is the same as that described earlier for vitamin D₃. 25-OH-D₂ was first isolated in 1969 from the blood of hogs fed massive doses of vitamin D₂. The chemical synthesis of 25-OH-D₂ 4b has not yet been reported although it has been achieved at the Upjohn Company a few years ago.

In the present communication an improved approach to this synthesis is described. As the starting materials were used the known PTAD-diene protected 22-aldehyde 1 and the side chain fragment, sulfone 5. The carbanion derived from sulfone 5 was combined with the aldehyde 1. The following reductive elimination of the product afforded exclusively trans-olefin 2. The removal of the PTAD protecting group, irradiation of



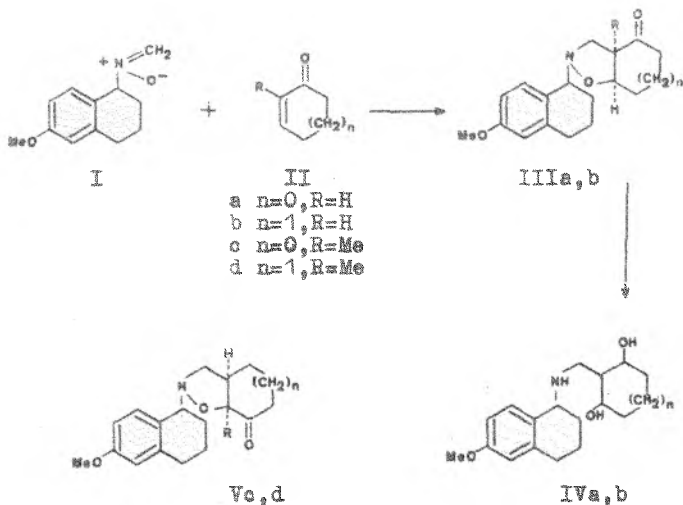
5,7-diene and thermal isomerization of previtamin resulted in the formation of vitamin D analog 3. After deprotection of 25-ketone the reaction with CH_3MgJ provided the mixture of 25-hydroxy-vitamin D_2 4b and its 24-epimer 4a. HPLC separation afforded both compounds in the pure state. The reported method of 25-OH- D_2 synthesis may be easily applied in the synthesis of radiolabelled analogs of high specific activity.

A NOVEL APPROACH TO THE SYNTHESIS OF
11-AZASTEROID SYSTEM

by B. Nawrot and H. Zając

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

1,3-dipolar cycloaddition of the new nitrene I to the conjugated enones II yields cycloadducts III which were hydrogenolyzed to the aminoalcohols IV by means of Hg (Al) in THF-H₂O. Cycloaddition of nitrene I to the enones IIc and IIId takes however a different course yielding cycloadducts V.



Rationalization of the regioselectivity of the cycloadditions in terms of frontier orbitals has been given.

CHEMICALS IN THE SECRETION OF SCALE INSECTS
THE STRUCTURES AND THEIR ROLES

Y. Naya, F. Miyamoto, T. Iwashita, H. Komura, K. Yoshihara, M. Tempesta,*
J. Pawlak,* and K. Nakanishi

Suntory Institute for Bioorganic Research, Wakayamadai, Shimamoto-cho,
Mishima-gun, Osaka, 618 Japan

During our investigation of the secretion from three species of scale insect, orchard pests (Ceroplastes ceriferus, rubens, and floridensis), many sesterterpenoids of three new skeletal classes have been isolated and characterized. Some sesterterpenoid alcohols are contained in the complex "cyclic wax" mixture in the form of esters with C_{10} - C_{32} fatty acids. This cyclic wax covers the insect body, presumably as a protective coat. The waxy secretion of rubens works as a kairomone, which induces ovipositional behavior, in its natural enemy Anicetus beneficus.¹ An enantiomeric series of sesquiterpenes has been found in the secretion of different species of the same genus infesting the same host tree. The body pigment works as an antifeedant against predatory ants. Application of two dimensional homonuclear spin correlation to structure elucidation will be presented.

* Visiting Scientist in 1982.

1) S. Takahashi(Kyoto University, Japan), private communication.

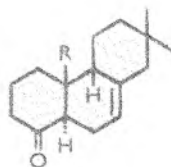
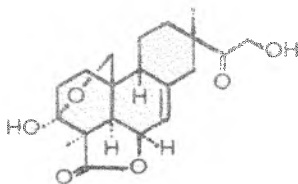
A SYNTHETIC APPROACH TO THE ANNONALIDE SKELETON

Fulvia Orsini¹, Francesca Pelizzoni¹ and Zdeněk Wimmer²

¹Institute of Organic Chemistry, University of Milan,
20133 Milan, Italy

²Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 156 10 Prague 6,
Czechoslovakia

A partial synthetic approach to the natural diterpenoid compound annonalide (1) was studied, concerning the substitution of the position 4 of the ring A of a model skeleton (2) in order to introduce there a starting group for the formation of the five-membered lactonic ring.

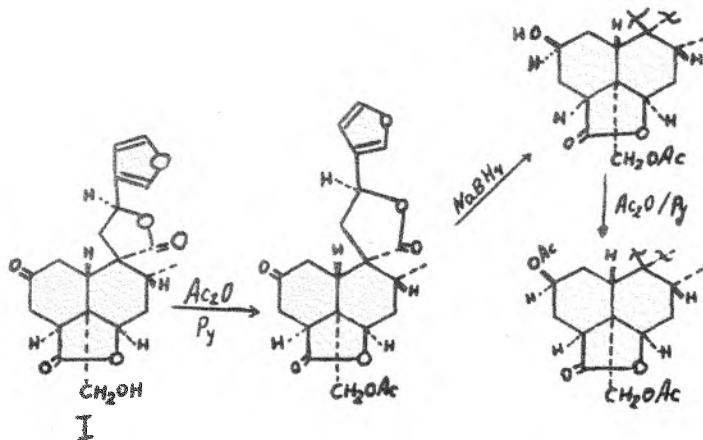


2-KETO-19-HYDROXYTEUSCORDIN, A NEW NEO-CLERODANE
DITERPENE FROM TEUCRIUM SCORDIUM L.

