CZECHOSLOVAK ACADEMY OF SCIENCES

5th CONFERENCE ON ISOPRENOIDS

LIBLICE, SEPTEMBER 1973

The Conference is organized by the Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague

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- - -

P L E N A R Y L E C T U R E S

D. Arigoni

Ayecetin, Structure and Biosynthesis.

W.A. Smit, V.F. Kucherov, N.V. Semenovsky

Electrophilic Cyclisation as a Biogenetically like Method for Synthesis of Cyclic Terpenes.

T.W. Goodwin

Phytosterol side chain Biosynthesis.

A.M. Daniewski

New Aspects of Total Syntheses of Steroids.

K.D. Barrow

The Structure and Biosynthesis of the Fusicoccins.

K. Schreiber

Chemical Degradation of Steroidal Solanum Alkaloids to Pregnane Derivatives.

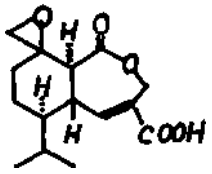
AVOCETIN: STRUCTURE AND BIOSYNTHESIS

D. Arigoni

Eidgenössische Technische Hochschule, Zürich

Avocetin, a new metabolite from the fungus Anthostoma avocetta, has been shown by extensive chemical degradation to possess structure I.

The suspected sesquiterpenoid nature of the compound has been substantiated by subsequent biosynthetic studies. Specifically, the compound is formed from farnesyl-PP via a bicyclic intermediate, formation of which involves an unexpected and stereospecific 1,3-hydride-shift. The stereochemistry of the formation of the isopropyl group will be discussed in detail and extension of these findings to the biosynthesis of longifolene in higher plants will be presented.



I

COMPUTER CONSTRUCTION OF STANDARD STEROID MODELS

P. Sedmera[a], A. Vítek[b] and Z. Samek[b]

[a] Institute of Microbiology of Czechoslovak Academy of Sciences, Prague

[b] Institute of Organic Chemistry and Biochemistry of Czechoslovak Academy of Sciences, Prague

Numerical models of several basic steroid skeletons were constructed by computer on the basis of geometric considerations using only the weighted averaged values of the natural coordinates. The resulting Cartesian coordinates were used to evaluate the geometric factors in the calculation of long-range shielding effects in the PMR spectra. Examples involving the effects of axially symmetric polar groups are given.

STRUCTURAL IMPLICATIONS OF METHYL SIGNALS IN PROTON MAGNETIC RESONANCE SPECTRA OF TRITERPENES

M. Budešínský[a], P. Sedmera[b] and A. Vystrčil[c]

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[b] Institute of Microbiology, Czechoslovak Academy of Sciences, Prague

[c] Department of Organic Chemistry, Charles University, Prague

PMR spectra (100 MHz) of about 250 triterpenoid derivatives with lupane skeleton were measured and the methyl signals in positions 4α, 4β, 10β, 8β, and 14α have been assigned. The shielding increments of 75 different substituents in individual positions were determined by the least-squares method (using an electronic computer). The possibilities of methyl signals assignment and the application of the additivity principle of shielding increment values of substituents to structural analysis of triterpenes are discussed.

STRUCTURAL ASSIGNMENT OF SECONDARY AND TERTIARY METHYL GROUPS OF NATURAL SESQUITERPENES BY PMR SPECTROSCOPY

Z. Samek

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

No abstract.

CHIROPTICAL PROPERTIES OF DITERPENOIDS WITH AROMATIC RING C

G. Snatzke

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No abstract.

Circular Dichroism of Substituted Steroidal Dienes

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University of Poznań Poland
Chemistry Department, Stanford University, USA

The effect of achiral substituents placed in the plane of the σ bonds of the chiral diene system upon the magnitude of the Cotton effect of $\widetilde{\pi} \rightarrow \widetilde{\pi}^*$ transition was investigated.

A number of compounds of different substitution patterns were subjected to C. D. measurements and the results are discussed in connection with the existing C. D. theories.

THE STERIC COURSE OF THE INITIATION STEP OF ELECTROPHILIC ISOPRENOID CYCLISATION

W.A.Smit, M.T.Mustafaeva, A.V.Semenovsky, V.F.Kucherov
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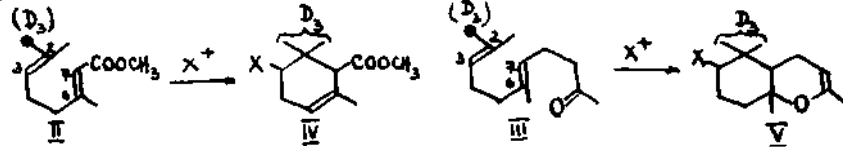
Methods for the synthesis of trans-$CD_3(CH_3)C{=}CHCH_2CH_2COCH_3$(I) were developped and corresponding D_3-analogs of geranic ester(II) and geranylacetone (III) were prepared from I.With the use of these model compounds the steric course of the initial step of electrophilic cyclisation -that of the addition of "external" electrophile X^+ to 2,3-double bond- was studied for the set of the known initiators.The stereospecificity of the reaction was evaluated with the help of P.M.R.-data for gem-substituents in the cyclic products IV and V. It was shown that complete stereospecificity could be achieved only for reagents like CF_3COOHg^+ or RS^+. On the other hand complete nonstereospecificity was observed for the proton-induced cyclisation of II and III. It was also found that in the case of carbocationic initiators (e.g. $X^+ = CH_3OCH_2^+$ or CH_3CO^+) one may observe both stereospecific and non-stereospecific course of the reaction depending on the nucleophilicity of 6,7 -double bond. For example, the addition of these reagents to 2,3-double bond in II proceeds in non-stereospecific manner, whereas the same reactions with III reveal comparatively high-degree of stereospecificity.



II IV III V

A NEW ANIONOTROPIC REARRANGEMENT OF STEROIDS AND ITS MECHANISM

T.V.Ilyukhina and A.V.Kamernitsky

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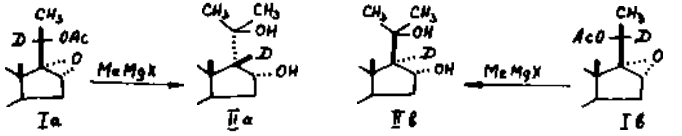
The study of the previously discovered rearrangement [1] of the steroid acetoxy-epoxides under the action of MeMgX was carried out with the use of deuterated analogs-epimeric at C-20 20-deutero--20-acetoxy-16α,17α - epoxy-steroids (I).It was shown that 3,16α, 20-trihydroxy-20-methyl-pregnanes (II),resulting in this case,contain all the deuterium present in I. Thus this rearrangement is proved to include the hydride shift. This fact as well as the known analogies permits to suggest the mechanism of this novel rearrangement as proceeding via the formation of chelate complex with the participation of the carbonyl oxygen atom of the acetoxy-group and oxygen atom of the oxide ring,followed by intramolecular 20→17 hydride shift.In the case of β-configuration of 20-acetoxy-group the rotation around C-17–C-20 bond is necessary for the chelation and thus the reaction proceeds with the retention of configuration at C-17.The name Akhrem's rearrangement is proposed for this reaction.



Ia IIα IIβ Iβ

References

1. A.A.Akhrem, T.V.Ilyukhina, Izv.Akad.Nauk SSSR, Ser.khim.1, 192 (1966); 3,710 (1967).

SYNTHESIS AND REACTIONS OF VICINAL SUBSTITUTED HALOGEN CARBAMOYLOXY STEROIDS

P. Große and K. Ponsold

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Vicinal substituted halogen carbamoyloxy steroids were synthesized from vicinal halogen hydrins of steroids

a) by reaction with isocyanates and

b) by reaction with phosgene to the chloroformic acid esters and following reaction with amines or ammonia.

By heating under solvolytic conditions these compounds react under O-5 ring closure to cyclic carbonates of the corresponding cis-diols. A connection between the configuration of the vicinal substituents and the reactivity to O-5 ring closure is given.

