National Committee of Chemistry
Polish Academy of Sciences

FOURTH POLISH NATIONAL STEROID CONFERENCE

Jadwisin – 1971

The Conference is organized by the Institute of Organic Chemistry,
Polish Academy of Sciences, Warsaw

POLISH ACADEMY OF SCIENCES

F O U R T H P O L I S H

NATIONAL STEROID CONFERENCE

JADWISIN 1 9 7 1.

The Conference is organized by the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw.

Honorary Committee :

Chairman : E. ZAWADA, M.Sc., Minister of Chemical Industry

Members : Prof. B. BOBRAŃSKI, D.Sc. Member of the Academy

Prof. J. MICHALSKI, D.Sc., Member of the Council of the Academy

H. TARCHALSKA, M.Sc. Director of the Union of the Pharmaceutical Industry "Polfa"

E. WARDZIŃSKI, M.Sc., Vice-Director of the Union of the Pharmaceutical Industry "Polfa"

Prof. M. WIŚWIÓROWSKI, D.Sc., Member of the Academy

Organizing Committee :

Chairman : Prof. M. KOCÓR, D.Sc., Director of the Institute of Organic Chemistry, Warsaw

Scientific Secretary of the Conference : W. SOBÓTKA, D.Sc.

Members : A. DANIEWSKI, Ph.D.

W. DANIEWSKI, Ph.D.

M. GUMUŁKA, Ph.D.

W. GUSTOWSKI, Ph.D.

W. KROSZCZYŃSKI, Ph.D.

A. KUREK, Ph.D.

A. SCHMIDT-SZAŁOWSKA, Ph.D.

F. WERNER-ZAMOJSKA, Ph.D.

J. WICHA, D.Sc.

C O N _ E N T S

P l e n a r y L e c t u r e s

Z. BOROWIECKI

Bridged Carbonium Ions

E. CASPI

Aspects of the Biosynthesis of Polyprenoids

R.N. CHAKRAVARTI

Indian Dioscoreas as a Source for Intermediates for Steroid Industry

V. HEROUT

Research on Phytochemistry of Some Lower Plants

K. SCHAFFNER

Photochemistry of Steroidal Ketones and Related Compounds

K. SCHREIBER

Recent Advances in the Chemistry of Plant Steroids

G. SNATZKE

New Application of CD in the Field of Natural Products

M. ZEIRAL

Controlled Transformation of Double-Branched Steroidal Olefins into α-Azido-Ketones

STRUCTURAL ELUCIDATION OF A NEW C_{28}-STEROIDAL LACTONE OF THE WITHANOLIDE TYPE

G. Adam, M. Hesse

Institute of Plant Biochemistry

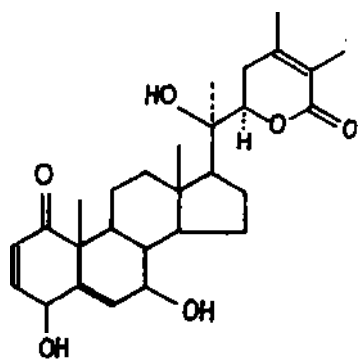
of the German Academy of Sciences at Berlin,

Halle, DDR

Institute of Organic Chemistry,

University of Zürich, Schweiz.

From the Solanaceae Dunalia australii (Griseb.) Sleum. a new C_{28} steroidal lactone has been isolated. On the basis of IR, UV, NMR, ORD and mass spectrometrical data and chemical transformation the structure is regarded as (20R : 22R)-4β.7β.20-trihydroxy-1-oxo-witha-2.5.24-trienolide (I).



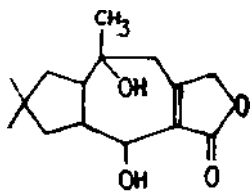
A NEW METHOD FOR SIDECHAIN DEGRADATION OF CYCLOARTENOL

G. Adam. B. Voigt and K. Schreiber
Institute of Plant Biochemistry
of the German Academy of Sciences at Berlin,
Halle, GDR.

A new method for stepwise sidechain degradation of the pentacyclic triterpene cycloartenol giving under preservation of the cyclopropane ring 4.4.14α-trimethyl-9β.19-cyclo-5α--pregnane 3β-ol-20-one has been described. A modified reaction sequence leading to the lanostane series yields the corresponding $\Delta^{9,11}$-unsaturated 20-keto-pregnane derivative.

MASS-SPECTROMETRY OF SOME SESQUITERPENES. FRAGMENTATION OF LACTARORUFIN A AND ITS DERIVATIVES UNDER ELECTRON IMPACT

E. Baranowska, W.M. Daniewski
Institute of Organic Chemistry
Polish Academy of Sciences, Warsaw



Electron impact studies of lactarorufin A ($C_{15}H_{22}O_4$) and its derivatives allowed to establish the correlations between the fragmentation modes and their structures.

The loss of water from molecular ion in lactarorufin A is accomplished in two ways : first by elimination fo the tertiary hydroxyl group with an adjacent hydrogen atom and secondly

by expulsion in which hydrogen atoms from both hydroxyl groups are ejected. The second mode of water elimination led to the formation of an internal ether which also could by easily obtained by chemical methods. The loss of the cyclopentane ring from the molecular ion gave the characteristic fragment at m/e 170 ($C_8H_{10}O_4$). This ion contains the lacton ring and both hydroxyl groups and appears in mass spectra of the keto-derivative (at m/e 168) and of the monoacetate of lactaro-rufin A (at m/e 212).

The possible origin of other major fragments has been determined using high resolution mass spectrometry and deuterium labelling.

THE MASS SPECTROMETRY OF (±)-9-AZA-D-HOMOGONA-3-ONE ETHYLENE KETALS

E. Baranowska, K. Łypaczewicz, W. Sobótka
Institute of Organic Chemistry,
Polish Academy of Sciences, Warsaw.

The mass spectra of (±)-9-aza-D-homogona-3-one ethylene ketals were determined and the influence of carbon-carbon double bond as well as the carbonyl group on their fragmentation behaviour was established. In all spectra the ketal moiety containing ions at m/e 99 and 101 were observed. [illegible] - dominant decomposition pathway, due to the C_1–C_{10} bond rupture, led to the azonium fragments. The presence of the C_6 carbonyl group effected the process of the partial ketal group elimination, giving rise to M^+–C_2H_5O ions. Fragments formed by the HDA process from ring A were observed in the

spectrum of the ketal with a cyclic cis-vinylogous amide system in the ring B. The other characteristic feature in the spectra of the examined compound was the appearance of M^{+}-101 ions. The insertion of nitrogen atom into the steroid skeleton, with the ethylene ketal group changed its usual fragmentation pattern.

A NEW ROUTE TO 17-ETHYLIDENE-1,3,5(10)-ESTRATRIENS

K. Barnikol-Oettler, G. Teichmüller
Scientific Laboratories of VEB Jenapharm, Jena GDR
Department of Organic Chemistry

17-Ethylidenesteroids have become more important in building up the 17-acetoxy-side-chain by the industrial utilisation of the total synthesis of C_{18}-steroids.

A new method for preparing 17-ethylidenesteroids from 17α-ethinyl-17β-trimethylsiloxy-steroids by Birch-reduction will be discussed. It is characterized by the selective reduction of the ethinylgroup in the presence of the aromatic system in the A-ring without changing the aromatic structure. The new variant is of general application and yields of 80-85% of 17-ethylidenesteroids were obtained.

The configuartion of the synthesized 17-ethylidenesteroids are investigated by NMR-spectroscopy and will be discussed as well.

EFFETS STÉRIQUES EN SÉRIE DIMÉTHYL-6,6 BICYCLO(3,1,1) HEPTANIQUE (DÉRIVÉS DE 1α ET DU β-PINÈNES)

Y. Bessière-Chretien

École Normale Supérieure

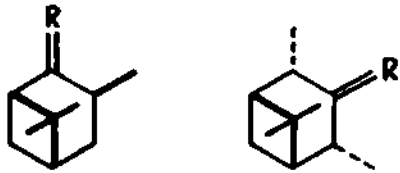
Laboratoire de Chimie, Paris

Après avoir préparé un certain nombre de cétones en 2 et en 3, et d'hydrocarbures à double liaison exo en 2 et en 3, nous avons effectué des séries de réactions nous permettant d'évaluer les encombrements stériques provoqués par les substituants ou par la conformation des molécules, en cis ou en trans par rapport au pont gem-diméthylé.

Les résultats exposés seront ceux :

- de la bromhydratation des hydrocarbures à méthylène en 2 (avec transposition);
- de l'époxydation et de l'hydroboration d'hydrocarbures à méthylène en 2 ou en 3;
- de la réaction de Corey sur des cétones en 2 ou en 3;
- de la réduction par divers hydrures complexes de cétones en 3.

Pour donner une très brève conclusion, nous pourrions dire que, parmi les dérivés étudiés, les deux extrêmes sont :



avec R = CH_2 ou O

le premier ayant le côté trans nettement favorisé et le second, le côté cis relativement plus favorisé que le côté trans.