G.Papanov and P.Malakov

Plovdiv University, Department of Organic
Chemistry, 24 "Tsar ASSEN" Street, 4000 Plovdiv
Bulgaria

From the aerial parts of *Teucrium scordium* the previously known diterpenoids teucrin E and teucrin H₄ have been isolated. In addition, a new neo-clerodane diterpene, 2-keto-19-hydroxyteuscordin (I), has also been obtained from the same source. From its spectral properties (IR, ¹H NMR, ¹³C NMR and MS) and chemical transformation the structure and stereochemistry of I have been established as 19-hydroxy-15,16-epoxy-neo-cleroda-13,(16),14-diene-2-one-18,6:20,12S-diolide.



**HALOKETENE ADDITION TO THE EXOMETHYLENE DERIVATIVES
OF STEROIDS**

Z. Paryzek and K. Blaszczyk

Institute of Chemistry, Adam Mickiewicz University
Poznań, Poland

The cycloaddition of haloketene to steroids containing the exomethylene group in various positions was investigated as a method of the synthesis of spiro-steroids.

The addition of dichloroketene to the 3-methylene-5 α -cholestane gave a mixture of two isomers of dichloro-spirocyclobutanones. These isomers were separated and their structure and stereochemistry were determined on the basis of spectral data. Steroidal dichlorospirocyclobutanones were reduced to spirocyclobutanone and oxidized to spiro-lactones.

Reactions in other positions of steroidal skeleton have also been investigated and results will be discussed.

REARRANGEMENTS OF 9-SUBSTITUTED LANOSTANES.
MECHANISTIC CONSIDERATIONS.

Z. Paryzek and R. Wydra

Department of Chemistry, Adam Mickiewicz University
Poznań, Poland

In skeletal rearrangements of steroids and triterpenoids the important factors determining the pathway of a reaction are: structure of the substrate, reaction conditions, steric (conformational) and electronic effects.

Recently, a series of rearrangements induced by the rupture of C₉-X bond (X=leaving group) in lanostane have been investigated.

Several main pathways were observed in these reactions leading to structurally important triterpenoid skeletons.

The synthesis of 3 β -acetoxy-5 α -lanosta-8,11-dien-7-one and of 3 β ,11 α -diacetoxy-5 α -lanost-8-en-7-one as possible intermediates in the rearrangement of 9 α ,11 α -epoxy-5 α -lanostan-7-one was carried out.

Taking into consideration these new results indicating the participation of secondary carbocations in some of these rearrangements an attempt is undertaken to draw preliminary conclusions regarding the mechanisms of these reactions.

NEW METHOD OF SYNTHESIS 2-ISOPROPENYL-2-HEPTENAL
 INTERMEDIATE PRODUCT OF OBTAINING SEX PHEROMONE
 AONIDIELLA AURANTII (MASHALL)

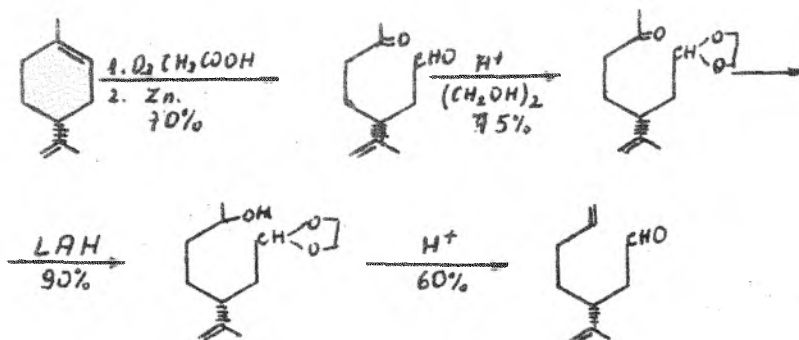
Jerzy Podlejski

Technical University of Łódź Poland, Institute
 of General Food Chemistry

Clive A. Henrich and others have undertaken investigation of the synthesis of two sex pheromones occurring in *Aonidiella aurantii* (Maskell). They have obtained the intermediate product for the synthesis (Z)-3-methyl-6-isopropenyl-3,9-decadien-1-yl-acetate the 6-isopropenyl-2-heptenal by a 9 steps synthesis starting from (S)-carvone. The final yield was about 12% those calculated on (S)-carvone.

In this experiment leaving the + limonene as the substrate in the 4-steps simple synthesis the 4-isopropenyl-2-heptenal with the yield of 28% was obtained.

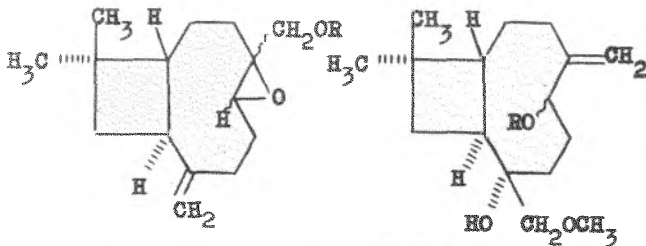
The scheme of the synthesis is presented bellow.



14-HYDROXYCARYOPHYLLENE-4,5-OXIDE, A NEW
SESQUITERPENE FROM BETULA PUBESCENS

N.D.Pokhilo, V.A.Denisenko, V.L.Novikov, N.I.Uvarova
Pacific Institute of Bioorganic Chemistry, Far East
Scientific Centre, Academy of Sciences of the USSR,
Vladivostok

From unsaponifiable part of foliar ether extract of *Betula pubescens* a new sesquiterpene, 14-hydroxycaryophyllene-4,5-oxide (I), has been isolated. The reaction of I with KOH under refluxing in methanol produced diol (III) in 35% yield, probably, as a result of simultaneous transannular interaction of one molecule of the water with epoxide ring and exocyclic methylene group. Treatment of I and III with acetic anhydride in pyridine at room temperature gave monoacetates II and IV respectively. The structures of compounds I-IV were determined by IR, MS, ^1H and ^{13}C -NMR data. Stereochemistry of epoxide ring in I is the subject of a further study.