By heating under basic conditions the title compounds react preferably under N-5 ring closure to 2-oxazolidones and if the basic conditions are strong enough by hydrolysis of the oxazolidones to cis-amino alcohols too. Connections between the nature of the substituent at the carbamoyloxy group (e.g. aliphatic, aromatic or sulfonic acid group) and the reactivity of the compounds to N-5 ring closure on one hand and between the steric arrangement of the vicinal groups and the reactivity to N-5 ring closure on the other hand are presented.

DELTA-7-STEROLS IN SOME BULGARIAN PLANTS

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Bulgarian Academy of Sciences, Sofia

No abstract.

A NOVEL REACTION OF 16α,17α - EPOXY - 16β-METHYLSTEROIDS

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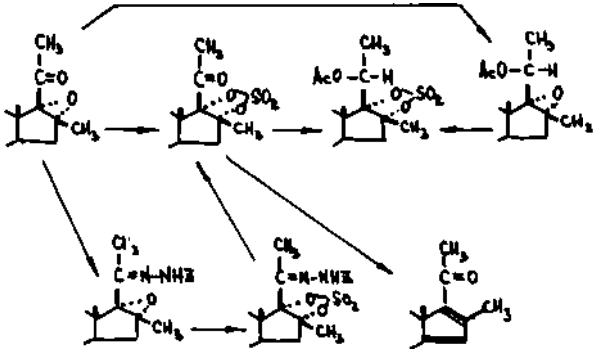
The reaction of 16,17α -epoxy-16β-methylsteroids with sulphuric acid and acetic anhydride results in 16,17-cyclosulphates of 16,17α - dihydroxy-16β-methylsteroids. The direction of the reaction does not depend on the presence of carbonyl- or hydrazone - or acetoxy groups at C-20.The structure of these cyclic sulphates is proved both by physico-chemical and chemical methods. The new reaction is common at least for ditertiary oxides and includes the opening of the epoxide ring by action of acetylsulphuric acid to give monoacetylsulphate and then intermolecular acylation by mixed anhydride. The 16,17α -cyclosulphates of Δ^4 -3-keto-, $\Delta^{1,4}$ - 3-keto-, $\Delta^{4,6}$ - 3-keto -, Δ^4 -3-keto-6α -methyl-, Δ^4 -3-keto -6α -chlor-and Δ^4 -3-keto-21-acetoxysteroids were obtained in this way.



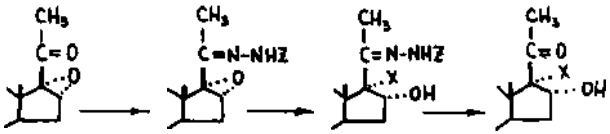
A NOVEL REACTION FOR SYNTHESIS OF 17α-SUBSTITUTED 16α-HYDROXY-20-KETOSTEROIDS

A.V.Skorova, A.A.Akhrem, A.V.Kamernitzky and A.M.Turuta

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

Under acidic conditions the hydrazones of 16α,17α-epoxy--20-ketosteroids undergo a selective cleavage of the C_{17}-O -bond accompanied by introduction of a hydroxy or acetoxy group at 17-position. This observation allows to develop a general method for the synthesis of 17α-substituted 16α-hydroxy-20-ketosteroids. The method consists in the reaction of hydrazone of ketooxides with the suitable nucleophilic reagents. Thus the reaction of 20-hydrazone of 16,17α--epoxy-20-ketosteroid with methanol, thiolacetic acid or hydrazoic acid followed by removal of hydrazone protection results in 17α-methoxy-, 17α-thiol- or 17α-azido-16α-hydroxy--20-ketosteroids respectively in high yields.

The method may be also used in monocyclic series.



X = OMe, SH, N_3

AN UNUSUAL REACTION OF 3β-ACETOXY-16α,17-EPOXY-5-PREGNEN-20-ONE WITH DIMETHYL SULFOXIDE

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b) Institute of Chemistry of the University of M. Kopernik, Toruń

In continuation of our investigations on dimethyl sulfoxide oxidation of steroid epoxides we attempted to oxidize 3β-acetoxy-16α,17-epoxy-5-pregnen-20-one with DMSO.

The oxidation was carried out at 98 - 100°C for 30 hours under introduction of air through a capillary. After normal working up two crystalline products have been isolated. The structure of these products will be discussed.

The results of this reaction differed from similar reactions carried out with other steroidal epoxides. In the reaction of 4β,5-epoxy-17α-methyl-17β-hydroxyandrostan-3-one, 3β-acetoxy-5β,6-epoxyandrostan-17-one and 6α,7-epoxyandrost-4-en-3,17-dione with DMSO we obtained α-hydroxyketones in every case.

SYNTHESIS OF THE NOVEL TYPE OF 16,17-SUBSTITUTED STEROIDS--16,17-EPIMERIC THIOCARBONATES

A.M. Turuta, A.A. Akhrem, Z.I. Istomina and A.V. Kamernitzky

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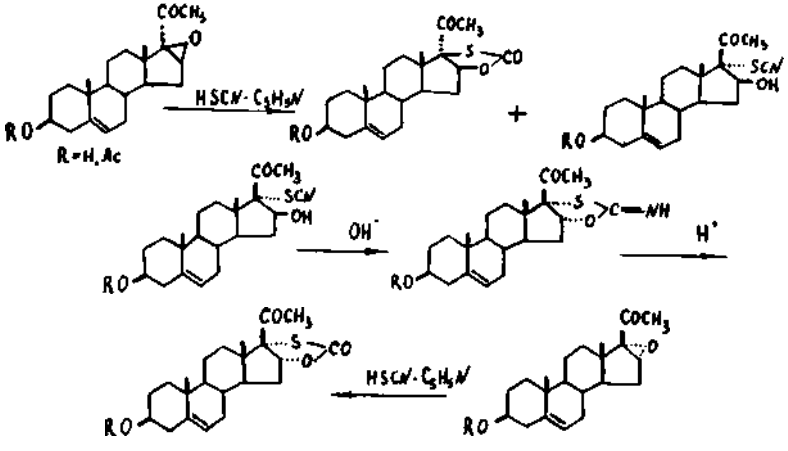
The method of directed synthesis for the new class of steroid compounds-16(O),17(S)-thiocarbonates have been developed. Epimeric 16,17-epoxypregnenolones were used as starting material. The interaction of the 16,17-epoxypregnenolones with thiocyanic acid proceeds with cleavage of a carbon to oxygen bond at C-17 with the introduction of SCN-ion in α-position to carbonyl group. The following intramolecular cyclization of the vicinal thiocyanohydrins and hydrolysis of the cyclic imines gives the title compounds. The cyclization of the trans-16β, 17α-thiocyanohydrin is accompanied by epimerization at C-16. The structure and the configuration of obtained products was proved by CD and NMR spectra.



16-SUBSTITUTED STEROIDS CONTAINING NITROGEN

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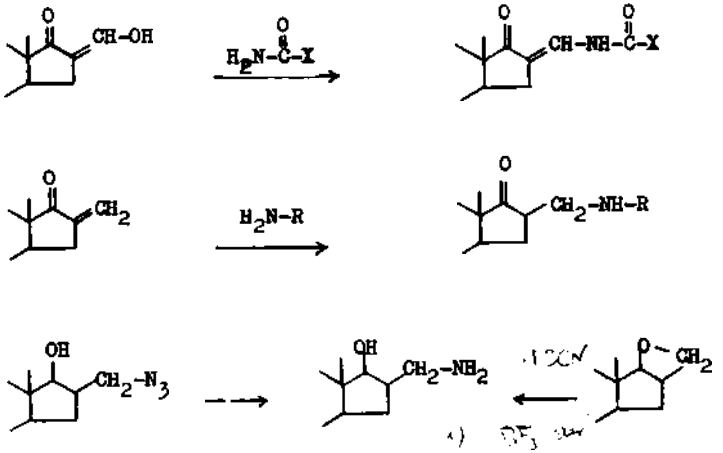
Institute of Organic Chemistry of
the József Attila University, Szeged, Hungary

Condensation reactions of 16-formyl-17-keto-steroids were carried out with acid amides, urethanes, amino acids and formamide. - The addition of primary amines to 16-methylene--17-keto-steroids gave 16-alkyl-aminomethyl derivatives. - 16-Aminomethyl-17-hydroxy-steroids were prepared by the reduction of 16-azidomethyl-17-hydroxy compounds and by the Ritter reaction of the four-membered ring ether.