REACTION OF MYRTENIC ACID WITH N-BROMOSUCCINIMIDE

L. Borowiecki, E. Heca

Institute of Chemistry, N. Kopernik University, Toruń

In the series of investigations of myrtenic acid we tried to carry out the addition reaction. These attempts were unsuccessful, however, except hydrogenation.

In the present paper the reaction of myrtenic acid and methyl myrtenate with N-bromosuccinimide was studied.

From the consideration of the structure of myrtenic acid and methyl myrtenate is evident, that only one possibility of substitution by bromine (from N-bromosuccinimide), namely in the position C-4 with formation of 4-bromomyrtenic acid and methyl 4-bromomyrtenate respectively can be taken in account.

The reaction of myrtenic acid with N-bromosuccinimide gave a small amount of a solid product (m.p. 119-121°) which is probably 4-bromomyrtenic acid.

The isolation of larger amounts pure 4-bromomyrtenic acid was very tedious and therefore allylic bromination of methyl myrtenate was carried out.

We obtained a stable bromoderivate, which after reduction with lithium aluminium hydride gave two products; one of them was identified as myrtenol.

The obtained bromoderivate was converted by silver acetate in an acetate, which was hydrogenated in the presence of the Adams's catalyst. Reduction of this saturated acetate with lithium aluminium hydride, yielded a glycol, to which the structure of 4,10-pinandiol was assigned.

The attempts of bromination of myrtenol and myrtenyl acetate by N-bromosuccinimide were also carried out.

TRIFLUORACETATES OF STEROIDS

E.M. Chambaz, G. Defaye

Biochimie, CEN-G., Grenoble, France

A systematic study of trifluoroacetate derivatives of hydroxy steroids was undertaken in order to evaluate their gas chromatographic properties. Their volatility and their stability are satisfactory for gas phase analysis and they may be interesting for high sensitivity measurements by electron capture detection.

Various experimental conditions for the synthesis of these derivatives are presented. A particular case is represented by the structure containing an enolisable keto group (testosterone, or more generally Δ-4 3-keto compounds). In this case the formation of enol esters can be avoided by the use of trifluoroacetyl-imidazole.

The nature of the derivatives obtained was studied by NMR spectroscopy and mass spectrometry.

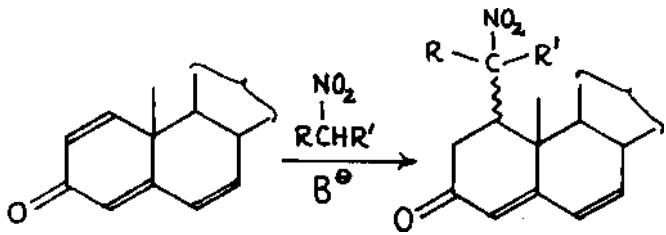
The chemical shift due to the CF_3 substituant can be characterized by NMR study of the 19-F signal. Its value can be correlated to the position of the original hydroxy group on the steroid skeleton.

The use of these derivatives is therefore of potential value in the structural characterization of naturally occuring steroids.

ON THE MICHAEL REACTION WITH STEROIDAL 3-KETO-1,4,6-TRIENES

T. Cynkowski, M. Gumułka, M. Kocór
Institute of Organic Chemistry
Polish Academy of Sciences, Warsaw

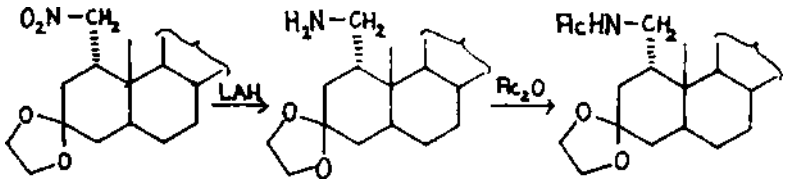
Nitroalkanes react with steroidal 3-keto-1,4,6-trienes giving the corresponding 1-substituted nitroalkil-3-keto-4,6--dienes. The stereochemistry of this Michael addition depends on the length of the alkil chain of the reagents i.e. nitromethane adds exclusively from the less hindered side of the steroid to give 1-alfa-nitromethyl-3-keto-4,6-dienes, whereas its homologes yield a mixture of 1-alfa- and 1-beta- substituted products. The rate of beta-substitution increases with increasing number of carbon atoms in the nitroalkane, but the total yield of both isomers becomes lower due to steric hinderance.



The structure of the adduct was proved by spectral analysis especialy by NMR and CD.

The adducts have been reduced by $NaBH_4$ to the corresponding 3-beta-alcohols and oxidized by organic peracids to 6-alfa-7-epoxides. The ketones could be also converted by standard methods to the 3-ethylenedioxycompounds. The latter were submitted to LAH reduction yielding a mixture of compounds from

which a noncrystalline very polar base was separated and converted to N-acetylated products.



An addition with KCN to 3-keto-1,4,6-trienes as well as with 3-keto-1,4-dienes was also performed.

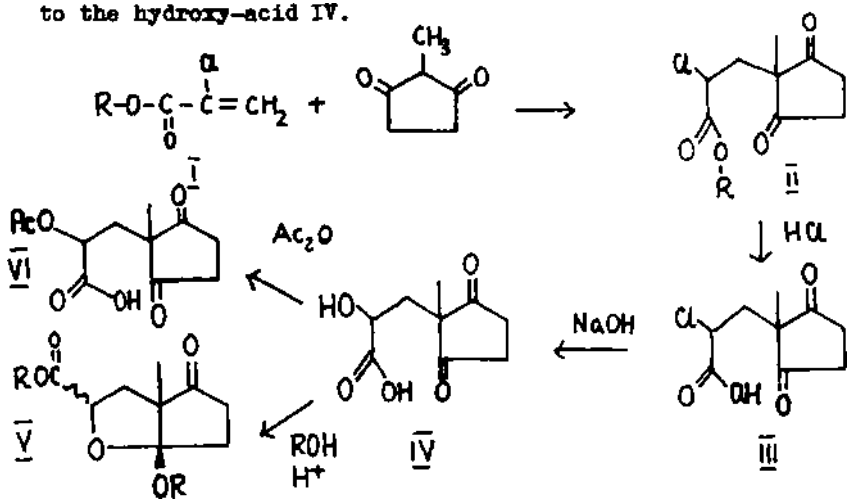
NEW INTERMEDIATES POTENTIALLY USEFUL FOR THE SYNTHESIS OF STEROIDS

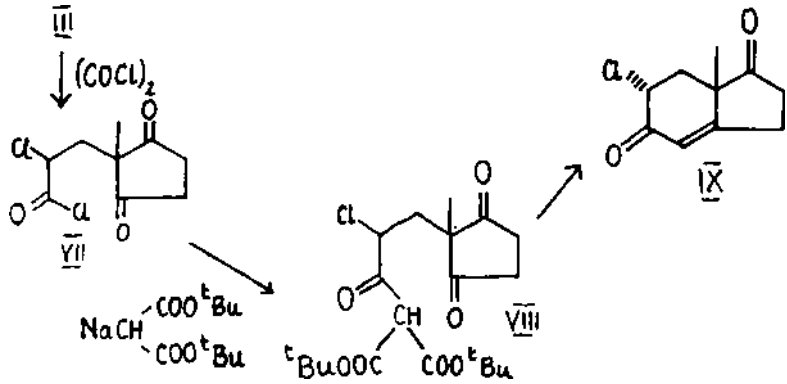
A.R. Daniewski, M. Kocór

Institute of Organic Chemistry

Polish Academy of Sciences, Warsaw

The α-chloroacrylates I react. smoothly with 2-methylcyclopentane-1,3-dione in methanolic solution giving 2-methyl--2(β-carbomethoxy-β-chloroethyl)-cyclopentane-1,3 dione II. This ester can be hydrolyzed to the chloroacid III and next to the hydroxy-acid IV.





The compound IV reacts with alcohols giving the mixture of two diastereoisomers ketalesters V, and when reacted with acetic-anhydride gives the acid VI. The chloroacid III can be converted in excellent yield to the acid chloride VII with oxalyl chloride. The acid chloride VII was converted to 5,6,7,8-tetrahydro-6-chloro-8-methyl-indane-1,5-dione IX via the malonate derivative VIII.

STRUCTURE OF LACTARORUFIN A

W.M. Daniewski, M. Kocór

Institute of Organic Chemistry,

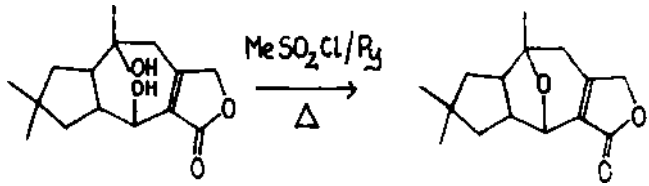
Polish Academy of Sciences, Warsaw.

