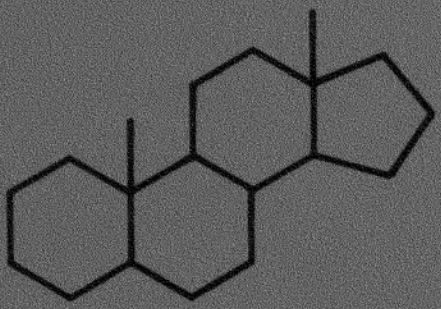
POLISH ACADEMY OF SCIENCES
INSTITUTE OF ORGANIC CHEMISTRY

XI CONFERENCE ON ISOPRENOIDS



ABSTRACTS OF PAPERS

Jachranka, 16–21 September, 1985

POLISH ACADEMY OF SCIENCES
Institute of Organic Chemistry

11th Conference on Isoprenoids

Abstracts of Papers

Jachranka 16th - 21st September, 1985

List of Plenary Lectures.

One hour

D.H.R Barton
Old Problems in Steroid Chemistry with New Solutions.

E. Caspi
Aspects of Estrogens Biosynthesis.

A. Fiecchi
Synthesis of Biologically Active Steroids and Analogs.

M. Julia
Biomimetic Syntheses of Isoprenoids.

A.V. Kamernitzky
Chemical Modification Approach to the Correlation between Steroid Structure and Action.

J.P. Kutney
Thujone, a Chiral Synthon for the Synthesis of Biologically Active Natural Products.

P. Magnus
The Synthesis of Isoprenoids Using Organometallic Chemistry.

K. Mori
Recent Results in the Synthesis of Bioactive Isoprenoids.

K. Nakanishi
Structural Studies on Bioactive Natural Products.

W. Oppolzer
Recent Progress in Enantioselective Synthesis of Natural Products.

G. Stork
Ionic and Radical Routes to the D Vitamins.

M. Vandewalle
The Synthesis of Some Cyclopentanoid Mono and Sesqui-terpenes.

R. Wiechert
On Steroidal Anti-hormones.

Half hour

J. ApSimon
Trichothecene Sesquiterpenes.

P. Baeckström
Photooxidation as a Tool in Terpenoid Synthesis.

M. Budesinsky
Structural Analysis of Sesquiterpene Lactones by FT - NMR.

F. Camps
Studies on Clerodane Diterpenoids and Drimane Sesquiterpenoids with Insect Antifeedant Activity.

D.P. Curran
Tandem Radical Cyclization Approach to Linear Condensed Cyclopentanoid Sesquiterpenes.

W.M. Daniewski
Recent Advances in Chemistry of Lactarius.

B.M. Fraga
Chemical and Microbiological Synthesis of Gibberellins.

G. Frater
Asymetric Induction with Chiral Ketenes. Synthesis of (-)Blastmycinone.

M. Hirama
A New Method for the Diastereospecific Functionalization of Acyclic Olefins.

G. Jommi
Aspects of Isoprenoid Synthesis.

P. Kocienski
New Synthetic Approaches to Spiroketal Antibiotics.

A.M. Moiseenkov
Synthesis of Polyprenols.

L. Novak
Synthesis of Faranal, the Trail Pheromone of Pharaoh's Ant.

K. Ponsold
On the Synthesis of 19-Nor-cardenolides and Analogous Compounds.

G. Quinkert
Aspects of Natural Products Synthesis.

E. Tsankova
Chemical Transformations of Terpenoids.

A. Zabża
Chemical Approach to Correlation of Dynamic Structure and Biological Activity of Juvenoids.

BIOSYNTHESIS OF NUATIGENIN-3-MONOGLUCOSIDE BY AN ENZYME PREPARATION FROM OAT (AVENA SATIVA) LEAVES

Kalinowska, M. and Wojciechowski, Z.A.
Institute of Biochemistry, Warsaw University,
02-089 Warsaw, Żwirki i Wigury 93, Poland

Young oat leaves contain steroid glycosides: avenacoside A and B which are derivatives of nuatigenin (3β,26-dihydroxy,22,25-epoxy-furost-5en). In our studies on biosynthesis of avenacosides we have demonstrated that an enzyme is present in the cytosol fraction from 7-day-old oat leaves which catalyzed the glucosylation of nuatigenin using UDP-glucose as the sugar donor. Chromatographically identical reaction products were formed when the enzyme preparation was incubated with unlabelled nuatigenin and labelled UDP-[^{14}C]-glucose or with [^{14}C]-nuatigenin and unlabelled UDP-glucose. The above product was identified as nuatigenin 3-O-monoglucoside by comparison with authentic nuatigenin 3-O-β,26-O-β-diglucoside, nuatigenin 3-O-β-monoglucoside and nuatigenin 26-O-β-monoglucoside obtained by combined chemical and enzymatical hydrolysis of avenacoside A and B. The glucosyltransferase present in the cytosol fraction of oat leaves seems to be highly specific for nuatigenin. In the reaction catalyzed by this enzyme nuatigenin is glucosylated at much higher rate than other steroid sapogenins such as isonuatigenin or diosgenin. Phytosterols are not glucosylated at all.