REACTION OF SOME VICINAL DIBROMIDES WITH SILVER FLUORIDE IN WATER

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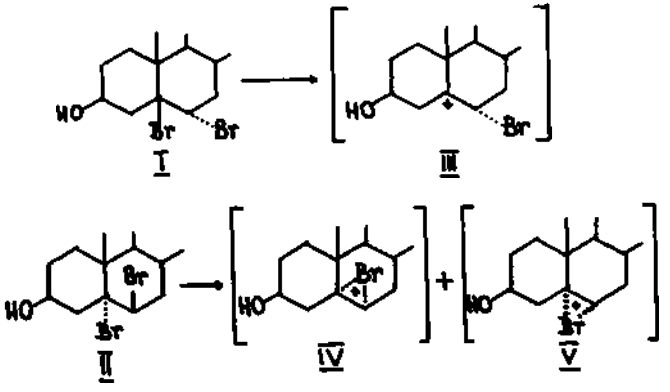
Czechoslovak Academy of Sciences, Prague

Earlier[1] we have reported reaction of 3β-acetoxy-5,6α-dibromo-B-nor-5β-cholestane with silver fluoride in water leading to 3β-acetoxy-5,6β-epoxy-B-nor-5β-cholestane and B-nor-5--cholestene-3β,4β-diol monoacetates. In this paper we discuss the behaviour of homologous dibromides I and II respectively under identical conditions. Product distribution in the former case is interpreted in terms of C_5-Br ionisation and subsequent reactions of the carbonium ion III. In the latter case we bring evidence for the formation of both epibromonium ions IV and V.



1. A. Kasal, Coll.Czech.Chem.Commun. 37, 3095 (1972)

B-NORANALOGUE OF CORTISOL

V. Šanda, J. Fajkoš and F. Šorm

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Czechoslovak Academy of Sciences, Prague 6

B-Noranalogue of cortisol was synthesized by two unambiguous routes. Starting from cortisol the 15-step reaction sequence was accomplished by using selective protective reactions followed by the ring contraction method developed by Šorm and Dyková[1]. By an alternative route, involving biological hydroxylation, identical compound was prepared from B-noranalogue of Reichstein's substance S, the synthesis of which has been described previously[2].

1. Šorm F. and Dyková H.: Coll.Czech.Chem.Commun. 13, 407 (1948)
2. Šanda V., Fajkoš J., Šorm F. and Protiva J.: Coll.Czech. Chem.Commun. 37, 2807 (1972)

FURTHER MICHAEL ADDITIONS TO STEROIDAL 3-KETOTRIENES

T. Cynkowski and M. Kocór

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Polish Academy of Sciences, Warsaw

No abstract.

SOME STEROIDAL AZIDES AND THEIR REACTIONS

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No abstract.

FURTHER ADDITION REACTIONS TO STEROIDAL 3-KETO-1,4,6-TRIENES

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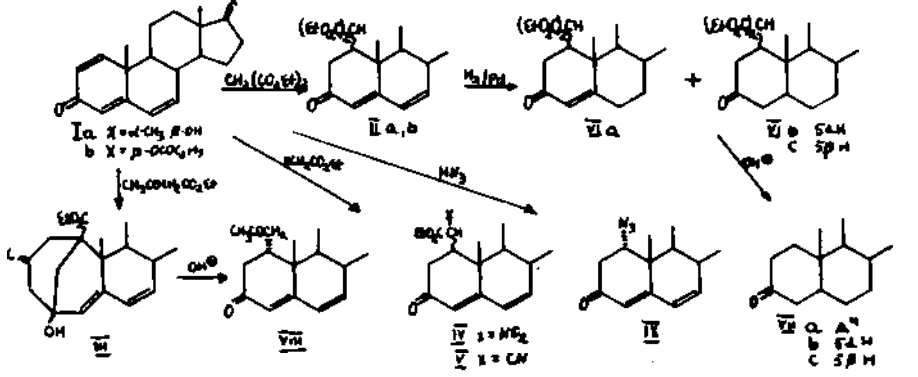
3-keto-1,4,6-trienes I react with activated methylene groups /Michael reaction/ yielding the adducts IIa, IIb, III, IV and V. The malonate adducts IIa and IIb resp. were catalytically hydrogenated affording partially and fully saturated ketones VIa, VIb and VIc resp. The latter compounds have been used as hapten formation promotors in the investigation of steroidal metabolism in animals. The adduct III is formed as the result of two subsequent reactions i.e. the normal Michael addition and the aldol reaction of 3-keto group with methyl from acetoacetate moiety. The action of alkali on III affords the 1-acetonyl derivative VIII formed via hydrolysis, retroaldol reaction and decarboxylation.

The trienes Ia or Ib resp. react also very easily with hydrazoic acid to give 1-azido-3-keto-4,6-dienes IX, very susceptive to alkali and acids.



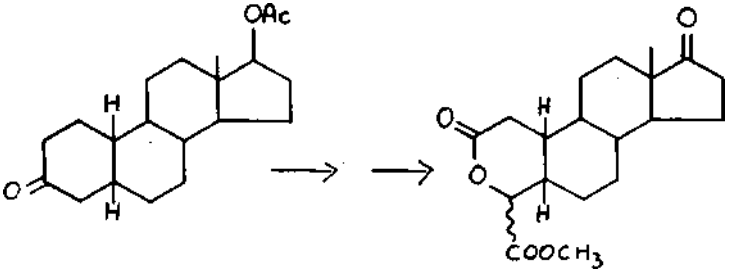
SYNTHESIS OF SOME OXADERIVATIVES OF 19-NORSTEROIDS

M.Kocór and A.Kurek
Institute of Organic Chemistry
of the Polish Academy of Sciences
Warsaw, Poland

19-Nor-5β-androstan-17β-ol-3-one acetate /I/ has been converted into the 3-oxasteroids II and III by a series of reactions, proceeding via 2,3-secoderivatives..

The structures of the new compounds II and III were confirmed by spectral and analytical data.

The possibility of dehydrogenation of II and III to steroidal α-pyrone derivatives will be discussed.



I

II 4α $COOCH_3$

III 4β $COOCH_3$

THERMOLYSIS OF STEROIDAL NITRATE ESTERS

F. Hodoşan and Mirela Niculescu

Institute of Chemistry, Cluj, Romania

Following spectrometrically the thermal cleavage of the ONO_2 group in a series of relatively simple sterol mononitrates, correlations could be established between the measured half times and steric (structural) factors. Thus in a conformer pair the thermal decomposition of the axial nitrate group proceeds faster than that of the equatorial one. The steric hindrance, as well as a homoallylic double bond, increases the decomposition rate considerably. A marked influence of the configuration at C-5 was observed in the 6β-nitrato steroids.
The reaction products were: unsaturated compounds, ketones, alcohols, and in certain cases nitriles or nitro derivatives.