In our previous papers we reported the isolation, and the partial structure of lactarorufin A, a new sesquiterpenoid lactone from Lactarius rufus.

On the basis of further chemical transformations, degradation, and full chemical and spectral analysis the structure of lactarorufin A was established.

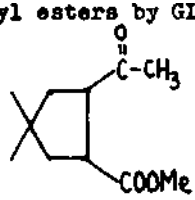
The position of geminal methyl groups was found by examination of the NMR spectrum of internal ether derivative of

lactarorufin A which was formed in the reaction of lactarorufin A with mesyl chloride in hot pyridine.

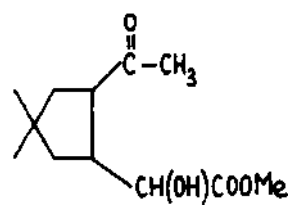


The LAH reduction of the internal ether yielded an easily acetylable diol; the NMR spectra of both of them being very characteristic, thus definitely confirming the existence of the lactonic ring.

The presence of cyclopentane ring in the molecule was proved by RuO_4/KIO_4 degradation of anhydrolactarorufin A monoacetate which yielded the acids I and II isolated as their methyl esters by GLC.

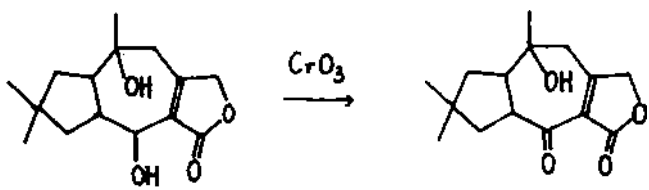


I m/e 198



II m/e 228

The position of lactonic carbonyl group was found on the basis of the UV absorption of the ketoderivative of lactarorufin A at λ_{max} 235 nm obtained by CrO_3 oxidation of lactarorufin A.



Further support of the structure of lactarorufin A was obtained by examination of $Eu/dpm/_3$ shifted pmr spectrum of lactarorufin A monoacetate.

APPLICATION OF THE PROTON MAGNETIC RESONANCE SHIFT REAGENTS. STEREOCHEMISTRY OF LACTARORUFIN A.

T.M. Daniewski, A. Ejchart, J. Jurczak, L. Kozerski, J.S. Pyrek
Institute of Organic Chemistry
Polish Academy of Sciences, Warsaw.

Continuing our research on the structure and stereochemistry of lactarorufin A, a new sesquiterpenoid lactone, isolated from Lactarius rufus, we examined $Eu(dpm)_3$ shifted pmr spectra of some derivatives of lactarorufin A.

It was found that the coupling constants were not changed with the increased concentration of $Eu(dpm)_3$. On the basis of the analysis of the correlation between the $Eu(dpm)_3$ induced shift and the distance of all protons from the coordination center, and the discussion of coupling constants, the stereochemistry of the junction between seven and five membered rings was established, together with the relative conformation of the chiral centers of the molecule.

THE INFLUENCE OF STERIC HINDRANCE ON BIOTRANSFORMATION OF SOME SATURATED AND UNSATURATED STEROIDKETONES BY RHODOTORULA MUCILAGINOSA

J. Dmochowska, A. Siewiński
Department of General Chemistry,
College of Agriculture, Wroclaw

A series of biotransformations with the title microorganism

was investigated using following compounds as substrates :

4-methyltestosterone, 19-nortestosterone, 4-chlortestosterone, 4-chlorandrostendione, 19-norandrostendione, 4-methyldihydrotestosterone and 19-nordihydrotestosterone.

The results were compared with analogical reactions for testosterone and androstene-3,17-dione.

It was observed, among others, that the methyl group in position 4 as well as the lack of methyl group in position 10 had an inhibiting influence on reduction of α,β -unsaturated system in ring A. In case of 4-chloro-testosterone the reduction gave, as the main product, the corresponding allyacohol.

From these results it may be concluded, that the substituents, such as methyl group or chlorine in ring A, have a significant steric influence on biotransformation of α,β --unsaturated ketone in position A.

SOME OXIDATION REACTIONS WITH TRITERPENOIDS

M.H.A. Elgamal, M.B.E. Fayez

National Research Centre, Dokki, Cairo, Egypt

and

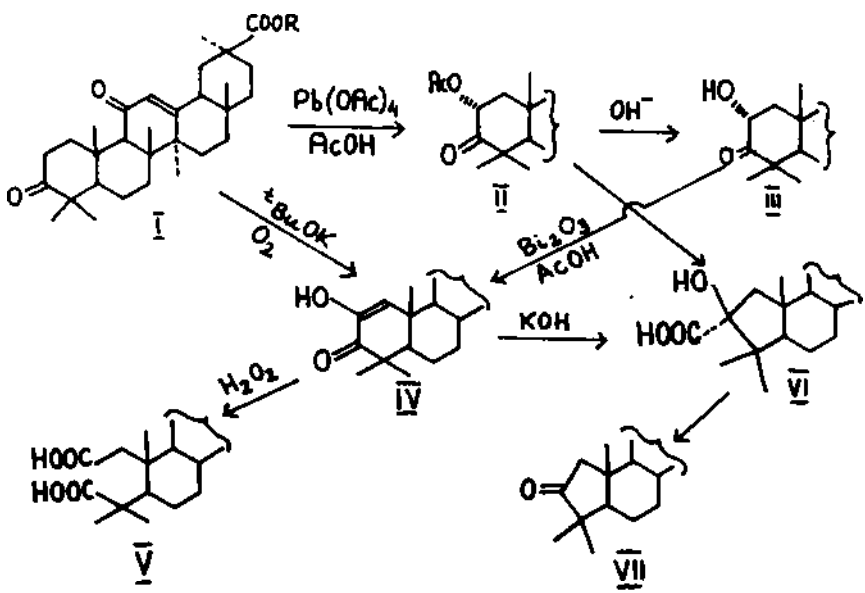
G. Snatzke

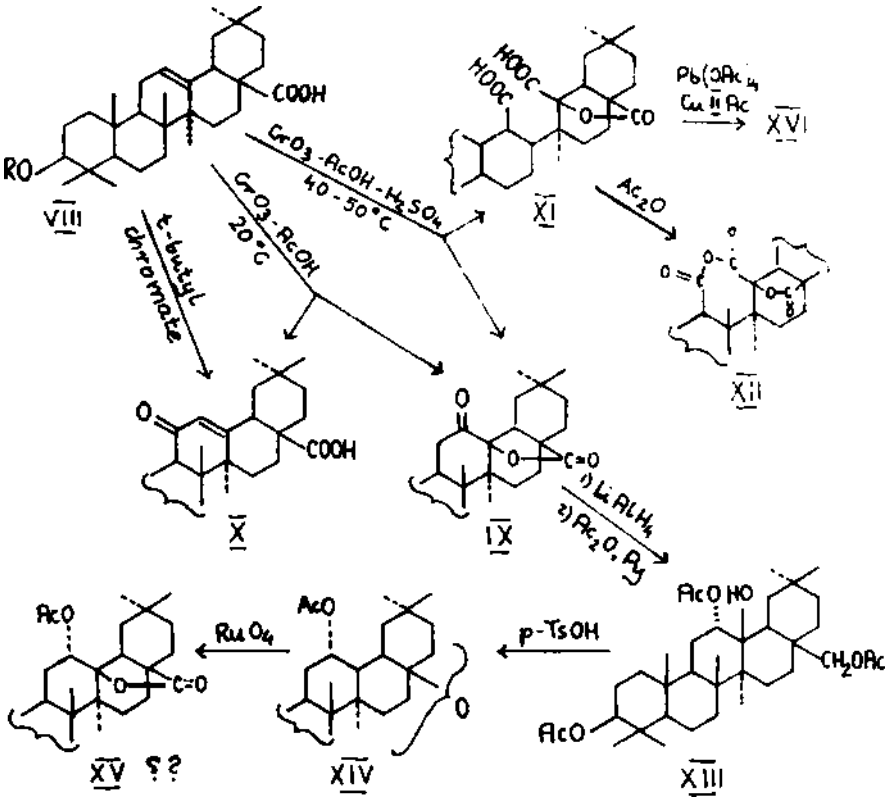
Org. Chem. Institut der Universität Bonn, DBR

Some glycyrrhetic and oleanolic acid derivatives with modified A and C rings have been prepared and their CD spectra studied. Treatment of the 2α-ketol III[1] with Bi_2O_3 or direct oxidation of I with k-t-butylate in oxygen atmosphere afforded the diosphenol IV which upon further oxidation with H_2O_2 gave a dicarboxylic acid (V) formed by cleavage of the 2-3 bond.

Action of strong alkali on the diosphenol IV or II in presence of air led to the contraction of ring A. The resulting A-nor acid (VI) was oxidised with $Pb(OAc)_4$ to give the A-nor--ketone VII.