(I) R = H

(II) R = Ac

(III) R = H

(IV) R = Ac

MOLECULAR REARRANGEMENTS OF SOME SESQUITERPENES
IN SUPERACIDS

M.P.Polovinka, S.A.Osadchy, D.V.Korchagina, Yu.V.Gatilov,
Zh.V.Dubovenko, V.A.Barkhash

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

Stable carbocations have been generated from some sesquiterpenes isolated from oleoresins of conifers (α - and γ -muurolenes, γ - and δ -cadinenes, zonarene, 10-epizonarene, isocadinene, α -copsene, etc.). The structures of the carbocations have been established (by ^1H , ^{13}C NMR), their molecular rearrangements and reactions with nucleophiles have been studied. The mechanisms of the rearrangements are suggested. The results of experimental observations of rearrangements are compared with the predictions provided by molecular mechanics calculations. The effects have been studied of the structures of substrates and the reaction conditions (the temperature of generating of ions and that of "defreezing" of them, acidity of a medium) on the pattern of skeletal rearrangements in superacids.

A SYNTHETIC APPROACH TO CARDIOTONIC 19-NOR STEROIDS

K. Ponsold and M. Wunderwald

Central Institute of Microbiology and Experimental
Therapy of the Academy of Sciences of the GDR, Jena

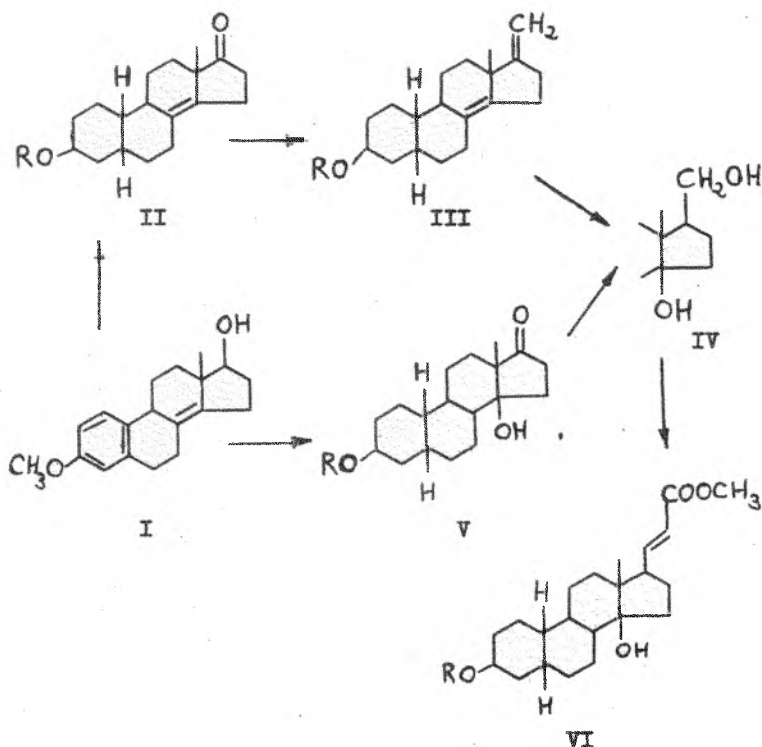
19-Nor-analogous of cardiotonic steroids are not easily available and therefore the knowledge on their biological activity is very limited. We looked for procedures for the synthesis of such compounds. As starting material we used 8(14)-dehydroestradiol methyl-ether I, easily available by Torgov total synthesis.

We investigated two ways for the introduction of essential elements of cardiotonic steroids (AB-cis ring junction, 3 β - and 14 β -hydroxy groups and a 17 β -configured side chain) in the estratetraene I. By the well known Birch procedure and following oxidation I can be transformed to 19-nor-androstene-4,8(14)-diene-3,17-dione. From this the AB-cis configured compound II was prepared by two selective hydrogenation steps and acylation of the hydroxy group. Wittig reaction of II gave the methylene compound III. On boronation of III the 17 β -hydroxymethyl compound IV could be isolated as main product. An alternative route for the synthesis of IV was the transformation of the estratetraene I to the ketone V by a procedure developed by Langbein¹⁾ and

1) G. Langbein et al., WP 128 564

coworkers, introduction of the methylene group in position 17 by Wittig reaction, silylation of the 14 β -hydroxy function, boronation and hydrolysis of the silylether group.

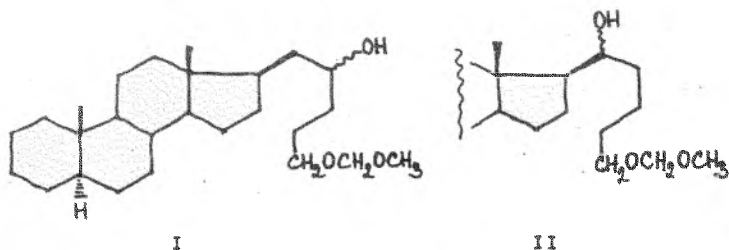
From the key compound IV, having all essential functions of cardiotonic steroids in the skeleton, the acrylic acid methylester VI (a ring open cardenolide) was prepared by oxidation of the hydroxymethyl group to the aldehyde and following Wittig-Horner reaction.