Our results indicate that glucosylation of nuatigenin in position 3 (but not in position 26) is the first step in the biosynthesis of sugar chains of avenacosides A and B.

INVESTIGATIONS ON DEACETYLASE FROM SUNFLOWER SEEDS

Zofia Kasprzyk, Ewa Szymańska and Wirginia Janiszowska

Institute of Biochemistry, University of Warsaw, 02-089 Warszawa, Żwirki i Wigury 93, Poland.

Previous studies have shown that crude enzymatic preparations obtained from sunflower seeds catalyse the deacetylation of tetraacetylglucosides of abscisic acid, gibberelins and oleanolic acid. During the hydrolysis of these compounds the ester-glycoside bond present in these compounds was not splitted.

In the present study, it was shown that enzymatic activity of deacetylase decreased 3 to 5 times in sunflower seeds during 6 months of storage depending on variety and different temperature conditions /+18, +5 and -20°C/. The highest decreasing in -20°C was observed.

The measurements of deacetylase activity of subcellular fractions obtained by differential centrifugation of the homogenate demonstrated that this activity was mainly associated with microsomal fraction / 12 times higher specific activity than that of homogenate/.

Acetone powder obtained from 16 000 x g supernatant showed no deacetylase activity, whereas acetone powder preparation from the precipitate between 30-60% of ammonium sulfate saturation of the same supernatant had 4 times higher enzymatic activity than the supernatant.

BIOSYNTHESIS AND DEGRADATION OF JUVENILE HORMONE IN CORPORA ALLATA OF GALLERIA MELLONELLA. JUVENILE HORMONE ACID METHYLATION IN PREPUPAL WING DISCS.

J.R.Wiśniewski[1],M.Muszyńska-Pytel[2], K.Grzelak[3],M.Kochman[1]
[1]Div.Biochem.,Inst.Org.Phys.Chem., Technical University of Wrocław,[2]Dept.Invertebrate Physiol.,Warsaw University, [3]Inst. Biochem.Biophys.,Polish Acad.Sci.,Warsaw.

It was demonstrated in Galleria mellonella that secretion of juvenile hormone/JH/ by corpora cardiaca-corpora allata complex/CCCA/ is a resultant of biosynthesis of the hormone and of its degradation. The rate of JH biosynthesis by CCCA is highest in the beginning of penultimate and last larval instar. The rate is markedly reduced before last larval ecdysis and after the second day of the last instar. During the post-feeding period, the JH synthesis again attains high values. In opposite, the JH esterase activity in CCCA is very low in the beginning of the last instar and it rapidly increases after the second day of this stage. At least 95% of JH degradationin these glands occurs via ester bound hydrolysis. Thus the secretion of JH in CCCA is possible till the second day of last larval instar. After larval-pupal reprogramming JH-acid is relased by CCCA. The imaginal wing discs of mobile prepupa exhibit the ability of methylation of JH-acid. We believe that,since after larval-pupal reprogramming, some tissues should be protected from JH, whereas other require an exposition to this hormone. Therefore the possible physiological function of CCCA at this stage of development would be to supply larval peripheral cells with biologically inactive JH-acid. In tissues requiring JH to maintain normal development /e.g wing discs/ the hormone is resinthetized from JH-acid.

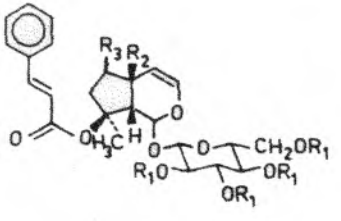
IRIDOIDS FROM VERBASCUM SPECIES

K. Seifert[1], J. Schmidt[1], N.T. Lien[2] and S. Johne[1]

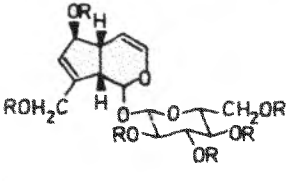
[1] Institute for Plant Biochemistry, Halle, Academy of Sciences of the GDR
DDR-4020 Halle/Saale, Weinberg 3

[2] Institute for Chemistry, National Research Centre of the SRV, Hanoi, SR Vietnam

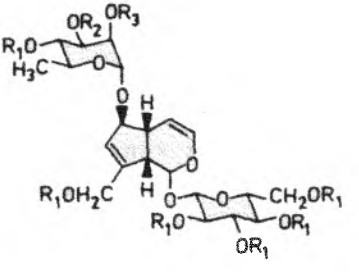
The occurrence of iridoids from 16 Verbascum species was investigated. The negative ion mass spectroscopy of the acetylated compounds was very useful concerning the appearance of a molecular ion. The fragmentation behaviour of the iridoids under positive and negative ionization is compared and discussed.