Selective oxidation of oleanolic acid acetate (VIII) with chromic acid at 20° afforded mainly the ketolactone IX[2] and the α,β-unsaturated ketone X as a byproduct. The latter compound also could be obtained in good yield by direct oxidation of VIII with t-butyl chromate. When oxidation of VIII with CrO_3-H_2SO_4 is carried at 40-50° the main product was the dicarboxylic acid XI[3] besides a small amount of IX. Reduction of IX with $LiAlH_4$ gave a tetrol. Unexpectedly, the treatment of the triacetate XIII with p-toluene-sulphonic acid afforded an ether XIV. The presence of ethereal linkage in XIV is supported by its oxidation with RuO_4 to the lactone XV. Degradative oxidation of XI with $Pb(OAc)_4$ led to a new product XVI which is under study. A discussion is given of the stereochemical assignments in various products.





APPLICATION OF THE PROTON MAGNETIC RESONANCE SHIFT REAGENTS TO THE STUDY OF TRITERPENOIDS

A. Ejchart, J. Jurczak, L. Kozerski, J. St. Pyrek

Institute of Organic Chemistry,

Polish Academy of Sciences, Warsaw.

A new triterpenoic triol isolated from sunflower flowers was examined by proton magnetic resonance spectroscopy using shift reagents. On the basis of the analysis of $Eu(dpm)_3$ shifted spectra of mono- and bifunctional triterpenes, we

have found the correlations between the change of chemical shifts of methyl protons and the protons surrounding the functional groups and the concentration of the complex, as well as the correlations between the change of the chemical shifts and the distance from the coordination centre. Using the above correlations for trifunctional compound and its derivatives or degradation products we have established the position of hydroxyl groups in the molecule.

AN ATTEMPT TO SEMIQUANTITATIVE INTERPRETATION OF THE $\pi \rightarrow \pi^*$ COTTON EFFECTS OF THE UNSATURATED STEROIDAL SYSTEMS

J. Gawroński, M. Kiełczewski
Institute of Chemistry, A. Mickiewicz University, Poznań

Despite the successful correlation of the sign of the Cotton effect of the principal $\pi \rightarrow \pi^*$ transition of the olefin with its geometrical structure through the octant rule or through the olefin chirality concept as well as of the $\pi \rightarrow \pi^*$ Cotton effect of the dienes by means of the diene chirality rules or using the allylic axial chirality rule, some apparent exceptions were noted. Moreover, no attempt to semiquantitative interpretation of these Cotton effects has been made.

In this report we wish to propose a simple method for semiquantitative treatment of the $\pi \rightarrow \pi^*$ Cotton effects of enes and polyenes in steroidal and other rigid systems.

This method is based on the assumption that the substituents in the proximity of the chromophore give the

contribution to the magnitude of the Cotton effect depending on the nature of the substituent and its vectorial distance from the chromophore.

A possible application to various unsaturated steroidal systems is discussed.

REACTIONS OF KETONES OF 3α,5-CYCLO-5α-CHOLESTANE SERIES WITH DIAZOMETHANE

J. Ulhaus, V. Černy, F. Šorm

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

$AlCl_3$-catalyzed reaction of 3α-5-cyclo-5α-cholestan-6-one with diazomethane leads to a mixture of homologous ketones; their structures and reactions are discussed. Analogous homologization of 3α,5-cyclo-5α-cholestan-2-one is reported.

A SYNTHETIC APPROACH TO THE (±)-9-AZA-3-METHOXY--METHYL-D-HOMOGONA-13(14)-EN-17a,6-DIONE SYSTEM

B. Grabowski, W. Sobótka

Institute of Organic Chemistry,
Polish Academy of Sciences, Warsaw

The enaminoketone and aromatic ring systems of (±)-9-aza--D-homogona-3ξ,17a-dimethoxy-5(10),13(14),15(16),17(17a)--tetraen-6-one has been used for its conversion into the litle compound by the route, O-alkylated and O-protonated vinylogous amide derivative to C-10 angularly alkylated 9-azasteroid skeleton followed by the Birch reduction and Jones oxidation respectively. Stereochemistry of the four

isomeric aminoketones isolated in the second step of the synthetic pathway has been discussed. A modification of the above procedure involved removal of the carbonyl function at C-6 prior to the liquid ammonia reduction.

APPLICATION OF THE PROTON MAGNETIC RESONANCE SHIFT REAGENTS TO THE STUDY OF STEROIDS

M. Gumułka, A. Ejchart, J. Jurczak, L. Kozerski, J.St.Pyrek
Institute of Organic Chemistry
Polish Academy of Sciences, Warsaw

Tris (dipivalomethanato) europium $Eu(dpm)_3$ and tris (dipivalomethanato) praseodymium $Pr(dpm)_3$ were applied as shift reagents for PMR analysis of steroids. We have examined several mono- and dioxygenated steroids and their spectra have bean found to be almost of the first order. Assignements of skeleton protons signals were done on the basis of spin decoupling experiments. Chemical shifts of methyl protons in normal spectra were found from the analysis of plots of the chemical shift versus complex/substance molar ratios. The influence of the differently situated functional groups on the change of chemical shifts of signal characteristic for different fragments of steroid skeleton is discussed.

SOME TRANSFORMATIONS OF THE SIDE-CHAIN OF SOLASODINE

M. Havel, V. Černy, F. Šorm
Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences, Prague, Czechoslovakia

A series of new compounds derived from solasodine (I) was prepared by opening the ring E and F of solasodine. Deamination and hydroboration of some these compounds were studied; stereochemistry at $C_{(22)}$ and $C_{(25)}$ was established.

EPOXIDATION OF ISOMERIC CHOLEST-5-EN-3,4-DIOLS WITH PERBENZOIC ACID

K. Jaworski, I. Małunowicz
Department of General Chemistry,
College of Agriculture, Wrocław

The reaction between perbenzoic acid and isomeric cholest-5-en-3,4-diols in different solvents leads always to the mixture of isomeric 5,6-epoxydiols.

It has been proved that the ratio of 5,6α- and 5,6β-epoxides in the mixture depends on the configuration of the hydroxyl groups and on the solvent used as well. The deciding factor is the formation of hydrogen bonds between the peracid and the steroid or the solvent.

REACTIONS OF SOME B-NORSTEROIDAL BROMIDES WITH SILVER FLUORIDE

A. Kasal, J. Joska, F. Šorm

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

Additions of bromine, bromine fluoride, hypobromous acid, methyl hypobromite and acetyl hypobromite to Δ^5-unsaturated B-norsteroide are governed by Markownikoff rule; 5β-substituted 6α-bromoderivatives being formed. With exception of 3β-fluoro-6α-bromo-B-nor-5β-cholestan-3β-ol, the compounds lose bromine under treatment with silver fluoride, yielding epoxides, olefines and hydroxy derivatives. Synthetic use of that particular reactions is discussed.

THE OXIDATION OF 3-METHOXY-8,14-SECOESTRA-1,3,5(10),9(11)-TETRAENE-14,17-DIONE

M. Kocór, A.R. Daniewski, K. Guzewska

Institute of Organic Chemistry
Polish Academy of Sciences, Warsaw

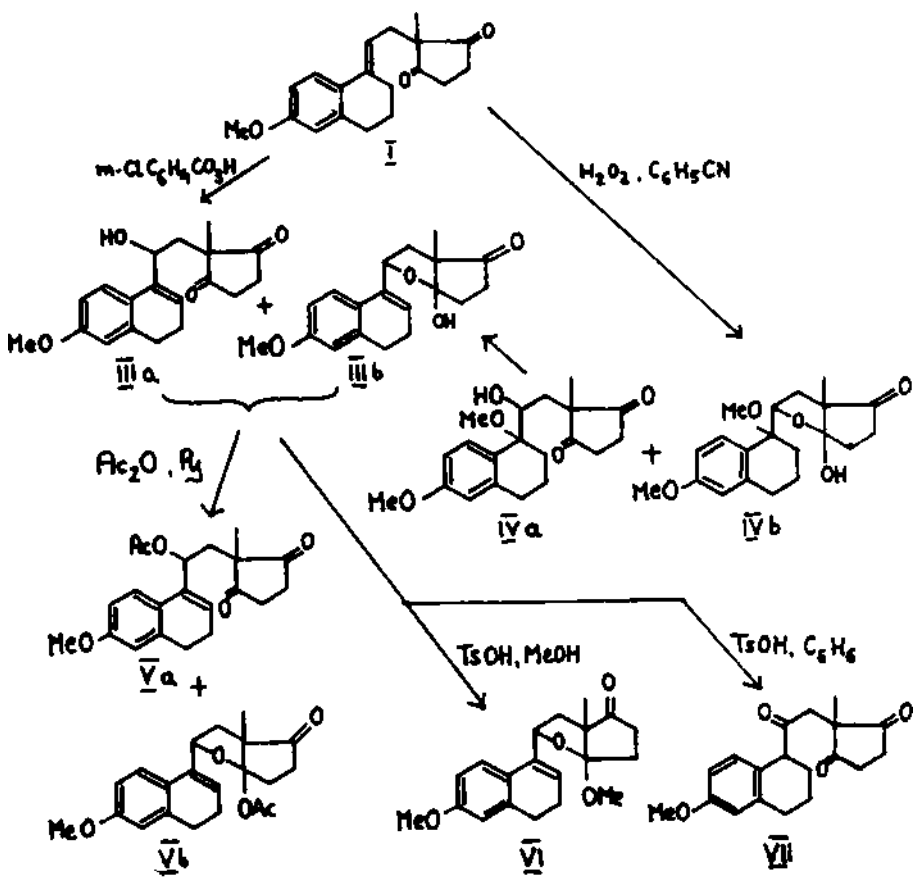
The title compound (I) was oxidized by DDQ to compound II which was next cyclized to 14,15-dehydroequilenin (IX). The compound (I) was epoxidized with m-chloroperbenzoic acid and 11,14α-epoxy-14β-hydroxy-3-methoxy-8,14-secoestra-1,3,5(10),8-tetraen-17-one was obtained, which equilibrated in solution with alcohol IIIa.