PREPARATION AND ABSOLUTE CONFIGURATION AT C₍₂₂₎ OF
21,26,27-TRINOR-5 α -CHOLESTANE-22,25-DIOL DERIVATIVES

V. Pouzar, P. Drašar, I. Černý, and M. Havel
Institute of Organic Chemistry and Biochemistry,
Czech. Acad. Sci., 166 10 Prague 6, Czechoslovakia

5 α -Pregnan-21-ol was converted into 21-aldehyde by oxidation with pyridinium chlorochromate and then condensed with the lithium salt of 1-methoxymethoxy-2-propyne. The epimeric (22S)- and (22R)-25-methoxymethoxy-21,26,27-trinor-5 α -cholest-23-yn-22-ols isolated from the above reaction mixture were converted to correspond- (22R)- and (22S)-25-methoxymethoxy-21,26,27-trinor-5 α -cholestan-22-ols (I). For the chemical determination of the configuration at C₍₂₂₎ of the above compounds 22-substituted derivatives I were correlated with 20-substituted derivatives II of known configuration¹.



1. Pouzar V., Havel M.: Collect. Czech. Chem. Commun.
46, 2758 (1981).

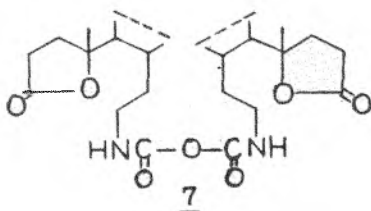
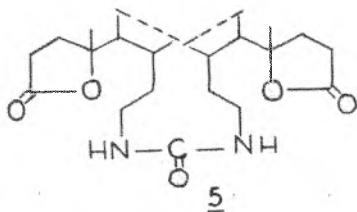
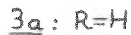
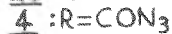
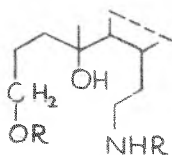
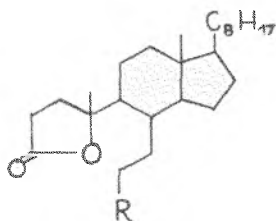
THE CURTIUS REARRANGEMENT OF 3-OXO-B-HOMO-A-NOR-5-OXA-
-5,5a-SECOCHOLESTAN-5a-OIC ACID AZIDE

by Władysław J.RODEWALD and Jadwiga FRELEK

Department of Chemistry, University, 02093 Warszawa

In search for physiologically active analogs of steroids hormones, studies were undertaken to transform natural systems by modifying the steroidal skeleton so as to replace carbon by nitrogen. Replacement of tetragonal carbon at the ring juncture by trigonal nitrogen seemed to be of particular interest in view of an expected relation to numerous physiologically active alkaloids. Syntheses of several 5-aza-analogs we have already reported. In this communication we present transformations of lactone-acid 1, previously obtained from cholesterol, into heterosteroids with nitrogen atom or atoms in rings A and B as well as at the ring juncture A/B in position 5 of steroidal skeleton. As a next reaction has been a replacement of the carboxyl groups in compound 1 into the primary amine group to obtain lactone-amine 2a and/or dihydroxy-amine 3a with the five-membered lactone ring cleaved. For this reason lactone-acid 1 was subjected to modified Curtius reaction to furnish the acid azide 4 as a main product. However, the obtained compound 4 heated in acetic acid did not undergo rearrangement to the expected amine 2a, but a disubstituted derivative of carbamide 5 and N-acetyl-lactone-amine 2b were formed. Heating

of the acid azide 4 in dimethyl formamide solution afforded izocyanate 6 which subjected to alkaline hydrolysis gave, besides carbamide 5, the disubstituted derivative of carbamic acid anhydride 7. However, compound 6 hydrolyzed in 5% hydrochloric acid afforded the free lactone-amine 2a in 40% yield and the mentioned above compounds 5 and 7 as by-products.



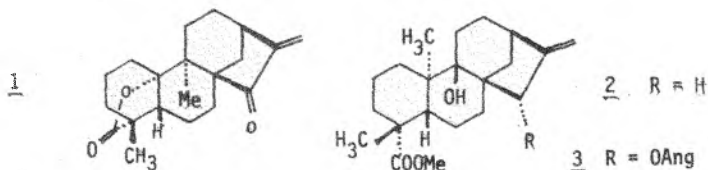
CONSTITUENTS OF Viguiera maculata and V. stenoloba.

STRUCTURE REVISION OF STENOLOBIN.

Alfonso Romo de Vivar and Guillermo Delgado.

Instituto de Química de la Universidad Nacional Autónoma de México. Circuito Exterior. Ciudad Universitaria. Coyoacán. 04510. México, D. F.

Recently we described the diterpenoid constituents of Viguiera insignis and pointed out the similarities between the diterpenoids of some sections of Viguiera and Helianthus. We now describe structure determination of 15-oxo-zoapatlin 1, a new tetracyclic diterpenoid lactone of rearranged kaurenoid type isolated from V. maculata, and the structure revision of the biogenetically related diterpene stenolobin 2, isolated from V. stenoloba. A new diterpene hydroxy-diester, 15- α -angeloiloxo stenolobin 3 was also isolated from this specimen.



Comments are offered on the biosynthesis and chemotaxonomic implications of these compounds.

CONTRIBUTIONS TO THE CHEMISTRY OF 2-ALKYL-CYCLOPENTANE-
1,3-DIONES - IMPORTANT BUILDING BLOCKS FOR THE
SYNTHESIS OF NATURAL PRODUCTS

H. Schick, B. Pogoda and S. Ballschuh

Central Institute of Organic Chemistry of the Academy
of Sciences of the GDR, Berlin,
German Democratic Republic

2-Alkyl-cyclopentane-1,3-diones are well known as important intermediates for the total synthesis of steroids (1). In last years they found also growing interest as building blocks for other classes of natural products (2 - 5). Therefore examples of the general reaction behaviour of these valuable intermediates and of some of their derivatives are represented.