1: $R_1 = H, R_2 = OH, R_3 = \beta\text{-}OH$
2: $R_1 = Ac, R_2 = OH, R_3 = \beta\text{-}OAc$
3: $R_1 = R_2 = H, R_3 = \alpha\text{-}OH$
4: $R_1 = Ac, R_2 = H, R_3 = \alpha\text{-}OAc$



5: R = H
6: R = Ac



7: $R_1 = R_2 = R_3 = H$
8: $R_1 = R_2 = R_3 = Ac$
9: $R_1 = R_3 = H, R_2 = (E)\text{-Cinnamoyl}$
10: $R_1 = R_3 = Ac, R_2 = (E)\text{-Cinnamoyl}$
11: $R_1 = R_2 = H, R_3 = (E)\text{-Cinnamoyl}$
12: $R_1 = R_2 = Ac, R_3 = (E)\text{-Cinnamoyl}$

IRIDOID GLYCOSIDES OF LIGUSTRUM VULGARE

Joanna Diak

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

In the course of phytochemical analysis of ornamental shrub Ligustrum vulgare L. two iridoid glucosides have been isolated.

The ethanolic extracts of the fresh leaves and ripe fruits of the plant were partitioned between $CHCl_3$ and H_2O. Aqueous phases evaporated in vacuo were subjected to SiO_2-column chromatography. TLC-detection showed the presence of iridoid compounds in the fractions eluted with 10, 15% MeOH in $CHCl_3$. Two amorphous compounds were isolated from the fractions. They yielded D-glucose on hydrolysis with β-glucosidase.

The spectral data of the aglycones suggested their iridoid structures which are under investigations.

TERPENOIDS FROM CREPIS BIENNIS

Wanda Kisiel

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

Silica gel column chromatography of the ethanolic extract of the roots of Crepis biennis L. /Compositae/ afforded a non-crystalline compound which turned out to be β-sitosterol-3-O-β-D-glucopyranoside esterified with oleanolic acid.

Evidence of the attachment of the glucose moiety to the carboxyl group of the acid was provided by alkaline hydrolysis which yielded β-sitosterol-3-O-β-D-glucopyranoside and oleanolic acid.

The position of the ester residue at C-6 of glucose was deduced from the shifts of sugar protons in the ^{1}H-NMR spectra of the compound and its acetyl derivative.

Oleanolic acid, β-sitosterol and its glucoside were also isolated and identified by comparison with standard samples.

BIOLOGICALLY ACTIVE COMPOUNDS FROM MELIACEAE

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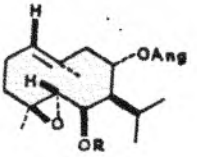
7000 Stuttgart 70, W.-Germany

From Azadirachta indica A.Juss. and Melia azedarach L. we have isolated several highly oxidized tetranortriterpenoids related to azadirachtin, and two lactams related to salannin which show biological activity. The structure determination using high resolution NMR will be reported, and a revised structure based on NMR data will be suggested for azadirachtin.

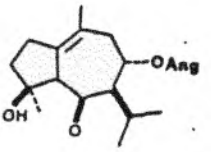
CONFORMATIONAL STUDIES ON SESQUITERPENE ALCOHOLS ESTERS FROM *LASERPITIUM HALLERI* CRANTZ

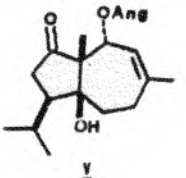
Giovanni Appendino[1], Pierluigi Garboldi[2] and Gian Mario Nano[1]
1: Istituto di Chimica Farmaceutica, Fac. di Farmacia, Torino
2: Laboratorio di Chimica Organica della Facoltà di Scienze, Milano

Investigation of the ripe fruits of *L.halleri* Crantz gave 2 couples of new germacrane (I,II) and guaiane (II,IV) esters and a daucane derivative previously isolated from a plant of the *Compositae* family, whose stereochemistry was revised to V. The spectral properties and the chemical reactivity of the natural germacrane derivatives I an II as well as of several derivatives and analogs, were related to peculiar conformational features. Some unusual conformations were detected, typified by the double chair form of VI, which represents a new molecular geometry for germacrane derivatives. The conformational importance of homoconjugation in germacra-1(10),4-dienes is discussed.



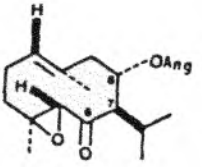
	R
I	Ac
II	H





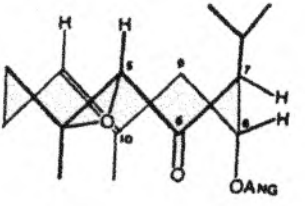
V

	R
III	Ac
IV	H



VI

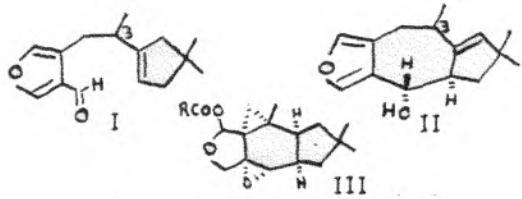
≡



CHEMICAL CORRELATION OF SECO-LACTARANE AND LACTARANE SESQUITERPENES

M.De Bernardi, G.Fronza, A.Scilingo, G. Vidari and P.Vita-Finzi
Dipartimento di Chimica Organica - Via Taramelli 10 - 27100 Pavia (Italy)

Many sesquiterpenes isolated from species of the Russulaceae family (Basidiomycetes) contain the lactarane and seco-lactarane skeleton, e.g. lactaral (I) and furosardonin A (II)



They seem to derive from the velutinal esters(III), either by chemical degradation and transformation or by direct enzymatic conversion of (III) (1,2). The configuration of C-3 is probably significant in order to establish the way of opening of the cyclopropane ring. Moreover direct chemical correlation between the two classes of sesquiterpenes (I) and (II) was never realized. In this paper we report our results on the Lewis acid catalysed intramolecular ene reaction of seco-lactarane derivatives, furanes and lactones, which are cyclized in this way to lactaranes. Furthermore the chemical correlation of these compounds with sesquiterpenes of known configuration at C-3 will be discussed.