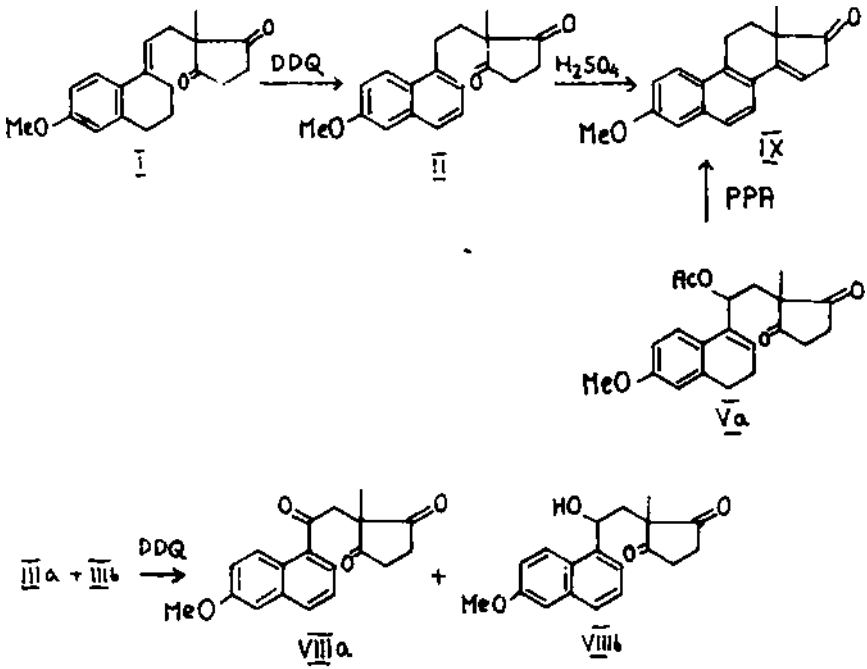
The compound (I) when reacted with hydrogen peroxide and benzonitrile in basic conditions gave IVa and IVb as viscous oil, which on standing decomposed to III b. The alcohol (IIIb) when acetylated with acetic anhydride affored a mixture of acetates Va and Vb.

The acetate Va was cyclized with PPA to give 14,15--dehydroequilenin (IX).

The alcohol IIIb was oxidized with DDQ to give the mixture of compounds VIIIa and VIIIb.

The compound IIIb can be transfered under acidic conditions to VI or VII in very good yield.





THE REACTION OF STEROID AZOMETHINES WITH ACETIC ANHYDRIDE

M. Kocór, W. Kroszczyński
Institute of Organic Chemistry
Polish Academy of Sciences, Warsaw

Some new steroid azomethines (steroids containing pyrroline ring condensed with A or D ring of the steroid nucleus) have been synthesized in order to investigate the reaction of azomethines with acetic anhydride. The reaction yielded as the main products the corresponding acetylaminoketones. In one case a cyclic byproduct has been isolated.

REDUCTION OF STEROIDAL KETONES WITH TRIS TRIPHENYLPHOSPHINE NITROGEN COBALT$^{(I)}$ HYDRIDE

M. Kocór, E. Małunowicz, S. Pyrlik

Institute of Organic Chemistry
Polish Academy of Sciences, Warsaw

Saturated and conjugated steroidal ketones with the carbonyl group in positions 3,7,17 and 20 were reduced with one mole of $CoHN_2[(PPh_3)_3]_3$. The yields of the reduction were varying from 20–80%, and were depending on the position and saturation of the carbonyl groups according to the rule: Δ^4-3-ketones > Δ^6-7-ketones > 3-ketones > 17 ≅ 20-ketones. The stereochemistry of the obtained alcohols obeyed the classical rule of the attack from the less hindered side i.e. the β-alcohols were obtained.

3β-acetoxy-pregna-5,16-dien-20-one yielded as the main product of the reduction the saturated 20-ketone (75%), which means that the reaction was 1,4 and not 1,2--addition.

REACTIONS OF B-HOMOCHOLESTANOLS WITH LEAD TETRAACETATE

L. Kohout

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

In connection with our stereochemical studies on B-homosteroids, the reaction of 7- and 7a-hydroxy derivatives of B-homo-5α-cholestane with lead tetraacetate was investigated.

On treatment with lead tetraacetate the 7β -alcohol afforded a 7β,19-oxide. The products of reaction of 7α - and 7aα-alcohols with lead tetraacetate are similar; both alcohols gave cyclic α-oxides(7α,9α- and 5α,7aα, resp.). When 7a -alcohol was treated with lead tetraacetate, 7aβ, 19-oxide was obtained. The structure of the product obtained was determined by NMR and mass spectroscopy. The flexibility of the seven membered-ring B is discussed.

OXIDATION OF DERIVATIVES OF Δ^5-STEROIDS WITH TERT.-BUTYL CHROMATE

T. Kołek, I. Małunowicz

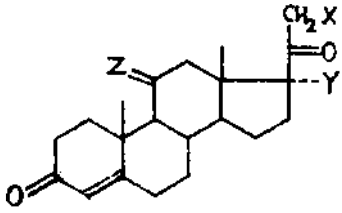
Department of General Chemistry,
College of Agriculture, Wrocław

Oxidation of various 3,17-disubstituted Δ^5-steroids and 4,4-dimethyl homologes of some of them leads mainly to the products of allylic oxidation, i.e. to Δ^5-7-oxo compounds. The byproducts of this reaction has been also investigated to explain the mechanism of their formation.

THE RELATION BETWEEN THE COURSE OF MICROBIAL REACTIONS AND THE STRUCTURE OF STEROIDAL SUBSTRATES

W.Kotula, R. Jaworska, I.Rysymontt, J.Golonka, M.Iwaszkiewicz
Department of Hormones, Pharmaceutical Institute, Warsaw

The relation between the course of the enzymatic reaction of steroids of the general formula given below and their structure was investigated :



where : X - H; OH; OAc

Y - H; OH;

Z - H; H; H,OH; O;

The experiments were carried out in submerged culture of the bacterial strain denoted with symbol J-1-2R in Pharmaceutical Institute collection under constant transformation conditions.

The following steroid compounds were used : 17α,21-dihydroxy-pregn-4-ene-3,20-dione and its 21-acetate, 17α,21-dihydroxy-pregn-4-ene-3,11,20-trione and its 21-acetate, 11β,17α,21-trihydroxy-pregn-4-ene-3,20-dione and its 21-acetate, pregn-4-ene-3,20-dione and 21-hydroxy-pregn-4-ene-3,21-dione.

The results of the experiments were following :

1) The substrate lacking oxygen in position 21 and no hydroxyl in position 17α was converted to the metabolites which did not contain the Δ^4-3-ketone moiety.
2) The substrate containing oxygen in position 21 and lacking hydroxyl in position 17α was completely unreactive with respect to the enzymic system of the above mentioned bacterial strain.
3) The substrates containing oxygen at C_{21} and in position 17α but containing no oxygen at C_{11} were monohydroxylated in still unknown position. The reaction was one-directional and its yield was practically quantitative.

4) The substrates containing oxygen substitutents in positions 21, 17α and 11 were dehydrogenated in position 1-2.

SOME NEW ROUTES TO CHLORMADINONE

G. Langbein, E. Menzer, R. Wesemann

Department of Organic Chemistry

AK VEB Jenapharm, Jena, GDR

Syntheses of Chlormadinone (I) are still of great interest, because it is an valuable active principle for manufacturing contraceptives.

New routes to reach that aim have been worked out. Some of them are discussed in this paper.

The first one is the surprising result that I is formed in yields up to 40% by simple treatment of 17(α)-acetoxy-progesterone with $CuCl_2$ in acetic acid. Additionally to I a second main product is formed in yields up to 30%, which could be reconized as the well known 6-Dehydro-17(α)--acetoxy-progesterone. The reaction mechanism of this transformation is discussed.