TOTAL SYNTHESIS OF B-SUBSTITUTED STEROIDS

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Academy of Sciences of USSR, Moscow

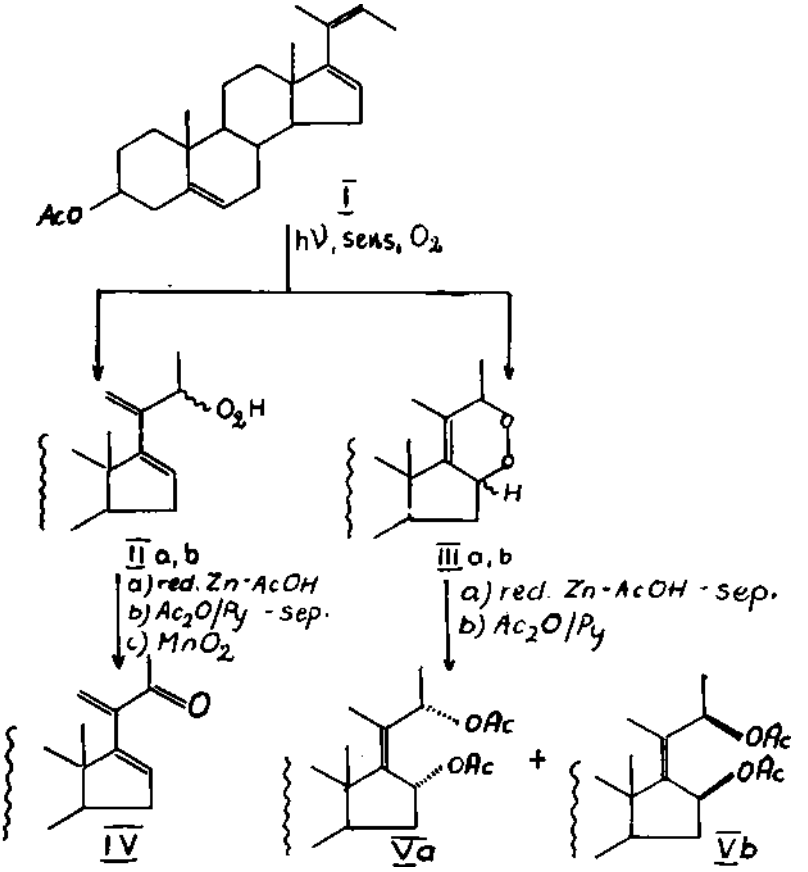
No abstract.

Photooxidation of 3β-acetoxy-24-norchola-5,16,20/22/-triene

by M. Kocór and W.M. Wojciechowska
Institute of Organic Chemistry of Polish Academy of Sciences, Warsaw.

The title compound, obtained by standard method from 16-dehydropregnenolone acetate was irradiated with visible light in the presence of methylene blue. Two pairs of compounds were obtained, to which we assigned on the basis of spectral data the structures IIa,b or IIIa,b, resp. In a series of reactions presented below the hydroperoxides IIa,b were converted into compound IV. The separation of both isomers was achieved at the stage of acetates/ reaction b /.

The epidioxides IIIa,b were reduced by Zn-acetic acid, and at this stage separated into both diastereoizomers, and subsequently acetylated to Va or Vb resp.



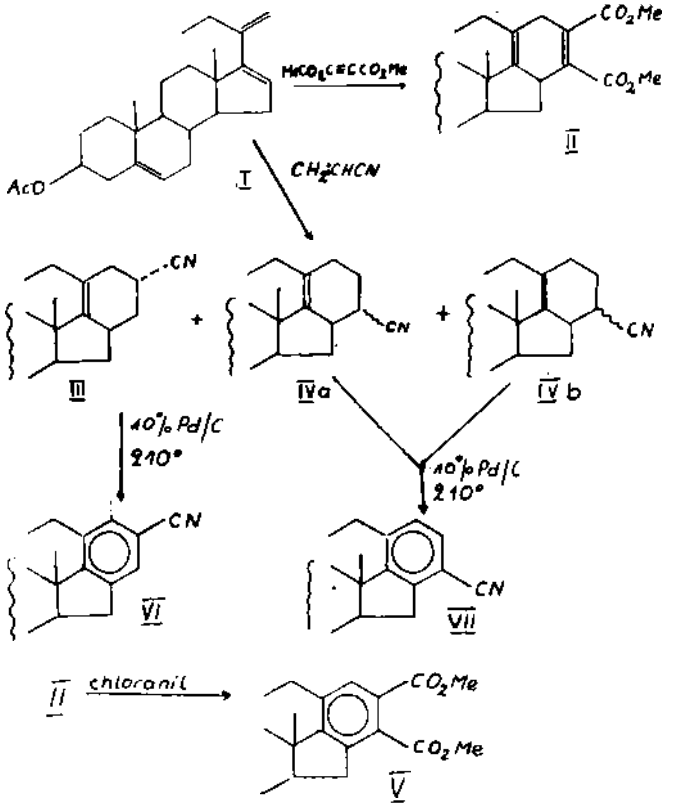
DIELS-ALDER ADDITION TO 3β-ACETOXY-24-NORCHOLA-5,16,20/22/-TRIENE

M. Kocór and W.M. Wojciechowska

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw

The title compound was submitted to Diels-Alder reaction with methyl acetylenedicarboxylate and acrylonitrile.

The structure of the adducts II, III and IVa,b has been elucidated on the basis of spectral data and their aromatization to benzene derivatives V, VI, and VII.



STEREOSPECIFIC REDUCTION OF DOUBLE BONDS IN STEROID SERIES

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No abstract.

STEREOCHEMISTRY OF DEHYDRATION OF ISOMERIC 20-HYDROXY-30--NORDERIVATIVES OF LUPANE

J. Klinot, E. Klinotová, N. Hovorková and A. Vystrčil

Department of Organic Chemistry,

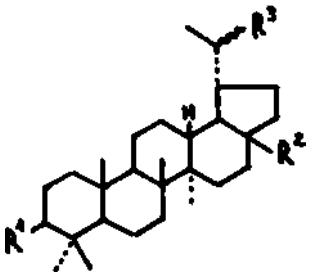
Charles University, Prague

On reaction of (20R)-3β,28-diacetoxy-30-norlupan-20-ol with phosphorus oxychloride or tosyl chloride in pyridine $\Delta^{19(20)}$-olefin with exocyclic double bond is formed predominantly in addition to a small amount of (20S)-chloro derivative. On reaction of (20S)-isomer under the same conditions substitution is preferred and (20R)-chloro derivative is formed as the main product; in olefinic fraction $\Delta^{20(29)}$-olefin and rearranged product were identified. The structures of the products have been elucidated by chemical transformations and infrared, ultraviolet and NMR spectra. The steric course of dehydration is discussed with respect to the interactions of the side chain with 12-methylene group in transition state and on its basis the assignment of configuration to isomeric 20-hydroxy-30-norderivatives is confirmed.

ABSOLUTE CONFIGURATION AND CONFORMATION OF LUPANE SIDE CHAIN DERIVATIVES

A. Vystrčil, Z. Blecha, V. Křeček, V. Pouzar
Department of Organic Chemistry, Charles University, Prague 2

Reduction of several 30-nor-20-lupenone derivatives yielded $C_{(20)}$-epimeric hydroxy derivatives (I, II, R^3 = OH), which, according to their adsorptivity, $\nu_{(OH)}$ and chemical shifts of $C_{(20)}H$ and $C_{(30)}H_3$, form two configurationally homogeneous wholes. Using the benzoate rule configuration 20R and 20S was assigned. Coupling constants $J_{(19H-20H)}$ and C.D. of acetates I,II,R^3 = OAc indicate the dominant conformation at a given configuration on $C_{(20)}$. For the determination of absolute configuration on $C_{(20)}$ in 29-substituted lupane derivatives, the Baeyer-Villiger oxidation of epimeric 29-lupanal derivatives (I,R^3 = CHO) was used; simple conversions of (20R)- and (20S)--lupan-29-al derivatives enabled the assignment of absolute configuration to epimers I, R^3 = COOH, $COOCH_3$, COCl, $CONHC(CH_3)_3$, $COCH_3$, CH_2OH.



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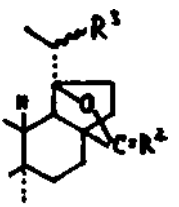


II

NEW TRANSFORMATIONS OF DIHYDROLANOSTEROL

O.E. Edwards and Z. Paryzek*

National Research Council of Canada, Ottawa, Canada

The deamination of a 9α-aminopregnan-11-one derivative resulted in migration of the methyl group on C-10 to C-9. Attempts have been made to extend this reaction to the lanostane series, to provide a method for synthesis of the cucurbitane skeleton.