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2. O.Sterner, R.Berrman, J.Kihlberg, J.Oluwadiya,B.Wickberg,M.De Bernardi,F. De Marchi, G.Fronza, G.Vidari and P.Vita-Finzi, J. Org. Chem. in press.

PHENOLS AND CHROMENES FROM LACTARIUS AZONITES

M.De Bernardi, G.Fronza, G.Mellerio, G.Vidari and P. Vita-Finzi

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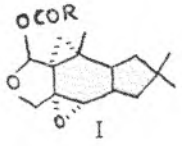
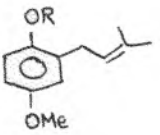
A few Lactarius species, belonging to the Section Plinthogali, e. g. Lactarius azonites, do not contain sesquiterpenes, like velutinal esters (I) and their derivatives, which seem peculiar to most Russulaceae species with pungent and acridic taste.

When fresh specimens of Lactarius azonites are injured, the colour of the flesh and of the juice of these mushrooms turns red in a short time, while the taste of the juice quickly becomes very pungent.

We have found that the very simple phenol ester (IIb) is the only responsible of all these transformations. The compound (IIb) is rapidly degraded to the free phenol (IIa) which is enzymatically oxidized through C-C and C-O couplings. Dimers and trimers like (III) and (IV), containing the chromene system, were isolated. Structures have been confirmed by synthesis.

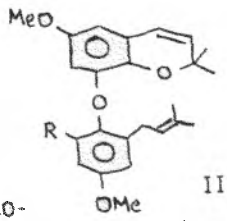


I

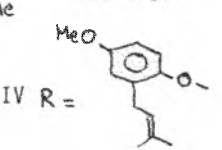


IIa R = H

IIb R = $CH_3(CH_2)_{16}CO$-



III R = H



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E.Conca, M.De Bernardi, G.Fronza,M.A.Girometta,G.Mellerio,G.Vidari and P.Vita-Finzi, Tetrahedron Letters, 22,4327 (1981)

TRITERPENES FROM AMARACUS DICTAMNUS

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and
Eszter GACS-BAITZ*

Institute of Organic Chemistry, University of Palermo, Palermo, Italy

*Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

From the aerial parts of Amaracus dictamnus (= Origanum dictamnus), family Labiatae, collected in the island of Crete (Greece), several triterpenoids were extracted.

Two minor constituents were identified as 21α-hydroxy--oleanolic acid and 21α-hydroxy-ursolic acid. Their structures were elucidated by MS, ^{1}H-NMR and ^{13}C-NMR. The first acid was found in nature only once previously, the second is a new natural product.

THE CRYSTAL STRUCTURE OF THE METHYLESTER OF 3α,6α-DIACETOXY-10-OXO-11(12)-KEMPEN-20-OIC ACID, A DITERPENE FROM NASUTITERMES COSTALIS SOLDIERS.

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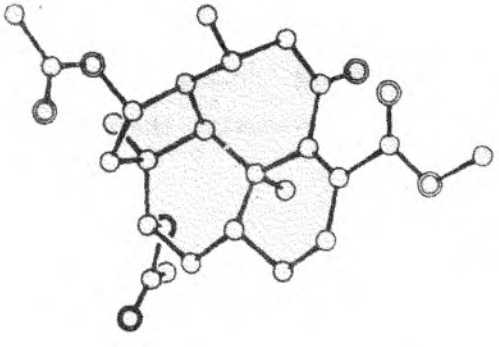
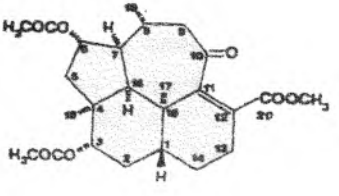
+) Istituto di Strutturistica Chimica C.N.R., C.P. n. 10 Monterotondo Stazione - Rome (Italy)
°) Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences - 166 10 Prague (Czechoslovakia).

The major constituents of the frontal gland secretion of the Nasutitermes Costalis soldiers are diterpenes whose structure is based on the trinervitane skeleton. The minor components are diterpenes which derive also from the kempane or secotrinervitane polycyclic systems. We report the crystal structure of one of these minor components, the methylester of 3α,6α-diacetoxy-10-oxo-11(12)-kempen-20-oic acid.

Crystals grown from ethanol are orthorhombic, S.G. $P2_12_12_1$, a=6.540(1), b=11.743(2), c=30.504(6) Å, $C_{25}H_{34}O_7$, M=446.52, Z=4, Dc=1.27 g.cm^{-3}, Cu-Kα radiation. The structure has been solved by multisolution direct methods and refined to R=0.08 with 1383 significant reflections.