The second route comprises :
firstly a section dealing with the introduction of an alkoxy or acyloxy substitutent in position 7 of 3(β)--acyloxy-17(α)-acetoxy-5-pregnen-20-one, which is achieved by allylic bromination followed by treatment of the resulting 7 bromide with ions of the type $R\text{-}O^-$ or $RCOO^-$ respectively,

secondly a section dealing with the introduction of the chlorine atom in position 6 by direct chlorination, as well as

thirdly a section, which describes the important transformations of the new intermediates to the desired end-product : chlormadinone in high yields. / 5

The structure elucidation problems are discussed as well.

EPIMERIC 3-AMINOTARAXASTANES AND THEIR DERIVATIVES

R.S. Ludwiczak, H. Matuszelewska, I. Życzyńska-Bałoniak

Institute of Chemistry and Analysis
Department of Organic Chemistry
College of Medicine, Poznań

Taraxastenone oxime (IIc) was prepared, as described by Herrera Jiménez J. This paper deals with the preparation of Ψ-taraxastenone oxime (Ic) and of taraxastanone oxime (IIIc). The acetates of the oximes showed the following physical datas Id, 194-196°, $[\alpha]_D^{20} = +46°$, IId, 193-195°, $[\alpha]_D^{19} = +91°$, IIId, 218-220°, $[\alpha]_D^{20} = +12°$.

Catalytic reduction both of Ψ-taraxastenone oxime (Ia) and of taraxastenone oxime (IIc), in the presence of platinum, yielded a mixture of epimeric 3-aminotaraxastanes (III g, III i) which by crystallisation of the hydrochlorides could be separated into two homogenous hydrochlorides IIIe, m.p. 249-250°, $[\alpha]_D^{20} = +17°$ and IIIf

m.p. 324–326°, $[\alpha]_D^{20}$ = +20°. The hydrochloride m.p. 249–250° prevailed. The free amine (IIIg) separated from the latter melted at 190–196°, $[\alpha]_D^{20}$= +17°, acetate (IIIh), m.p. 278–280° $[\alpha]_D^{18}$= –11°.

The yield of the hydrochloride m.p. 324–326° was very poor.

A mixture of the epimeric 3–aminotaraxastanes was obtained, by reduction of taraxastanone oxime (IIIc) with sodium and n-amyl alcohol, but in this case the amine IIIi m.p. 195–196°, $[\alpha]_D^{20}$= +6°, (hydrochloride IIIf, m.p. 324–326°, acetate IIIj m.p. 294–295° $[\alpha]_D^{20}$= +7°) prevailed.

Analytic results and IR spectra of the amines and their derivates were in good agreement with those expected theoretically.

On the basis of molecular rotations differences of the free amines and their acetates the equatcrial configuration of the amino-group was ascribed to the 3–aminotaraxastane (IIIi) m.p. 195–198°, $[\alpha]_D^{20}$= +6°, and the axial to the 3–aminotaraxastane (IIIg) m.p. 190–196°, $[\alpha]_D^{20}$= +17°.

The N–methyl derivates were also prepared.

SYNTHESIS OF ISOMERIC (±)–9–AZA–D–HOMOGONA–-10–METHYL–13(14)–EN–3–ONES AND RELATED COMPOUNDS

K. Łypacewicz, W. Sobótka

Institute or Organic Chemistry

Polish Academy of Sciences, Warsaw.

A facile method of synthesis of (±)–9–aza–D–homo–steroid skeleton with the angular methyl group at C–10 and the

carbonyl group at C-3 has been elaborated.

The successive steps of the synthesis comprised the conversion of the cisoid vinylogous amide system into either O-alkylated or O-protonated derivatives followed by the sterically controlled insertion of an alkyl substituent or hydrogen atom at C-10. In the case of the enol-ether thus obtained its subsequent acid hydrolysis led to the cyclic aminoketone similar to that isolated in the direct alkylation of the O-protonated species. Further modification of the azasteroid skeleton involved removal of the carbonyl group at C-6 by Wolff-Kishner reduction, which afforded two stereoisomeric products of different configuration at C-5.

Functionalization of the double bond at the C/D ring fusion, directed towards insertion of the angular alkyl substitutent at C-13, has been performed by the synthesis of the corresponding epoxides prepared in the reaction of the unsubstituted model 9-azasteroid skeleton with HOBr generated from N-bromosuccinimide in aqueous acetic acid. An intermediate in the oxirane ring closure the bromo-acetoxy derivative was isolated.

IR, NMR, and MS spectral data of the free bases and their quaternary N-methyl derivatives were discussed to determine the stereochemistry of the title compounds.

IN VITRO TRANSFORMATION OF STEROIDS

B. Matkovics, M. Marián, Z. Rakonczay

Biochemical Research Group

Institute of Animal Physiology, "A.J." University, Szeged

Hungary

In our lecture in Jena in September 1967 we gave a summary of our results of "in vitro" iron (II) ascorbate hydroxylation; in non-steroid model compounds it was possible (i) to transform the methyl to hydroxymethyl group: $-CH_3 \rightarrow CH_2OH$, (ii) to hydroxylate numerous aromatic compounds, and (iii) to transform deoxycholic acid to cholic acid, i.e. the transformation $-CH_2- \rightarrow -CHOH$. The yield of these procedures is not very high and problems of isolation also arise.

For these reasons we made attempts later with two other "in vitro" methods :

A. Photochemical reactions : (i) UV light induced photolysis, (ii) study of the transformations resulting from the ionizing action of high-energy radiation sources.

B. The other field was the study of the roles and properties of (i) "in vitro" specific and (ii) non-specific hydroxylases, which play an important part in the intermediary transformation of steroids.

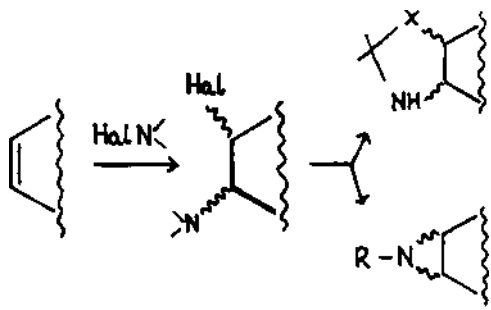
We report some details of our results obtained primarily on the transformations listed in the main groups A and B.

SYNTHESE STICKSTOFFHALTIGER STEROIDE DURCH ADDITION VON N-HALOGENVERBINDUNGEN AN STEROIDOLEFINE

K. Ponsold, W. Ihn, D. Eichhorn

Zentralinstitut für Mikrobiologie und experimentelle Therapie der DAW zu Berlin, Jena, DDR

Im Rahmen unserer Arbeiten über stickstoffhaltige Steroide untersuchten wir Additionsreaktionen von N-Halogenverbindungen an Steroidolefine (I). Die auf diese Weise leicht zugänglichen Verbindungen vom Typ(II) sind interessante Ausgangsmaterialien für die Synthese von heterocyclisch kondensierten Steroiden, insbesondere für die bisher wenig bearbeiteten Aziridine (IIIa - c)



III a = H
b = CN
c = COOR

Es wird über die Addition von Jodisocyanat (JNCO), Chlor- und Bromazid ($HalN_3$), Chlor- und Bromcyanamid (HalNHCN) sowie Mono- und Dichlorurethan (ClNHCOOR, Cl_2NCOOR) an Δ^2-, Δ^5- und Δ^{16}- Steroidolefine berichtet.

Aus den Additionsprodukten von Halogenaziden an Steroidolefine wurden bei der Reduktion Aziridine (IIIa) erhalten. Aus den Additionsprodukten von Halogencyanaminen bzw. Chlorurethanen entstanden bei der Alkalibehandlung N-Cyanaziridine (IIIb) bzw. N- Carbalkoxyaziridine (IIIc).

INVESTIGATION OF AN ENZYME FROM POTATO TUBERS, SAPONIFYING STEROID ACID ESTERS

Z. Procházka, Nguyen Gia Chan
Institute of Organic Chemistry and Biochemistry
Czechoslovak Academy of Sciences, Prague, Czechoslovakia

Our incidental observation that a 20 hours incubation of deoxycholic acid methyl ester with a suspension of freshly grated potato tubers results in its saponification induced us to investigate the specificity of the saponifying enzyme from the plant.

Esters of various steroid acids were submitted to the saponification test (incubation with a suspension of grated potatoes) and the correlation between the structure and the yield of saponification was observed. Structural factors are discussed which might be responsible for the differences in the yields of the enzymatic reaction under investigation.

3,17-BIFUNCTIONAL 17α-METHYL-5-AZAANDROSTANE DERIVATIVES - A SYNTHETIC APPROACH

W.J. Rodewald, J. Jaszczyński
Institute of Fundamental Problems of Chemistry,
University of Warsaw, Warsaw

A partial synthesis of the first 5-azasteroid having both oxygen functions at C-3 and C-17 in 17α-methyl-5-aza-androstane system : 3β,17β-diacetoxy-17α-methyl-5--azaandrosta-4,6-dione (VI) was performed in our laboratory.