Functionalization of carbons 5, 6, 8 and 9 in the lanostane molecule has been achieved by thermolysis of the epimeric 3β-acetoxy-11-oxolanostan-7-yl azidoformates. The structures of the products were deduced using ^{13}C mr and ORD-CD spectra.

A second approach to the cucurbitane skeleton using 9α-oxygenated lanostane derivatives will be described.

*On leave from the Institute of Chemistry,
A. Mickiewicz University, Poznan, Poland.

REDUCTION OF ESTRADIOL 3-METHYL ETHER WITH LITHIUM IN HMPA

M. Kotlarek, L. Jabłoński and S. Mejer

Institute of General Chemistry
Academy of Agriculture, Wrocław, Poland

6-Methoxytetralin as a model for A-aromatic steroids was reduced under different conditions using lithium and alcohol in HMPA /hexamethyl phosphoric triamide/. In most cases the formation of complex mixtures was observed after working up with hydrochloric acid. The product composition was found to be dependent to a high degree on the reaction conditions. The results analogical to those obtained by the Birch reduction were gained only at low temperature /-40°C/, and on gradual addition of a lithium solution in HMPA-THF to a solution of 6-methoxytetralin. Application of this procedure to estradiol 3-methyl ether resulted in a high yield of 19-nortestosterone.

THIO-STEROIDS

S. Schwarz and (Mrs.) G. Weber

VEB Jenapharm, Bereich Forschung und Entwicklung,
DDR-69 Jena, Otto-Schott-Str. 13

In the course of studying the synthesis of antifertile acting steroids, compounds containing sulphuric groups, attached to an aromatic A-ring became of interest. Accordingly, as examples in this field, compounds 1-4 have been prepared from estrone.

Structure elucidation of the synthesized compounds was performed by means of physical methods, e.g. CD-measurement in order to determine the chirality of sulphur in 2a and 2b. Compounds 1-4 have been investigated in bio-assay.

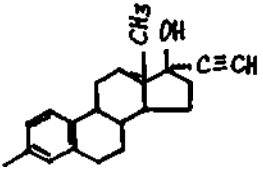
1 : $(CH_3)_2CH\text{-}S\text{-}R$

2a: (R)-$(CH_3)_2CH\text{-}SO\text{-}R$

2b: (S)-$(CH_3)_2CH\text{-}SO\text{-}R$

3 : $(CH_3)_2CH\text{-}SO_2\text{-}R$

4 : R-S-S-R



HYPOBROMITE OXIDATION OF CHOLESTEROL. A REINVESTIGATION

J. Gawroński, A. Gałat

Institute of Chemistry, A. Mickiewicz University,
Poznań, Poland

The two-phase cholesterol oxidation reaction by the alkaline hypobromite solution was studied. Under these conditions the Diels' acid was obtained with the yields approx. 50%, making this reaction convenient for preparation of the ring A-nor derivatives.

A number of other by-products of this reaction were separated and characterized. These products, along with the additional experiments carried out, provide an evidence that in the course of the reaction unique allylic oxidation occurs prior to the conversion of the 3β-hydroxy group into the carbonyl group.

STEREOCHEMICAL STUDIES OF SOME A-HOMOCHOLESTANE DERIVATIVES

H. Velgová, V. Černý and F. Šorm

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

In extention of our previous work[1-3] on 6β-acetoxy-A-homo-5α--cholestanes we prepared a series of 6β-acetoxy-A-homo-5α-cholestane derivatives bearing oxygen substituents at the 4a-position. Conformation of the A-ring in 4aα-hydroxy-, 4β-bromo--4aα-hydroxy- and 4β-bromo-4aβ-hydroxy derivatives and 4α-bromo- and 4β-bromo-4a-keto derivatives wee studied on the basis of IR, ORD and NMR measurements.

1. Velgová H., Černý V.: Coll.Czech.Chem.Commun. 35, 2408 (1970)
2. Velgová H., Černý V., Šorm F.: Coll.Czech.Chem.Commun. 36, 3165 (1971)
3. Velgová H., Černý V.: Coll.Czech.Chem.Commun. 38, 575 (1973)

THE SYNTHESIS OF SOME NEW STEROID GLUCOSIDES

P. Kočovský, K.K. Koshoev* and Ž. Procházka

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

On reaction of hydroxy steroids with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide mixtures of anomeric steroid glucosides have been prepared. These mixtures could not be separated directly either by crystallization or chromatography. Therefore, a combination of chemical and chromatographic steps had to be used in order to obtain pure anomers. Configuration of the glucosidic bond has been determined by PMR.

* On leave from the Institute of Organic Chemistry, Academy of Sciences of Kirghiz SSR, Frunze.

2,3,5-TRIPHENYLTETRAZOLIUM CHLORIDE AS OXIDATIVE REAGENT FOR 11β,17α,21-TRIHYDROXY-1,4-PREGNADIEN-3,20-DIONE (Prednisolone)

M.A. Smoczkiewicz and J. Jasiczak

Department of General and Analytical Chemistry,
Institute for Good Sciences,
School of Economics, Poznań, Poland, Marchlewskiego 146/150

Oxidation products of 11β,17α,21,trihydroxy-1,4-pregnadien-3,20--dione (mainly steroid-21-glyoxalic acid and 17-ketosteroid) were characterized by UV, IR and NMR spectra, also by chemical and elementary analysis after column and thin layer chromatography.

The authors propose two different mechanisms of the oxidation reactions depending on the presence or absence of water in the medium.

THE EFFECT OF THE NITROGEN ATOM IN THE SIDE CHAIN ON THE MICROBIAL DEGRADATION OF STEROID ALKALOIDS

I. Belič and H. Sočič

Biochemical Institute of the Medical Faculty, University of Ljubljana;
Chemical Institute " Boris Kidrič ", Ljubljana, Yugoslavia

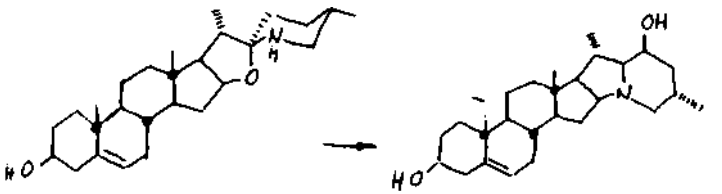
In contradistinction to the known microbial degradation of steroids, leading via 1,4-diene-3-keto intermediates to low molecular weight compounds, tomatidine is dehydrogenated by Nocardia restrictus to 1,4-tomatadiene-3-one, but no further degradation can be observed. The same results are obtained with dihydrotomatidines which have the ring F intact. When the ring F is opened, the amino group is acetylated and the resulting acetylated compound seems to be no good substrate for dehydrogenation by Nocardia restrictus.

SYNTHESIS OF THE STEROIDAL ALKALOID LEPTINIDINE

H. Ripperger, E. Höhne und K. Schreiber

Institute of Plant Biochemistry, Research Centre of Molecular Biology and Medicine of the Academy of Sciences of the GDR
Halle (Saale), German Democratic Republic

Leptinidine (II), the aglycone of glycosides occurring in the South American wild potato Solanum chacoense Bitt., was synthesized starting from tomatidenol (I). The stereochemistry of an intermediate and some stereoisomeric by-products has been investigated by means of IR-, NMR-, and ORD-spectroscopy as well as by X-ray analysis.



I II

A CONTRIBUTION TO THE CHEMISTRY OF BUXUS ALKALOIDS

Z. Votický and V. Paulík

Institute of Chemistry, Slovak Academy of Sciences
809 33 Bratislava

It has been found that the carbonyl group at C-3 of the steroid skeleton need not be a reliable chromophore, when determining the configuration of the neighbouring methyl group.

It has further been shown that artifacts of Buxus alkaloids are formed during the separation process due to the enhanced acidity of the hydrogen in α-position to the C-16 carbonyl group.