- 1) L. VELLUZ, J. VALLS and G. NOMINE, *Angew. Chem.* 77, 185 (1965)
- 2) K. TANAKA, F. UCHIYAMA, K. SAKAMOTO and Y. INUBUSHI, *JACS* 104, 4965 (1982)
- 3) P. T. LANSBURRY, A. K. SERRELIS, J. H. HENGEVELD and D. G. HANGAUER, *Tetrahedron* 36, 2701 (1980)
- 4) A. G. SCHULTZ and L. A. MOTYKA, *JACS* 104, 5800 (1982)
- 5) B. M. TROST and P. G. Mc DOUGAL, *JACS* 104, 6110 (1982)

RECENT INVESTIGATIONS ON SOME PLANT TERPENOIDS

K. Schreiber

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

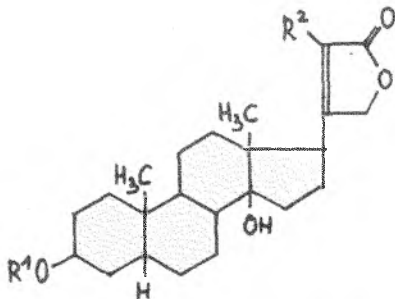
From plants of European, subtropical and tropical origin a number of new terpenoidal constituents representing different structural types have been isolated and structurally elucidated. The results of further investigations dealing with the biosynthesis and/or metabolism of terpenoids in plants especially in plant cell cultures are also reported.

CARDENOLIDE DERIVATIVES WITH AN UNSATURATED ALDEHYDE FUNCTION AT THE LACTONE RING

Barbara Streckenbach

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

Oxidation of 22-allyl-digitoxigenin-3-acetate 1 and 22-allyl-digitoxin 2 with selenium dioxide resulted in the introduction of an oxygen function into the unsaturated C-22 substituent of the cardenolide molecule. The isolated compounds were the 22-(3'-oxo-prop-1'-en-1'-yl)-derivatives 3 and 4 of 1 and 2, respectively. Other oxygenated compounds were not found. The inhibitory effect of 3 on Na,K-ATPase, the molecular point of attack of cardio-active steroids, was estimated to be about six times higher than that of the parent compound 1.



- | | | | |
|----------|---------------------------|----------|---------------------------|
| <u>1</u> | $R^1 = -COCH_3$ | <u>3</u> | $R^1 = -COCH_3$ |
| | $R^2 = -CH_2-CH=CH_2$ | | $R^2 = -CH=CH-CHO$ |
| <u>2</u> | $R^1 = -(D-Digitoxose)_3$ | <u>4</u> | $R^1 = -(D-Digitoxose)_3$ |
| | $R^2 = -CH_2-CH=CH_2$ | | $R^2 = -CH=CH-CHO$ |

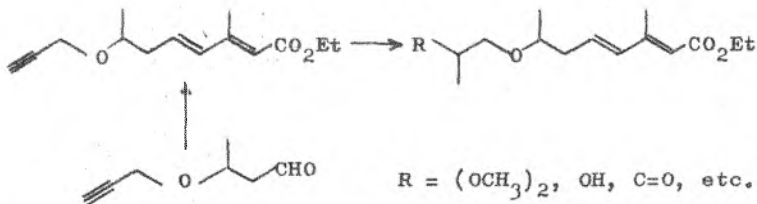
PREPARATION OF SOME 8-OXA ANALOGUES
OF JUVENILE HORMONE

L. Streinz and M. Romaňuk

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

The synthesis of several juvenoids derived from 2,4-dienic acid has been outlined using ethyl 3,7-dimethyl-8-oxa-2,4-undecadien-10-ynoate as a key intermediate. The appropriate aldehyde used for the synthesis of this compound has been prepared by the reaction of propargyl alcohol with crotonic aldehyde (see the Scheme). The reaction conditions have been studied.

The synthesized compounds exhibit juvenile hormone activity when tested topically on various unrelated insect species.



FIRST- AND SECOND-ORDER WESTPHALEN-TYPE REARRANGEMENTS

OF 5β -HYDROXY-STERIODS

Wojciech J. Szczepek

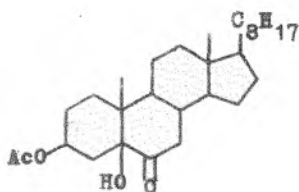
Department of Chemistry, Warsaw University

Pasteura 1, 02093 Warszawa, Poland

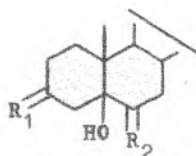
It is well known that no rearrangement products are obtained from 5β -hydroxy-steroids under traditional conditions of Westphalen rearrangement ^{1,2/} (KHSO_4 or H_2SO_4 - Ac_2O - AcOH) or backbone rearrangement ^{1,3/} ($\text{BF}_3 \cdot \text{Et}_2\text{O}$ - Ac_2O).

We now report the reactions of 5β -hydroxycholestanes 1, 2 and 3 with our new reagent ^{4/} (KHSO_4 -TFAA) leading to the respective rearranged products.

The rearrangement of hydroxyketone 1 in THF at r.t. with subsequent hydrolysis resulted in formation of hydroxyketones 4, 5 and 8. Under analogous conditions hydroxydiketone 3 gave diketones 6 and 7 as the main products. Treatment of hydroxyketone 1 with KHSO_4 -TFAA in TFA at r.t. and subsequent hydrolysis afforded rearranged hydroxyketones 9, 11, 12 and 13. Compounds 12 and 13 are formed from intermediate hydroxyketone - 3β -acetoxy- 5α -hydroxy-A-homo-B-nor- 5α -cholestan-4 α -one. Rearrangement of triol 2 in THF and subsequent hydrolysis gave rearranged diol 10 accompanied by normal dehydration products. The structures of all compounds were confirmed by chemical and spectroscopical methods.