This was accomplished by a several step conversion of 17α-methyl-B-nortestosterone acetate (I). Thus I was reduced (LATB -THF or $NaBH_4$ - MeOH) to allylic 17α-methyl-androst-4-en-3β,17β-diol-17-acetate (IIa) and further acetylated to diacetate IIb. Ozonolysis of IIa afforded 4,5-seco-5-ketoaldehyde IIIa, convertible into appropriate acid IIIb, which was characterised as its methyl ester IIIc. Oxiamation of the IIIc 5-keto group gave a mixture resolved into anti- and syn- oximes (IVa,b). As the methyl ester group appeared less convenient than benzhydryl, providing stereochemical control of the synthesis, the ketoacid IIIb was converted into benzhydrylic ketoester IIId and then - appropriate anti-oxime IVc. In a Beckmann-type reaction IVc furnished 3,17β-diacetoxy-3-carbobenzhydryloxy-17α-methyl--4,5-seco-5-azaandrosta-6-one Vb. Conversion of the lactam--triester Vb into lactam-acid Va by removal of the benzhydrylic carboxyl-blocking group was followed by an intermolecular N-acylation to the final 5-azasteroid VI, whose structure was confirmed by analytical and spectral data.

THE SECOND ORDER BECKMANN REARRANGEMENT OF STEROID KETOXIMES

W.J. Rodewald, B. Achmatowicz
Institute of Fundamental Problems of Chemistry,
University of Warsaw, Warsaw

In connection with the synthesis of 5-azaderivatives of cholestane, Beckmann rearrangement of : oxime of methyl ester of 3,5-seco-5-keto-B-norcholestan-4-oic acid and

oxime of methyl ester of 3β-acetoxy-3,5-seco-5-keto-B-norcholestan-4-oic acid, was performed. It was found that besides the "normal" Beckmann rearrangement (lactam's yield about 45%), fragmentation (the second order Beckmann rearrangement) took place, resulting in a mixtures of unsaturated nitriles (about 30% yield). It was shown that in the fragmentation reaction, both oximes gave rise to analogous pairs of isomeric nitriles, differing in double bond location, namely : methyl ester of 6-cyano-4,6,10--seco-5-norcholest-1(10)-en-4-oic acid, methyl ester of 6-cyano-4,6,10-seco-5-norcholest-10(19)-en-4-oic acid, methyl ester of 3β-acetoxy-6-cyano-4,6,10-seco-5-norcholest-1(10)-en-4-oic acid, methyl ester of 3β-acetoxy-6-cyano--4,6,10-seco-5-norcholest-10(19)-en-4-oic acid.

ISOLATION AND INVESTIGATION OF COMPONENTS OF CANTHARELLUS CIBARIUS

A. Schmidt-Szałowska, M. Kocór

Institute of Organic Chemistry

Polish Academy of Sciences, Warsaw

By continous extraction, reextraction and column chromatography a few interesting compounds from the edible mushrooms Cantharellus Cibarius were isolated. Among them ergosterol and its peroxide were identified. An unidentified compound "F" was also isolated and some experiments leading to its structure elucidation were undertaken. From the chemical and spectral data it appeared that the substance

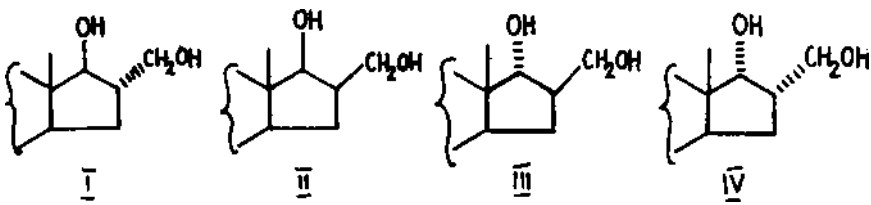
"P" is probably a polyhydroxytriterpene or an ergostane derivative.

Further work on structure determination is in progress.

THE NEIGHBOURING GROUP PARTICIPATION AND ACYL MIGRATION REACTIONS OF 16-HYDROXYMETHYL-17--HYDROXY-STEROID DERIVATIVES

Gy. Schneider, I. Weisz-Vincze, K. Kovács.
Institute of Organic Chemistry, University of Szeged
Hungary

The acetolysis of the 16α-acetoxymethylandrost-5-ene--3β,17β-diol 3-acetate-17-p-toluenesulphonate in the presence of KOAc gave 16α-acetoxymethylandrost-5-ene--3β,17α-diol diacetate with (AcO-6) neighbouring group participation. By this method we succeeded in preparing the fourth isomeric member of the series of 16-hydroxymethyl--17-hydroxy-steroids.



I II III IV

We have examined all four isomers in various ring closure and acyl migration reactions.

The solvolysis studies on the mixed acetic acid and p-toluenesulphonic acid esters of the four isomers gave additional data to the conformational analysis of the substituted D-ring of steroids.

SYNTHESEN 16,17-HETEROSUBSTITUIERTER ÖSTRATRIENE

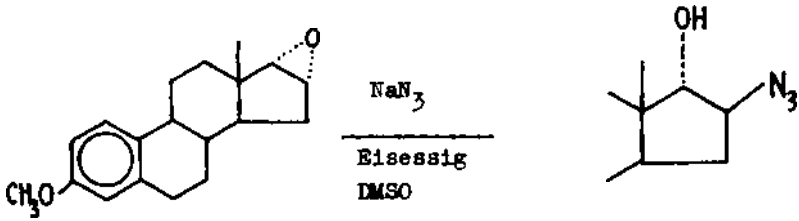
B. Schönecker, K. Ponsold, P. Neuland

Zentralinstitut für Mikrobiologie und experimentelle Therapie der DAW zu Berlin, Jena, DDR

Als Teil eines Programms zur Aufdeckung von Struktur-Wirkungs-Beziehungen wurden Östratriene mit verschiedenen Substituenten und verschiedener Konfiguration in 16- und 17-Stellung synthetisiert.

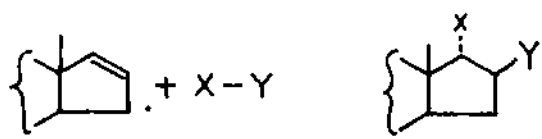
1. Synthese von Verbindungen mit 16β,17α-Konfiguration : Verbindungen dieser Konfiguration sind zugänglich

   a) durch Öffnung des 16α,17α-Epoxids I mit Nucleophilen



oder

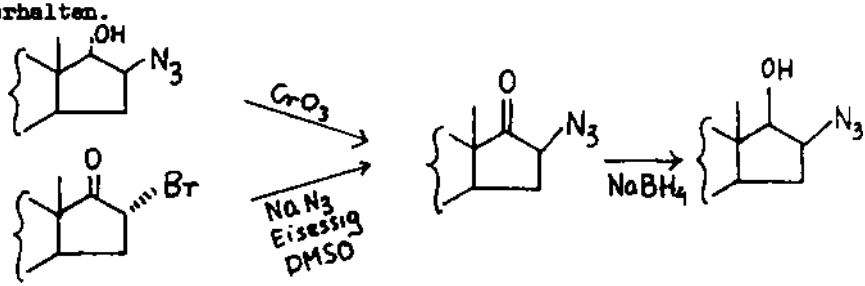
   b) durch elektrophile Addition an die Δ^{16}-Doppelbindung



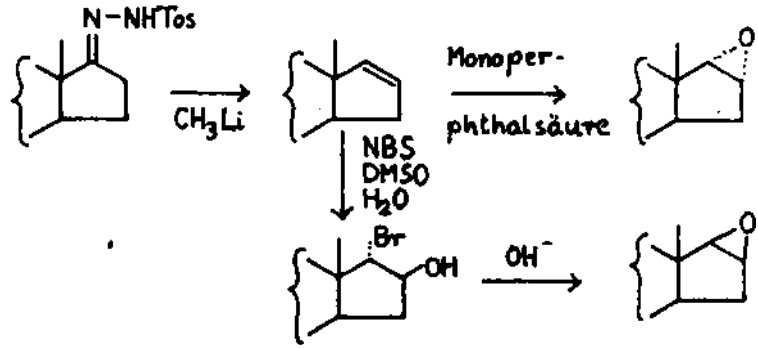
x – y : Br — OH, J — NCO, NCS — Cl

2. Synthese von Verbindungen mit 16β,17β-Konfiguration : Die Reduktion von 16β-substituierten 17-Ketonen mit Natriumborhydrid führt in sterisch einheitlicher Reaktion zu Verbindungen mit obiger Konfiguration. Die entsprechend substituierten Ketone werden entweder durch

Oxidation von 16β-substituierten 17α-Hydroxyverbindungen oder durch nucleophile Substitution aus 16α-Brom-17-Ketonen erhalten.