Synthesis of Some Mono- and Bis-Amino Pregnanes

Z. Tuba, J. Tóth and O. Szepesi
/Chemical Works of Gedeon Richter Ltd., Budapest X, Hungary/

In connection with our synthesis of mono- and bis-amino steroids, we have paid a little attention to the ring opening reaction of the 16,17-epoxy-20-keto systems, with different amines. The direct addition of amines to 16α,17α-epoxy-20-keto steroids, gives rise not to 16β-amino-17α-hydroxy-20-keto steroids as claimed in a series of patents, but rather to rearranged compounds which have a D-homo-steroid structure.

The piperidine adduct prepared by indirect route through the 20-ketal has a methyl peak at 134 cps in the n.m.r. spectrum, while the piperidine adduct prepared by direct route has a methyl peak at 84 cps and none further downfield. The well known tendency of 17-hydroxy-20-keto steroids to undergo D-homoannulations under basic conditions would produce such a methyl group.

We have separated the products and confirmed their structures by synthetic and spectroscopic methods.
The possible mechanism of the rearrangement will be given, too.

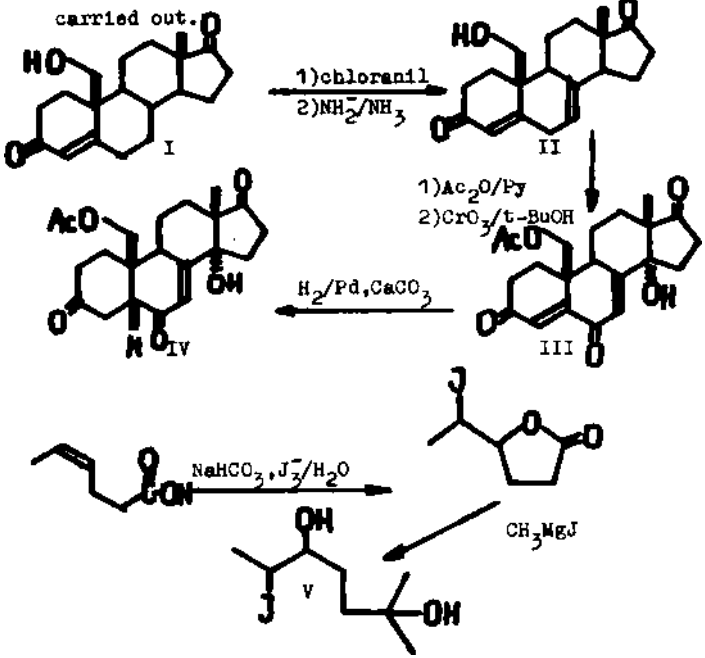
SYNTHESIS OF 19-HYDROXYANALOGUES OF STEROIDAL INSECT HORMONES

by M.Kocór and A.Cieplak

Institute of Organic Chemistry
Polish Academy of Sciences
Warsaw, Poland

Using 19-hydroxy-androst-4-ene-3,17-dione (I) as starting material in a series of reactions described below 19-acetoxy-5β-androst-7-ene-14α-ol-3,6,17-trione (IV) has been obtained.

The iodide (V) was prepared and some attempts of its attachment to IV in position 17 have been carried out.



PHYTOECDYSONES OF AJUGA TURKESTANICA AND SERRATULA SOGDIANA

I.L. Zatsny, B.Z. Usmanov, M.B. Gorovits, N.K. Abubakirov

Institute for Chemistry of Plant Products
Uzbek SSR Academy of Sciences, Tashkent, USSR

From the roots of A. turkestanica Bge. ecdysterone (I) (0,031%), cyasterone (II) (0,009%) and a new phytoecdysone - turkesterone (III) (0,043%), $C_{27}H_{44}O_8$, amorphous, $[\alpha]_D^{22}$ +52,0° (CH_3OH), $\lambda_{max}^{C_2H_5OH}$ 244 nm (lg ε 3,95); ν_{max}^{KBr} 3300-3500, 1660 cm^{-1}, have been isolated. The mass-spectrum of III displays base peaks at m/e 460, 442, 424, 379, 361, 343, 325, 99 and 81. The NMR-spectrum of III (C_5H_5N, HMDS): 1,12--C_{18}; 1,18-C_{19}; 1,24-C_{26} and C_{27}; 1,45-C_{21}. Acetylation of product III led to a mixture of amorphous 2,3,11,22-tetraacetate (IV), $C_{35}H_{52}O_{12}$ and 2,3,11,22,25-pentaacetate (V), $C_{37}H_{54}O_{13}$. NMR - spectrum of IV ($CDCl_3$): 0,85-C_{18}; 1,05--C_{19}; 1,13 and 1,18-C_{26} and C_{27}; 1,21-C_{21}. All the above data permit to identify III as 11α,20R - dihydroxyecdysone.

From methanolic extract of S. sogdiana Bge. leaves 0,17% of ecdysterone (I) and 0,027% of viticosterone E (VI) have been isolated and the latter partially being synthetised from I. Acetylation of I gave a mixture of 2,3,22-triacetate (VII) and 2,3,22,25-tetraacetate (VIII). By methanolic $KHCO_3$ hydrolysis of product VIII viticosterone E has been obtained.

MICROBIOL. HYDROGENATION OF 17α-ETHINYLESTRADIOL

K. Schubert, G. Rese and C. Hörhold

Central Institute of Microbiology and Experimental Therapy of the Academy of Sciences of German Democratic Republic, Jena

The first enzymatic hydrogenation of an aromatic system of steroids is described. 17α-Ethinylestradiol (17α-Ethinyl--1,3,5(10)-estratriene-3,17β-diol) has been transformed by Aspergillus flavus to 10β-Hydroxy-19-nor-ethisterone (17α--Ethinyl-10β,17β-dihydroxy-4-estrene-3-one).

HYDROXYLATION OF 16-METHYLENE DERIVATIVES OF PREGNANE SERIES WITH CUNNINGHAMELLA BLAKESLEANA

R. Míčková, J. Protiva and V. Schwarz

Research Institute for Pharmacy and Biochemistry, Prague

Microbial hydroxylation of 17α-acetoxy-16-methylene-4,6-pregnadiene-3,20-dione and its 6-chloro derivative with Cunninghamella blakesleana was studied. Formation of 15-hydroxy compounds was observed, in the former case accompanied by reduction of the 6,7-double bond. Dependence of the course of biotransformation on the structure of compounds substituted differently is discussed.

HYDROXYLATION OF PHENOL-STEROIDS IN C-2, C-4 AND BOTH POSITIONS

B. Matkovics

Biochemical, Genetical Groups of "A.J." University,

Szeged, Hungary

The C-2 and C-4 monosubstituted and the C-2,4 disubstituted phenolic steroids were synthesized by a combination or a direct application of the methods of Werbin and Heleway, Nieder and Vogel, and Patten.

The first prepared mono- and dinitro phenolic steroids were purified by column chromatography, and then reduced to the corresponding amines with Zn powder in acetic acid/HCl. The amines were converted to the diazonium chlorides, and finally by means of acetic acid/HCl and Zn dust in the presence of copper (II) sulphate to the corresponding mono- or dihydroxy phenolic steroids.

In all cases the two types of mono- and disubstituted estrone derivatives were reduced with sodium borohydride in methanol to the corresponding estradiol (17-β) derivatives.

The lecture gives an account of the experimental difficulties of the outlined method.

SOLID STATE PHOTOCHEMISTRY OF GIBBERELLIN A_3 DERIVATIVES

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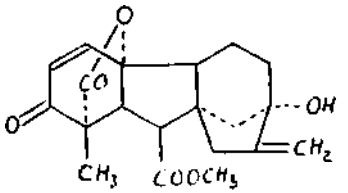
Institute for Plant Biochemistry
of the Academy of Sciences of German Democratic Republic
402 Halle / Saale, GDR

Photolysis ($\lambda_{max} > 300$ nm) of 3-dehydro gibberellin A_3 methylester (I) in the crystalline state leads under [2 + 2] cycloaddition to two stereoisomeric cyclobutane-type photodimers for which structures are proposed on the basis of physical data. Further irradiation of both compounds gives under loss of carbon dioxide the corresponding ring A aromatic dimers. The same photodecarboxylation process takes place upon photolysis of I as a thin film or of the crystalline free enone acid leading to the corresponding monomeric phenolic compounds.