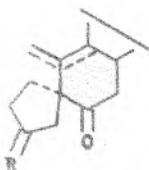


1



2 $R_1=R_2= \beta\text{-OH}, H$

3 $R_1=R_2= O$

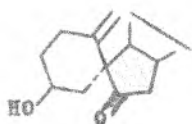


4 $R= \beta\text{-OH}, H; \Delta^{10(19)}$

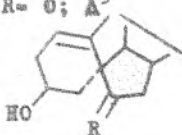
5 $R= \beta\text{-OH}, H; \Delta^9$

6 $R= O; \Delta^{10(19)}$

7 $R= O; \Delta^9$

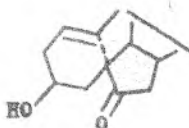


8

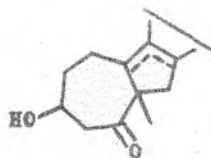


9 $R= O$

10 $R= \beta\text{-OH}, H$



11



12 Δ^9

13 Δ^8

1. G. Snatzke, H.-W. Fehlhauer, Ann., (1964) 676 188.
2. A.T. Rowland, J. Org. Chem., (1964) 29 222.
3. E.T.J. Bathurst, J.M. Coxon, M.F. Hartshorn, Austral. J. Chem., (1974) 27 1505.
4. W.J. Szczepak, Habilitation thesis. Warszawa, 1982.

RECENT DEVELOPMENTS IN THE STUDY OF THE STRUCTURE
ACTIVITY RELATIONSHIPS (SAR) OF CARDIAC GLYCOSIDES

R. E. Thomas

Department of Pharmacy, The University of Sydney,
Sydney, Australia, 2006

The study of cardiac glycoside SAR has proceeded through three stages. The first period could be called the classical period and was limited to the study of the many hundreds of naturally occurring cardiac glycosides. During this period, the glycosides were isolated, their structures determined and their biological activity measured using a variety of methods. The pharmacology of this period was dominated by the work of Chen & Henderson who used cat toxicity as a measure of cardiotoxic activity. This work led to the conclusion that the indispensable requirements for cardiotoxic activity were the 17 β unsaturated lactone, the 14 β hydroxyl group and the unique stereochemistry of the cardiac glycoside steroid.

The above assumptions began to be challenged during the second period of cardiac glycoside SAR study - namely the period of semi-synthetic modification. During this period, a number of investigators, including the present author, showed that it was possible to modify significantly the basic cardiac glycoside structure and still retain activity. It was shown that the lactone could be replaced by open chain structures of the type $-\text{CH}=\text{CH}-\text{C}=\text{A}$ (where A is a heteroatom). The 14 β hydroxyl group and the A/B cis configuration were also shown not to be indispensable. Considerable attention was also given to the sugar moiety which was shown to influence both pharmacokinetic and pharmacodynamic properties. Relatively minor changes in the

-2-

sugar moiety were shown to alter greatly the rate of drug-receptor interaction as well as changing potency by factors ranging up to several hundred-fold.

The third period of cardiac glycoside SAR study is the period of QSAR - quantitative structure activity relationships. Notable contributions have been the work of Repke et al., who determined activation energies for the interaction of cardiac glycosides with Na^+, K^+ -ATPase and the work of Fullerton et al., who determined the optimum configuration of the C17 side chain using potential energy calculations and computergraphics.

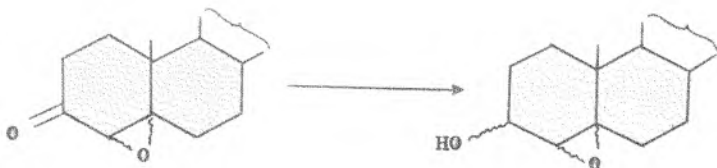
Based on all this work, a model of the digitalis receptor can be deduced, although the ultimate aim of SAR studies - namely the development of a safer drug has yet to be achieved.

THE REACTION OF α -EPOXYKETONES WITH DIBORANE

L. Tomaszewska, M. Zaidlewicz

Institute of Chemistry Nicolas Copernicus
Toruń, POLAND

The stereochemistry of reduction $4\alpha,5\alpha$ - and $4\beta,5\beta$ -epoxycholestan-3-one, $4\alpha,5\alpha$ - and $4\beta,5\beta$ -epoxy-17-methylandrostan-17 β -ol-3-one and $4\alpha,5\alpha$ - and $4\beta,5\beta$ -epoxypregnan-3,20-dione with borane-THF complex has been studied.



The structure of epoxyalcohols was confirmed by means of spectral /IR, H^1 -NMR/ and chemical methods.

NEW 3-HALOGENO-PREGNANE DERIVATIVES

J. Tóth, L. Boór, CS. Molnár

Chemical Works of Gedeon Richter Ltd.
Budapest, Hungary

Iminium salts have found widespread application in organic preparative chemistry. The Vilasmeier reagent, belonging to this groups of compounds, has been used several time in the conversion of steroids.

We have found that rather unreactive $\Delta^{1,4}$ -3-keto systems can be converted into $\Delta^{1,3,5}$ -3-halogeno derivatives under appropriate conditions:

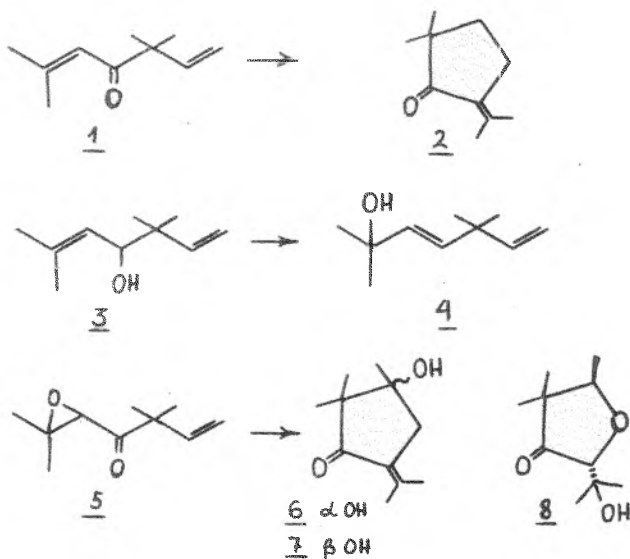


CYCLISATION OF ARTEMISIA KETONE AND ITS DERIVATIVES

E. Tsankova, E. Alexandrova and V. Enev

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

As a result of the acid-catalyzed cyclisation of artemisia ketone, 1 and 5,6-epoxy-artemisia ketone, 5 the cyclopentenone derivatives 2, 6 and 7 were obtained respectively, while artemisia alcohol, 3 undergoes allylic rearrangement yielding yomogi alcohol, 4. The cyclisation of 5 via oxymercuration-demercuration proceeds stereoselectively leading to the furan derivative 8. The structure of all the products has been determined by spectral data. The mechanism of the reactions will be discussed.



DITERPENES FROM THE DEFENSE SECRETION
OF NASUTITERMES COSTALIS SOLDIERS

Irena Valterová^a, Miloš Buděšínský^a, František Tureček^b,

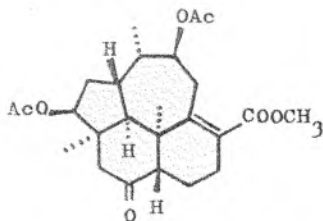
Jan Vrkoč^a

^aInstitute of Organic Chemistry and Biochemistry

^bJ. Heyrovský Institute of Physical Chemistry
and Electrochemistry

Czechoslovak Academy of Sciences, Prague, Czechoslovakia

Nasutitermes costalis is a highly evolved termite species which employs chemical weapons in defense. The composition of the soldiers frontal gland secretion has recently been investigated in detail. This secretion contains monoterpene hydrocarbons and polyoxygenated bicyclic, tricyclic and tetracyclic diterpenes. A new tetracyclic kempene-derived defensive compound (I) was found in the soldiers secretion. Structure determination based on mass and NMR spectra will be discussed.



I

OCCURRENCE OF BETULINIC ACID IN TISSUE CULTURES OF
SOLANUM AVICULARE FORST

T. Vaněk, T. Macek, I. Beneš, L. Novotný

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

During the analysis of chemical constituents of *Solanum aviculare* callus cultures (strain KL 9) also betulinic acid was found in a remarkable amount (3% on dry weight basis). This fact led us to the screening of betulinic acid content in other cultures of this species. The 50 strains tested were obtained in our laboratory and subcultured under constant conditions for more than 3 years. The analysis was performed by means of HPLC. The reasons why this compound appears in the tested tissue cultures in relatively large amounts, are under further investigation.

OXIDATION AND EPOXIDATION OF 4,4-DIMETHYL-A-HOMO-5-CHOLESTENES.

H. Velková, J. Zajíček

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

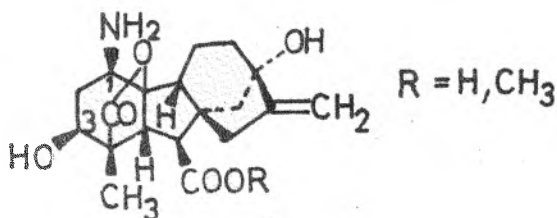
Oxidation of 3-substituted 4,4-dimethyl-A-homo-5-cholestenes bearing a hydroxy group in the position 4a with chromium trioxide-pyridine complex affords according to the configuration of the 4a-hydroxy group the corresponding unsaturated ketones or 5,6-epoxides as the main products. The 4a-hydroxy group does not exert any directing effect on the stereochemistry of epoxidation of the 5,6-double bond and 5 β ,6 β -epoxides are the only epoxidation products. The configuration of the 5,6-epoxidic ring was confirmed by ¹H-NMR data.

SYNTHESIS OF 1-AMINO-GIBBERELLINS

B. Voigt and G. Adam

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

The present paper describes the synthesis of gibberellin derivatives with 1 β -amino function which are of interest for affinity chromatography and radioimmunoassay of this phytohormone class. Starting compounds are 1 β -azido-gibberellins prepared by addition of hydrazoic acid to 3-dehydro-gibberellin A₃ followed by NaBH₄-reduction of the obtained 1-epimeric azidoketones. Reaction of 1 β -azido-gibberellin A₁ with propane-1,3-dithiol/triethylamine gives 1 β -amino-gibberellin A₁ in 75 % yield. In analogous reactions from 1 β -azido-gibberellin A₁-methyl ester and 1 β -azido-3-epi-gibberellin A₁ 1 β -amino-gibberellin A₁ methyl ester as well as 1 β -amino-3-epi-gibberellin A₁ were obtained. The stereochemistry of the synthesized compounds was determined by NMR-investigations.



TERPENE SYNTHESIS

Ernest Wenkert

Department of Chemistry (D-006), University of California-San Diego,
La Jolla, CA 92003, U.S.A.