The relative position of the substituents on the tetracyclic skeleton and the junctions of the rings indicate that the compound belongs to the kempane derivatives. However the structure has the the peculiarity of having in position 7 a hydrogen atom with α-configuration, which is a feature common to the trinervitane and rippertane skeletons. The molecule shows a dome-shaped arrangement of the rings with H(7), C(16), C(17) and C(18) protruding on the convex α-face.

CONSTITUENTS OF HIGHER FUNGI. DIHYDROXY LACTONES OF VARIOUS LACTARIUS SPECIES

By Włodzimierz Daniewski and Wojciech Kroszczynski

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

Monohydroxy lactone contents of Lactarius species are important chemotaxonomic features (1). Similarily dihydroxy lactones are also important. They possess insect deterrant activity, extreemly bitter taste, and therefore play an important role in the plant defence mechanism. The analyses of monohydroxylactone contents could be relatively easily performed by HPLC using simple solvent system (1) with conjunction with mass spectrometry. After having examined fractions of dihydroxy compounds of ethanolic extracts of various Lactarius species we found that their dihydroxylactone contents were different in every mushroom. The key compound was lactarorufin A. The isolation of dihydroxylactones was difficult even with HPLC. In some extracts i.e. Lactarius vellereus the mixture of dihydroxylactones is very complex. With the use of HPLC carried out in two modes (reverse and normal) new lactones were isolated and their structure determination will be discussed.

1. W.M. Daniewski, M. Kocor, T. Januszewski and A. Rymkiewicz, Polish. J. Chem., 55, 807 (1981). W.M. Daniewski, W. Kroszczynki, A. Wawrzun and A. Rymkiewicz, J. Liqu. Chrom., 7, 2915 (1984).

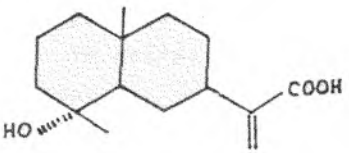
SQUITERPENES OF DITTRICHIA VISCOSA AND THEIR BIOLOGICAL ACTIVITY

By E. Błoszyk[a], M. Buděšinsky[b], W.M. Daniewski[c], M. Holub[b] and W. Kroszczynski[c].

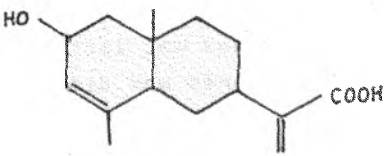
a Department of Medicinal Plants, Medical Academy, 60623 Poznan.
b Institute of Organic Chemistry and Biochemistry CSAV, 166 10 Prague
c Institute of Organic Chemistry PAS, 01 224 Warsaw, Poland.

In seeking for compounds possessing insect deterrant activity the species of Dittrichia viscosa (Compositae) was investigated. With the aid of column chromatography the following compounds were isolated: vachanic acid (1) or ilicic acid (2) m.p. 174-176 ,viscosic acid m.p. 149-150 (new compound), carabron (grandicin), inuviscolide and three new sesquiterpenoic lactones whose structures are investigated.

Vachanic acid, its methyl ester, and viscosic acid showed high insect deterrant activity when tested on storage pests (larvae and adults) Tribolium confusum, Sitophilus granarius and Trogoderma granarium.



Vachanic acid



Viscosic acid

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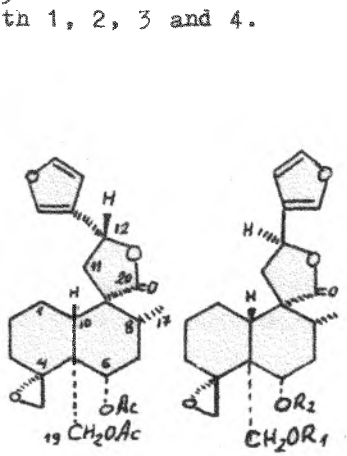
2. W. Herz, H. Chikamatsu, L.R. Tether, J. Org. Chem., 31, 1632 (1966).

THE STEREOCHEMISTRY OF MONTANIN C, TEUPOLIN I AND TEUPOLIN II

Peter Y. Malakov and G.Y. Papanov
Department of Organic Chemistry, Plovdiv University,
24 Tsar Assen Street, 4000 Plovdiv, Bulgaria

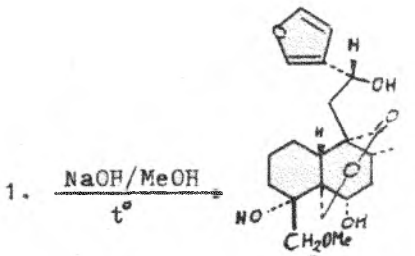
S u m m a r y

Using a chemichal transformation, it was possible to determine the stereochemistry at C-12 in Montanin C /1/, isolated from Teucrium montanum, and in Teupolin I /2/ and Teupolin II /3/, isolated from T. polium. This quantitative chemical transformation - opening of the γ-lactone ring and closing of a new δ-lactone ring between C-19 and C-20, took place on treating 1, 2 and 3 with sodium base in a methanol solution. As a result, 5 and 6 were yielded, in which the chemical shifts for H-11 and CH_3-17 in ^1H NMR differed significantly in comparison with 1, 2, 3 and 4.