Für die Δ^{16}-Verbindung, für das 16α,17α-Epoxid und für das als Ausgangsmaterial für 16α,17β-disubstituierte Östratriene in Betracht kommende 16β,17β-Epoxid wurden neue Synthesen entwickelt :



NEW STEROID SULFONATES WITH BIOLOGICAL ACTIVITY

S. Schwarz, G. Weber

Research Laboratories of VEB Jenapharm, Jena, DDR

Derivatives of 17α-ethynyl-estradiol (1) are of interest in view of their possible prolonged activity in the field of fertility control.

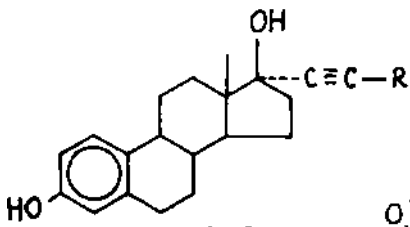
Starting from 1 and 2 sulfonates of the general formulas 3 and 4 have been prepared.

Esterification of the phenolic hydroxyl group in compounds 1 and 2 with alkyl-, cycloalkyl-, or aralkyl-sulfonylchlorides and tertiary amines needs temporary protection of the hydroxyl group at $C_{(17)}$ as well as special conditions of reaction with respect to the nature of the amine and the sequence of addition of the reagents. In this way a uniform course of reaction and a high yield of compounds 3 has been reached.

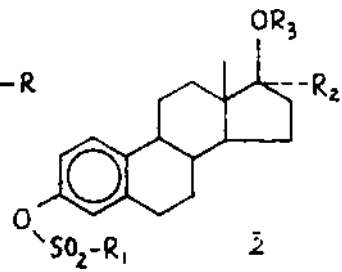
Treatment of 1 with corresponding amidosulfonyl-chlorides in dipolar aprotic solvents and in presence of sodium methylate gave rise to esters of the general formula 4. As byproducts 17-ketones of type 5 and their 16-dichlorinated derivatives 6 could be detected.

The structure of the synthesized compounds has been established by means of UV-, IR-, and ^{1}HNMR-spectroscopy.

Bioassay displayed for some of the sulfonates a long-acting estrogenic and antiovulatory effect, comparable to the activity of the well known QUINESTROL® (17α-ethynyl-estradiol-3-cyclopentylether).



1, 2

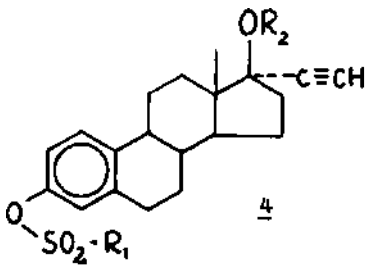


3

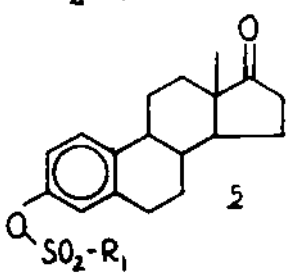
3 : R_1= Alkyl, Cycloalkyl, or Aralkyl ;

R_2= C≡CH, C≡C-Cl, CH=CH_2, or C_2H_5 ;

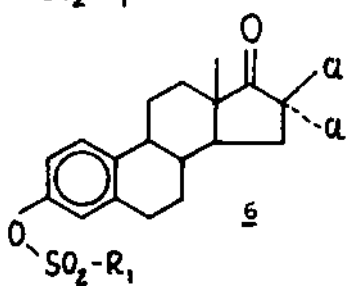
R_3= H, CH_3, $Si(CH_3)_3$, or Acyl.



4



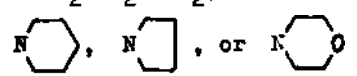
5



6

4, 5, 6 :

R_1= $N(C_2H_5)_2$, $N(i\text{-}C_4H_9)_2$, $N(CH_2\text{-}CH_2\text{-}Cl)_2$,



R_2= H or Acyl.

A STUDY ON OXIDATION OF 16α,17α-EPOXY-STEROIDS

A.M. Smoczkiewiczowa, J.B. Jusiczak

College of Economics

Division of General and Analytical Chemistry,

Poznań

3β-Acetoxy-16α,17-epoxy-5-pregnen-20-one was oxidized with such oxidants as $HClO_4$, HIO_4, DMSO-BF_3, commonly used for epoxides under different conditions.

The oxidation products i.e. a compound with trans-glycol group(when HIO_4 was used) or a substance with 17α-ol-16,20--dione structure (in the case of DMSO-BF_3) were investigated chemically and spectroscopically.

THE SYNTHESIS OF A AND D RING AZA STEROIDS

Z. Tuba, M. Bór

Chemical Works of Gedeon Richter Ltd., Budapest, Hungary

We present a new synthesis of 2-aza- and 17-aza-steroids namely of : 17-aza-5α-androstane-3-one, 17-aza-3-methoxy--1,3,5(10)-oestratriene, 2-aza-5α-cholestane and their derivatives e.g., 21-hydroxy-17-aza-5α-pregnane-3,20-one, 21-amino-17-aza-5α-pregnane-3,20-one.

The structure of these new compounds were confirmed by the common modern methods.

TOTAL SYNTHESIS OF 7-THIASTEROIDAL SYSTEMS

E.R. de Waard, J.W. de Leeuw, H.O. Huisman
Laboratory for Organic Chemistry, University of Amsterdam
Amsterdam, The Netherlands

The interesting physiological activities of 6-thiaestrone derivatives, synthesized following the known scheme by Torgov and collaborators, have stimulated the investigations of the 7-thiasteroidal systems. Difficulties experienced in the application of the Torgov's scheme to 7-thiasteroids necessitated the search for an alternative mode of ring annellation.

A useful reaction scheme has been developed comprising of synthesis of the 9,10-secoderivatives of the 7-thiaestrone skeleton, by addition of benzyl mercaptanes, to a suitable CD ring system. In the final step the 9,10 carbon to carbon bond is constructed.

The presence of the sulfur atom at β-position in regard to carbon atom 9 imposes some special problems in view of possible participation of the sulfur atom with the positive center at C_9 created prior to the ring closure.

The sulfur participation however can be made to facilitate the ring closure, when the proper functional groups are chosen.

In this way several 7-thiasteroidal systems of different oxidation stages have been prepared.

The generality of the approach is demonstrated by the use of other AB syntons which after linkage to the CD moiety can be converted into heterosteroidal systems.

SELECTIVE REACTION OF SOME STEROIDS WITH DIETHYL PYROCARBONATE

I. Weisz
North-Hungarian Chemical Works
P. Agócs, K. Kovács
Institute of Organic Chemistry
University of Szeged, Hungary

The selective reaction of the primary and phenolic hydroxyl groups of some di- and trihydroxy steroids with diethyl pyrocarbonate has been described. A simple method is suggested for the preparation of ethyl carbonates (cathylates) of steroids.

PREPARATION AND SOME REACTIONS OF 5,6-EPOXY-6--ACYLOXY-CHOLESTANES.

J. Wicha
Institute of Organic Chemistry
Polish Academy of Sciences, Warsaw

Methods of preparation and some reactions of epoxides substituted on oxirane ring have been investigated. The stable 5α,6α-epoxy-3β,6β-dibenzoxycholestane I was obtained on oxidation of 3β,6-dibenzoxycholest-5-ene II with m-chloroperbenzoic acid. The thermal rearrangement of I and its reactions with hydrogen chloride, boron trifluoride and magnesium bromide are discussed.

GRIGNARD REACTIONS OF ANDROSTENOLONE ACETATE

R. I. Zalewski

College of Economics

Division of General and Analytical Chemistry, Poznań

To study the yield and purity of 17α-alkyl-5β,17β-dihydroxy-5-androstene the androstenolone acetate was treated with various Grignard reagents in various systems of solvents.

All the 17α-alkyl steroids were studied spectrophotometrically, their IR spectra were taken as well as those in UV and visible region in concentrated sulfuric acid. The absorptivity in time showed the reaction between the steroid and sulfuric acid to be of the first order. The rate constants of the reaction were calculated.

The influence of the alkyl groups on the yield and rate constants is discussed.

AUTHOR INDEX

E. Małunowicz
B. Matkovics
H. Matuszelewska
M. Marián
E. Menzer
P. Neuland
K. Ponsold
Ž. Procházka
J.S. Pyrek
Z. Rakonczay
E. Reca
W.J. Rodewald
K. Schaffner
A. Schmidt-Szałowska
Gy. Schneider
B. Schönecker
K. Schreiber
S. Schwarz
A. Siewiński
A.M. Smoczkiewiczowa
G. Snatzke
W. Sobótka
F. Sorm
G. Teichmüller
Z. Tuba
S. Tyrlik
B. Voigt
E.R. de Waard
R. Weismann
I. Weisz-Vincze
I. Weisz
G. Weber
J. Wicha
R.J. Zalewski
E. Zbiral
I. Życzyńska-Bałoniak