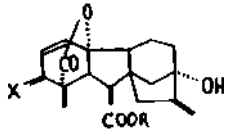


I

SOME NEW TRANSFORMATIONS IN THE SERIES OF GIBBERELLIC ACID AND RELATED DITERPENOIDS

E.P.Serebryakov, N.S.Kobrina, V.F.Kucherov
(Zelinsky Institute for Organic Chemistry, the USSR Academy of Sciences, Moscow)

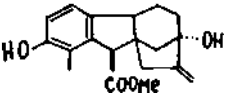
Attempts to transform gibberellin A_3(I) into the corresponding 3-keto-acid (II) on treatment with neutral MnO_2 lead to the dilactone (III). The photolysis of the 3-keto-gibberellin A_3 methyl ester (IIa) gives rise to the tetracyclic phenol (IV). The geometry of IIa implies that the reason for the easy photo-elimination of the lactone bridge may be due to the overlap between π -orbitals of the system c=c-c=o with the lactonic c-o σ -orbital. In the saturated keto-lactones (V-VII) an analogous overlap between π -orbitals of the keto-group and lactonic c-o bond also facilitates the photo-elimination of the lactonic bridge which in this case leads to cyclopropane-containing products.



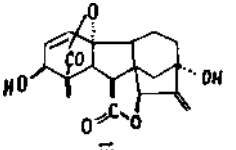
I X = $\langle^{OH}_{H}$, R=H

II X=O, R=H

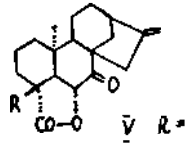
IIa X=O, R=Me



IV



III



V R=Me

VI R=H

VII R=CH_2OH

THE STRUCTURE OF 3-CARENE NITROSATE

J. Harmatha[a,b], T. Norin[b], Z. Samek[a]

[a] Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague
[b] Swedish Forest Products Research Laboratory, Stockholm

In order to study the possible structural changes of 3-carene in the process of nitrosation, the structure of 3-carene nitrosate and its degradation products was elucidated by means of PMR, IR and mass spectrometry. The 3-carene nitrosate, obtained under the conditions used (nitrosation by amyl nitrite + nitric acid + acetic acid at -20°C), is a dimer of two menthane units substituted in the positions 3 (-NO group) and 8 ($-ONO_2$ group) with the unchanged position of the 3-carene double bond. The paper gives details on structural analysis.

STEREOCHEMISTRY OF THE SESQUITERPENIC LACTONE MONTANOLIDE AND RELATED SUBSTANCES

M. Holub, Z. Samek and S. Vašíčková

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

Native sesquiterpenic lactones montanolide, isomontanolide, acetylisomontanolide and archangelolide have been correlated chemically. On application of PMR spectroscopy, CD and ORD measurements, and benzoate rule formulae with relative and absolute configuration were deduced for the mentioned native substances.

SYNTHESIS OF RING A-FUSED HETEROCYCLIC TARAXASTANE DERIVATIVES

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

Department of Organic Chemistry, Institute of Chemistry and Analysis, School of Medicine, Poznań, Poland

Taraxastan-3-one when treated with ethyl formate and Na-ethoxide gave 2-hydroxymethylenetaraxastan-3-one. Condensing the latter with hydrazine hydrate /80%/ taraxastan-[3,2-c]-pyrazole was obtained. Condensation with phenylhydrazine did not occur with cyclization to the pyrazole derivative /by IR and Mass spectr./ Addition of conc. HCl to the reaction mixture is necessary to produce taraxastan-[3,2-c]-N-phenylpyrazole. In an analogous way taraxastan-[3,2-c]N-/4" -nitrophenyl/-pyrazole, was prepared. However, the condensation of 2-hydroxymethylenetaraxastan-3-one with 2,4-dinitrophenylhydrazine yielded an uncyclized nitrogen derivative only /by IR/.

Condensing 2-hydroxymethylene-ψ-taraxasten-3-one with $H_2NOH \cdot HCl$ ψ-taraxasten-[3,2-c] -izoxazole was obtained. Fischer reaction of ψ-taraxasten- 3-one gave ψ-taraxasten- [3,2-b] -indole

THREE BISABOLOLOXIDES FROM Matricaria chamomilla L.

L. Novotný[a], K. Ubík[a], O. Motl[a] and V. Herout[a], H. Schilcher[b]

[a] Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague

[b] Scientific Department, SALUS-HAUS Company, Bruckmühl/Mangfall, West Germany

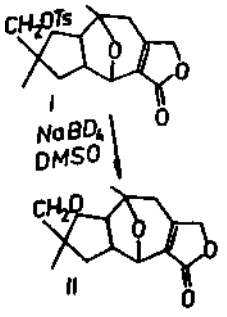
The structure of (-)-α-bisabololoxide-A, m.p. 99-100°, isolated more than twenty years ago by Šorm and co-workers from Matricaria chamomilla oil has been elucidated on the basis of spectral and chemical evidence.
Conditions of GC-separation of (-)-α-bisabololoxides-A,-B and C as well as their mass-spectral fragmentations will be discussed.

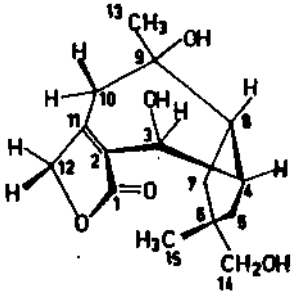
Structure of Lactarorufin B.

By W.M. Daniewski and M. Kocór

Institute of Organic Chemistry of Polish Academy of Sciences, Warsaw, Poland.

Lactarorufin B ($C_{15}H_{22}O_5$; m/e 282; $[\alpha]_D^{20}$ + 24°; m.p. 213°; λmax 218 nm, E 10100; νmax 3420, 3356, 3265 (OH), 1732 (CO), 1685 cm^{-1}(C=C); NMR (CD_3COCD_3) 2H AB quartet 5.13 (J_{AB} 19Hz), 1H d 5.53 (J 8Hz), 2H s 6.65, 2H m 7.2 - 7.8 superimposed with 2H broad s 7.47, 4H complex m 8.0 - 8.95, 3H s 8.75, 3H s 8.87) is a sesquiterpenoid lactone isolated from muahroom Lactarius rufus[1]. The comparison of the NMR spectrum of lactarorufin B with that of lactarorufin A[1,2,3,4], a sesquiterpene obtained by us from the same species, showed that in lactarorufin B one of the geminal methyls is replaced by hydroxymethyl group. By carrying out a series of chemical transformations connected with full spectral analysis of the derivatives obtained, it was proved that lactarorufin B is indeed the 14-hydroxy derivative of lactarorufin A. The $NaBD_4$ reduction of lactarorufin B -3,9-ether 14-tosylate (I) gave lactarorufin A--3,9-ether-14d_1 (II). The comparison of Eu(dpm)$_3$ shifted NMR spectra of lactarorufin A internal ether and that of the deuterated compound (II) showed univocally which of the geminal methyls has been oxidised. The above transformation also proved the stereochemistry of lactarorufin B shown by formula III.





III

1. W.M. Daniewski and M. Kocór, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 18, 585 (1970). 2. W.M. Daniewski and M. Kocór, ibid., 19, 553 (1971). 3. W.M. Daniewski, J. Jurczak, A. Ejchart, L. Kozerski and J.ST. Pyrek, ibid, 20, 151 (1972). 4. E. Baranowska and W.M. Daniewski, ibid., 20, 313 (1972).

Sesquiterpenoic Constituents of Lactarius Necator.

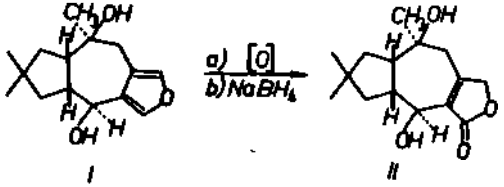
By W.M. Daniewski and M. Kocór

Institute of Organic Chemistry of Polish Academy of Sciences, Warsaw, Poland.