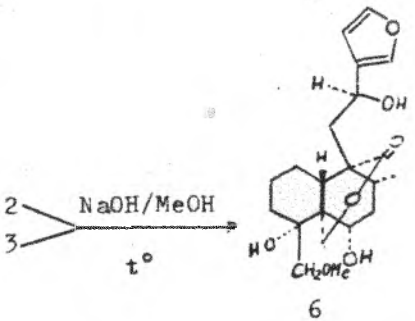
1

2. R_1=Ac; R_2=H
3. R_1=H; R_2=Ac
4. R_1=R_2=Ac



1. NaOH/MeOH, t°

5



2, 3 NaOH/MeOH, t°

6

SESQUITERPENE LACTONES OF CENTAUREA PSEUDOMACULOSA

S.M.Adekenov, G.M.Kadirberlina, A.D.Kagarlitskii
Institute of Organic Synthesis and Coal Chemistry
of the Kazakh Academy of Sciences
Karaganda, USSR

From air dried above ground material of Centaurea pseudomaculosa Dobrocz., collected in the Jschim river flood-lands of Celinograd region Kazakh SSR the following five crystalline compounds have been exracted with $CHCl_3$ and the extracts were separated on Si gel column.

Compound I, $C_{29}H_{50}O$, M^+ 414, mp 135-137° (petrol), $[\alpha]_D^{20}$ -34°, R_f 0,58, was identified as β-sitosterol.

Compound II, $C_{30}H_{50}O$, M^+ 426, mp 215-217° (petrol), $[\alpha]_D^{20}$ +51°, R_f 0,34 - taraxasterol.

Compound III, $C_{20}H_{26}O_7$, M^+ 378, mp 143° (EtOH, decom.), $[\alpha]_D^{20}$ +152°, R_f 0,22 - sesquiterpene lactone cnicin.

Compound IV, $C_{19}H_{24}O_7$, M^+ 364, mp 200° (EtOH, decom.), $[\alpha]_D^{20}$ +17,2°, R_f 0,62. JR ν_{max}^{KBr} cm^{-1} : 3370-3340 (-OH), 1760 (γ-lactone), 1710, 1280 (-O-C=O), 1660, 1635 (C=C). NMR (200 MHz, C_5D_5N, O-GMDS): δ 1,47 (s., 3H) - CH_3-C=C-; 4,02 (q., 1H, J_1=9Hz, J_2=15Hz) - H-C-O- ; 5,88 (d., 1H, J =5Hz), 6,28 (d., 1H, J =5Hz) - CH_2=C-C- . IV was identified as sesquiterpene lactone.

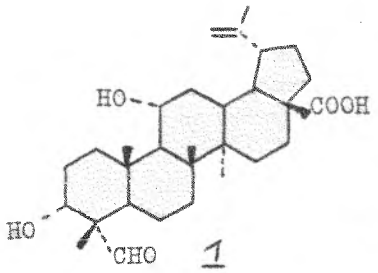
Compound V, $C_{19}H_{18}O_7$, M^+ 358, mp 189-190° (EtOH), R_f 0,33 - 5-hydroxy-6,7,3',4'- tetramethoxyflavone.

ISOLATION AND STRUCTURE OF A NEW TRITERPENES FROM THE VIETNAMESE PLANT ACANTHOPANAX TRIFOLIATUS

M. Lischewski[1], Ph. D. Ty[2], H. V. Phiet[2], L. Kutschabsky[3], J. Schmidt[1], A. Preiss[1], G. Adam[1]

1) Institute for Plant Biochemistry of the Acedemy of Sciences of the GDR, 4020 Halle/S., German Democratic Republic
2) Institute of Chemistry, National Research Centre of the SRV, Hanoi, SR Vietnam
3) Central Institute of Molecular Biology of the Academy of Sciences of the GDR, Berlin-Buch, GDR

Continuing our studies on vietnamese plants of medical and biological interest, we have examined the species Acanthopanax trifoliatus (Araliaceae) which is used in the Vietnamese folk medicine as a drug with Ginseng-like activity. We now report on the isolation and structure elucidation of the following new pentacyclic triterpenoid acids from leaves of this species: 3α,11α-dihydroxy-23-oxo-lup-20(29)-en-28-oic acid (1), 24-nor-3α,11α-dihydroxy-lup-20(29)-en-28-oic acid (2) and 24-nor-11α-hydroxy-3-oxo-lup-20(29)-en-28-oic acid (3).



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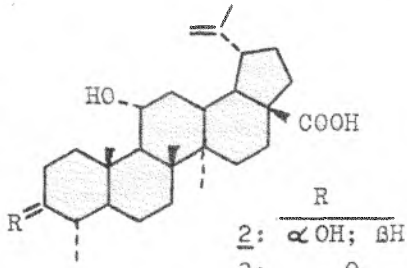


R

2: αOH; βH

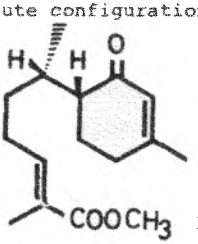
3: O

The structures of 1 - 3 were established by spectroscopic data (IR, MS, ^{1}H NMR, ^{13}C NMR), chemical transformations and X-ray analysis. The possible biosynthetic pathway in this plant is discussed.