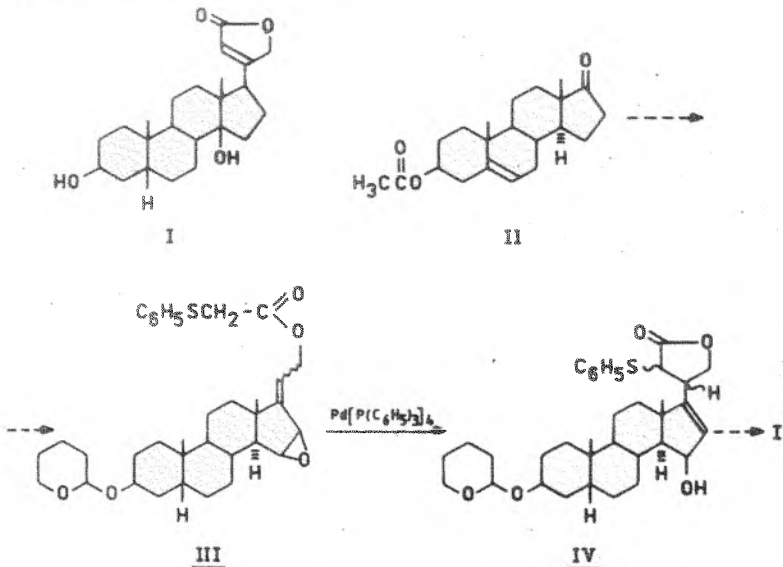
The use of α -diazocarbonyl compounds in terpene synthesis will be described. The general chemistry of unusual α -diazocarbonyl substances will be discussed.

SYNTHESIS OF DIGITOXIGENIN FROM 3 β -ACETOXY-5-ANDROSTEN-
-17-ONE INVOLVING PALLADIUM INDUCED REARRANGEMENT OF
ALLYLIC EPOXIDE

J. Wicha and M. M. Kabat

Institute of Organic Chemistry of the Polish Academy of
Sciences, ul. Kasprzaka 44, 01-224 Warszawa, Poland

A synthesis of digitoxigenin I from 3 β -acetoxy-5-
-androsten-17-one II has been developed in which the key
step involved rearrangement of allylic epoxide III to
butanellide IV induced by tetrakis(triphenylphosphine)-
palladium(0).

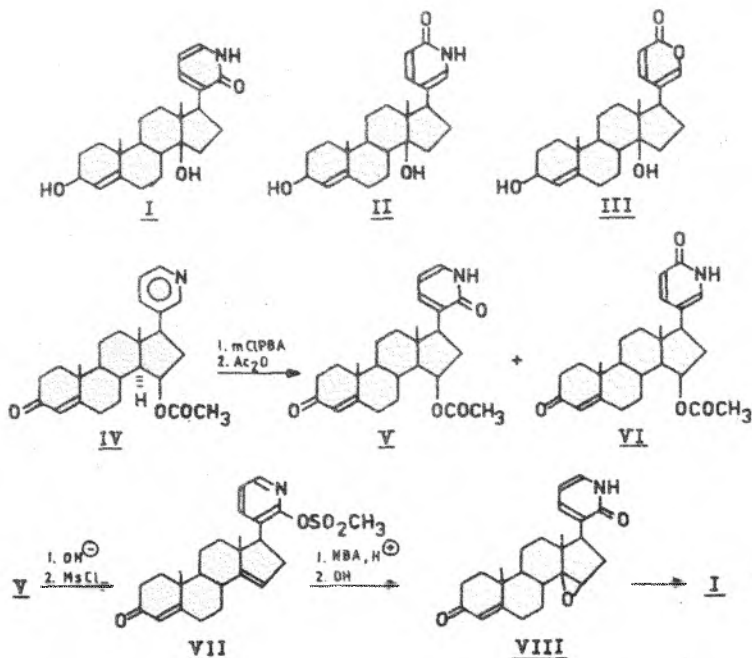


A SYNTHESIS OF PYRIDONE ANALOGUES OF SCILLARENIN

J. Wicha and M. Masnyk

Institute of Organic Chemistry of the Polish Academy
of Sciences, ul. Kasprzaka 44, 01-224 Warszawa, Poland

Isomeric pyridones I and II related to scillarenin III were synthesized from 3 β -hydroxy-5-androsten-17-one via intermediate IV previously described.¹ The main steps of the synthesis of compound I are shown on the following scheme. The synthesis of pyridone II was carried out in similar way.

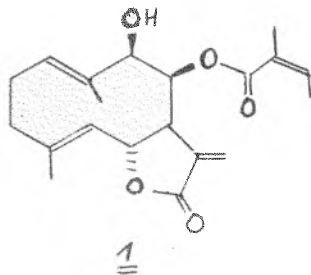


β, γ -DILACTONES FROM GRAZIELIA SPECIES

C. Zdero and F. Bohlmann

Institute for Organic Chemistry, Technical University of Berlin

The Brazilian Composite Grazielia serrata (Spreng.) K. et R. afforded in addition to known kaurene derivatives and 8β -angeloyloxy- 9β -hydroxy costunolide (1) a dilactone its structure and stereochemistry being elucidated by high field ^1H NMR spectroscopy and a few chemical reactions which clearly established the presence of a β, γ -dilactone which obviously was derived from 1. Similar dilactones have isolated from a further Grazielia and a Disynaphia species. The biogenetic relationships will be discussed.



CONFORMATIONAL ANALYSIS OF STEROID SIDE-CHAINS

F.J.Zeelen

Organon, Scientific Development Group, 5340BH Oss,
The Netherlands

The published X-ray structure determinations of more than 400 steroids contain a wealth of information concerning preferred conformations of steroids. This will be illustrated by discussing the conformation of the acetyl side-chain of progesterone derivatives and the conformations of the sterol side-chains of cholestanes and Δ^{22} -unsaturated sterols. Strong conformational preferences are found in all three series.

This information will then be used to interpret the stereoselectivity observed in a number of reactions, which are used to construct sterol side-chains.

I N D E X O F A U T H O R S

- Adam G.: 1,56,94
Akhrem A.: 2,3,4
Alexandrova E.: 90
Allevi P.: 5
Anastasia M.: 5
Appendido G.: 6
- Baekström P.: 8
Ballschuh S.: 80
Baram G.I.: 30
Barkhash V.A.: 73
Beneš I.: 9,92
Bernassau J.M.: 10
Błaszczyk K.: 69
Bohlmann F.: 98
Bończa-Tomaszewski Z.: 11
Boór L.: 89
Borowiecki L.: 13,14,15
Buděšínský M.: 9,91
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