Lactarius necator is a mushroom, widely distributed in central Europe, growing mainly in mixed forests.

Our preliminary experiments on isolation of its low molecular weight and neutral constituents have demonstrated, that it contains basically the same variety of sesquiterpenes as it has been isolated previously by us from Lactarius rufus[1]. The main difference in the composition of extracts of Lactarius rufus and Lactarius necator lies in the concentrations of the constituents, and therefore also in the ease of their isolation and separation. Generally Lactarius necator is richer in the less oxygenated sesquiterpenes from which the furanoid I could be separated relatively easily. The same compound was isolated by S. Nozoe et al.[2] from another fungi i.e. Pomitopsis insularis. Compound I can be regarded as biogenetic precursor of lactarorufins; we could demonstrate that it can be converted into lactarorufin A (II) by peracid oxidation and subsequent reduction with $NaBH_4$ in moderate yield.

Lactarorufin A although also present in Lactarius necator, was found in much lower concentration than in Lactarius rufus. Further experiments on isolation of other sesquiterpenes from Lactarius necator are in progress..



I II

1. W.M. Daniewski and . Kocór, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 18, 585 (1970).

2. S. Nozoe, H. Matsumoto and S. Urano, Tetrahedron Letters, 1971, 3125.

THE DITERPENOID COMPOUNDS OF THE OLEORESINS OF SOME SIBERIAN CONIFEROUS SPECIES

V.N. Pentegova

Institute of Organic Chemistry of Siberian Department of the Academy of Sciences, Novosibirsk, USSR

No abstract.

NEW DITERPENOIDES FROM TEUCRIUM CHAMAEDRYS L.

D.P.Popa and A.M.Reinbold

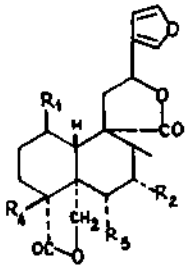
Chemical Institute of Moldavian Academy of Sciences,

Kishinev, USSR

In connection with the study of isoprenoids from the plants of the family Labiatae we have isolated from Teucrium chamaedrys L. four new diterpenoid bitter principles wich were named as teucrin B,E,F and G.

The investigation of teucrines by chemical and spectroscopic methods showed them to have the structures 1-4 respectively. It was established that teucrines are related to the diterpenoid furanolactones with a rearranged (4→5, 10→9) labdan skeleton, all they have in molecules two γ-lactonic rings, one of which is situated in α-position to furan, and another one in position C_4-C_5.On the basis of NMR and mass spectroscopic data was established the positions of hydroxy groups in (1-4), double bond in (3) and epoxy group in (4).

The stereochemistry of these substances was determined by ORD and CD measurements.

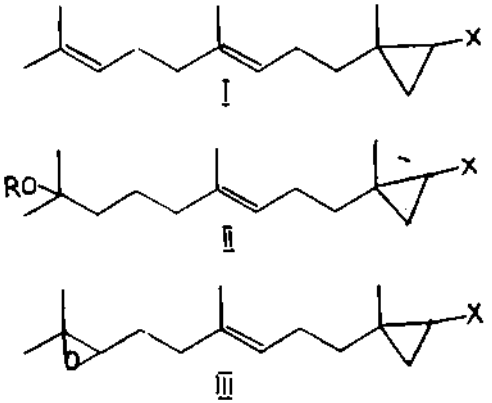


1. R_1= R_2=OH, R_3=R_4=H
2. R_1=R_2=R_4=H, R_3=OH
3. R_1=R_3=H, R_2=R_4=OH; Δ^2-
4. 2,3-epoxy-(3).

NEW JUVENOIDS WITH CYCLOPROPANE SYSTEM

M.Kocór, W.Sobótka and R.Sterzycki
Institute of Organic Chemistry
of the Polish Academy of Sciences
Warsaw, Poland

A modified Simmons-Smith reaction of farnecol afforded 1-hydroxy-2-methyl-2-/4,8-dimethylnona-3,7-dienyl/-cyclopropane used subsequently as the key compound for the synthesis of a series of 1,2,2-trisubstituted cyclopropane derivatives of the general formulae I, II and III resp., where X = CH_2OH, CH_2OMe, CO_2Me and R = Me, Et. Some of them revealed a moderate morphogenetical activity.



CYCLOTRICHOSANTOL, A NEW C_{31} 31-NOR-TRITERPENE

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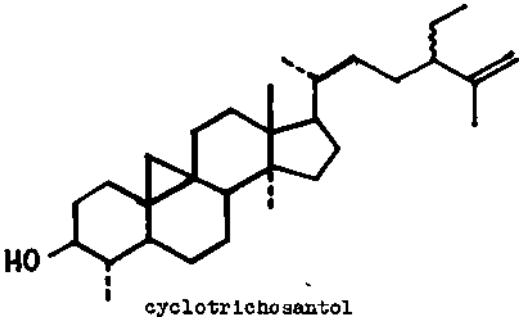
From the leaves of Trichosantes palmata L. /Cucurbitaceae/ cycloeucalenol and a new methylsterol - cyclotrichosantol /4α,14α-dimethyl-24β-ethyl-9:19-cyclo-cholest-25-ene-3β-ol/ were isolated. The structure of the latter compound was established on the basis of mass spectra of the parent alcohol, acetate, ketone and 26-nor-ketone, and was proved by the application of Eu/dpm/$_3$ shifted pmr spectrum.

Cyclotrichosantol is considered as the probable plant sterols precursor in the possible biosynthetic way:

cycloartenol → 24-methylene-cycloartenol → cycloeucalenol → cyclotrichosantol → 4α,14α-dimethyl-stigmast-8,25-dien-3β-ol → 4α-methyl-stigmast-7,25-dien-3β-ol → stigmast-7,25-dien-3β-ol → stigmast-7-en-3β-ol → α-spinasterol.



cyclotrichosantol

TRITERPENES OF DATURA INNOXIA MILL. STRUCTURE OF DATURADIOL AND DATURAOLONE.

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From the seeds of Datura innoxia Mill. /Solanaceae/ two new pentacyclic triterpenes, daturadiol /$C_{30}H_{50}O_2$/ and daturaolone /$C_{30}H_{48}O_2$/, were isolated. Their structures were established as 3β,6β-dihydroxy-olean-12-ene and 6β-hydroxy-3-oxo-olean-12-ene resp. on the following way:

Daturadiol was transformed to β-amyrin /3β-hydroxy-olean-12-ene/ by the monoacetylation, oxidation to ketoacetate and Wolff-Kiżner reduction; the presence of olean-12-ene skeleton was also proved by obtaining two characteristic products, by oxidation of daturadiol diacetate with selenium dioxide, i.e. : 11,13/18/-diene and 9/11/,13/18/-diene-12,19-dione.

The second hydroxyl group of daturadiol was shown to be secondary - axial /chemical and spectral evidences/. For the corresponding ketone, based on epimerization, deuteration and spectral properties, position 6 was established as the only possible one.

The second triterpene, daturaolone, was correlated with daturadiol as both were oxidized to the same diketone.

THE REVISED STRUCTURE OF FARADIOL AND ARNIDIOL

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The structures of faradiol and arnidiol were established as 3β,16β-dihydroxy-ψ-taraxerene and -taraxerene, resp. Earlier proposed structures were 3β,12ξ-dihydroxy-ψ--taraxerene and -taraxerene, resp.

The chemical and spectral properties will be discussed, and the reasons for the wrong structure determination will be given.

THE STRUCTURES OF FURAN SESQUITERPENES FROM NEPETA HINDOSTANA

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Two new furan sesquiterpenes were isolated from Nepeta hindostana: "NH-1" $C_{15}H_{18}O_3$ is a secondary alcohol containing $\alpha\beta$-unsaturated keto group and a trisubstituted furan ring, "NH-2" $C_{15}H_{20}O_4$ contains secondary and tertiary hydroxyl groups, and a trisubstituted furan ring, most probably with an oxo group the position 3.

The chemical and spectral properties and the possible structures will be discussed.

List of authors