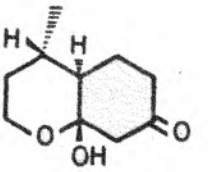
Abstract: RELATIVE AND ABSOLUTE CONFIGURATION OF ß-TURMERONE AND SOME NATURAL 1-BISABOLONES.

by W. Dummer, W. Kreiser and H. Preut University of Dortmund

The 1-bisabolone class of sesquiterpenes represents a rapidly growing natural product family mainly found in composites. As a typical example the carboxylic ester **I** isolated from Baeria chrysostoma is shown here. Most of the family members were discovered and their structure elucidated by Bohlmann, who also gave some spectroscopic evidence regarding the relative and absolute configuration at the two adjacent chiral centres.



I



II

After having synthesized some dozen natural compounds of this type in optically active forms during the last 15 years, we noticed that all of them displayed a very distinct chemical shift range for the secondary methyl group in the ^{1}H-n.m.r. spectrum. The natural diastereomer quite regularly resonated at about 0.80 ppm, whereas the signal belonging to the unnatural isomer was shifted downfield to 0.93 ppm. Regardless of the further molecular environment, the maximum deviations for 1-bisabolones were ± 0.03 ppm. From these observations we have deduced that all natural 1-bisabolones reported so far belong to the same relative stereochemical series.

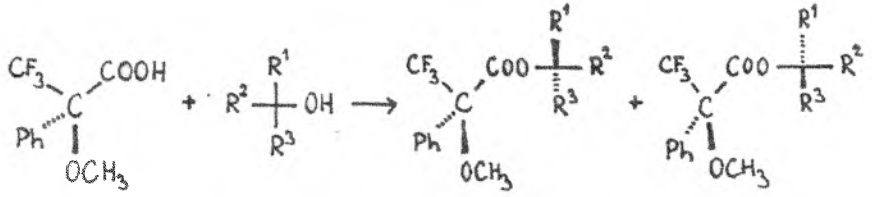
Starting from (-)-3-S-methyl-valerolactone of well established absolute configuration we synthesized the crystalline bicyclic derivative **II** and determined its relative structure by X-ray. The latter was transformed into several natural 1-bisabolones and into ß-turmerone. In this way we were able to deduce relative and also absolute configurations of these natural compounds.

A SIMPLE WAY OF DETERMINING THE ABSOLUTE CONFIGURATION OF ALCOHOLS.

Strnínz L., Valterová I., Wimmer Z., Budějínský M., Kořoutová J., Šaman D. and Romaňuk M.

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

In connection with our search for biologically active compounds and their metabolites in plant tissue cultures, several hydroxy derivatives were isolated and identified, and subsequent study of the stereoselective course of the biotransformations was performed. Our approach is shown below. A simple method of synthesis of diastereoisomeric esters (3) and (4) was found using one-step procedure involving reaction of an equimolecular amount of the acid (1) with the alcohol (2) in aprotic solvent in the presence of 2-chloro-1-methyl pyridinium iodide and 4-dimethylamino pyridine. Diastereoisomeric esters thus obtained were separated by HPLC and their absolute configuration established by the NMR.



(R)-(+)-(1) (2) (racemic) (3) (4)

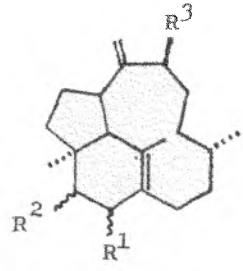
R^1, R^2, R^3 = H, alkyl group

CONFIRMATION OF THE ABSOLUTE CONFIGURATION OF THE TRINERVITANE SKELETON

Irena Valterová, Soňa Vašíčková, Miloš Buděšínský and Jan Vrkoč

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

Absolute configuration of the trinervitane skeleton has been confirmed by two independent methods. CD curves of the complexes of trinervitane-2,3-diols I - III with tris (dipivalomethanato)praseodym have been analyzed. ^{1}H-NMR spectra of the esters of alcohol IV with the respective R- and S-α-methoxy-α-(trifluoromethyl)-phenyl-acetic acid have been studied. Differences in the chemical shifts of these two esters are in accordance with the result of CD measurements and they confirm the absolute configuration proposed earlier[1].



I : $R^1 = R^2 = \alpha$-OH; R^3 = H
II : $R^1 = \alpha$-OH; $R^2 = \beta$-OH; R^3 = H
III: $R^1 = \beta$-OH; $R^2 = \alpha$-OH; R^3 = H
IV : $R^1 = R^2$ = H; R^3 = OH

1. Prestwich G.D., Tanis S.P., Springer J.P., Clardy J.: J. Amer. Chem. Soc. 98, 6061 (1976).

THE STRUCTURES OF VULGARIN AND ITS ISOMERS. — A REINVESTIGATION.

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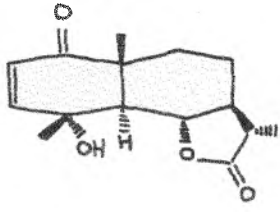
[a] Department of Chemistry, Addis Ababa University, P.O. Box 1176, Addis Ababa, Ethiopia

[b] Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

[c] Research Department, Swedish Tobacco Company, P.O. Box 17007, S-104 62 Stockholm, Sweden

During the identification of a sesquiterpene lactone from the ethiopian plant *Artemisia rehan* (Compositae) we found that there were several reports on compounds, which appeared to be identical with vulgarin (**1**).[1] Due to discrepancies in the reported spectroscopic data, we started a reinvestigation using different NMR-techniques.

The compound isolated from the ethiopian plant, vulgarin, barrelin and judaicin were found to be identical with the stereochemistry shown in **1**. These results also settles the epimeric relationship between various natural products of this series.



1

[1] T.A. Geissman and G.A. Ellestad, *J. Org. Chem.* **1962**, *27*, 1855; K.S. Rybalko and L. Dolejš, *Coll. Czech. Chem. Commun.* **1961**, *26*, 2909.

α-CYCLODEXTRIN AS STATIONARY PHASE FOR GC SEPARATIONS OF MONOTERPENE ENANTIOMERS.

Mikael Lindström,[a*] Johan Roeraade[b] and Torbjörn Norin[a]

[a] Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

[b] Department of Analytical Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Enantiomeric separations of pinene derivatives have been performed by gas chromatography on packed columns using α-cyclodextrin in formamide as stationary phase.[1,2] We have used this stationary phase for the preparation of micropacked columns as well as wall coated open tubular glass capillary columns. Important factors affecting the enantiomeric separation will be discussed. The concept has been applied for the investigation of the enantiomeric compositions of some monoterpenes in plants and insects.

[1] T. Kościelski, D. Sybilska, S. Belniak and J. Jurczak, *Chromatographia* **1984**, *19*, 292.

[2] T. Kościelski, D. Sybilska and J. Jurczak, *J. Chromatogr.* **1983**, *280*, 131.

STRUCTURE ELUCIDATION OF PENTACYCLIC TRITERPENE TRIOLS FROM CALENDULA OFFICINALIS FLOWERS

Bogusław Wiłkomirski

Institute of Biochemistry, University of Warsaw, 02-089 Warszawa, Żwirki i Wigury 93, Poland.

From the dry ligulate marigold / Calendula officinalis / flowers crude lipid fraction / 13% of dry weight/ was isolated. After alkaline hydrolysis the unsaponified fraction was obtained / 7% of dry weight/. This fraction was adsorbed onto silica-gel and applied to a silica gel column. Crude triterpene polyols were obtained from eluate containing 80-100% of chloroform in hexane. These compounds were acetylated and purified using TLC giving the mixture of triterpene triol triacetates / 0.055% of dry weight /.

The mixture of triterpene triol triacetates separated in TLC on four bands. Three of them corresponded with individual compounds, the lowest one separated in TLC-$AgNO_3$ impregnated on two bands. The purity of all bands was controlled by GLC.

The use of mass spectroscopy and ^{1}H NMR and chromatographical comparison with the original samples allowed to determine their structure as:

1. 3β,16β,28-olean-12-ene-triacetate
2. 3β,16β,28-lup-20/29/-ene-triacetate
3. 3β,16β,22α-tarax-20-ene-triacetate
4. 3β,16β,30-tarax-20-ene-triacetate
5. 3β,16β,21-urs-12-ene-triacetate

REDUCTION OF SOME 6-METHYLENE DERIVATIVES OF PREGNANE SERIES

M.K.Łypacewicz, R.Jaworska, T.Wasiak, S.Raczkowska, M.Malinowska, J.Smolińska

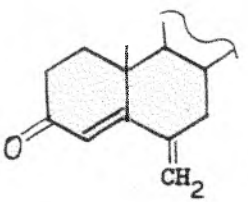
Institute of Pharmaceutical Industry, Warsaw

The course of reduction of exocyclic double bond at C-6 in pregnane series derivatives (I) was studied under conditions of catalytic hydrogenation and hydrogen transfer.

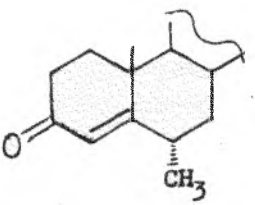
The reaction products of type II and III were identified by analytical and spectral means and their distribution under different hydrogenation conditions was determined.

It was found that the course of reaction is dependent on the substituents of steroid molecule, the kind of catalyst, the solvent and temperature.

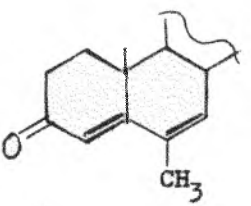
In some derivatives of 6-methylene-11β,17α,21-trihydroxy-4-pregnene-3-one there was observed the formation of endocyclic double bond at 6,7-position, which was resistant to reduction.



I



II



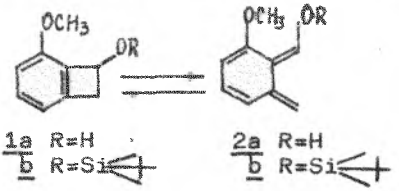
III

TERMOLYTIC CYCLOADDITION OF o-QUINODIMETHANES WITH 4-OXA-5α -2-ANDROSTEN-17β -ACETATE

KAZIMIERZ OLEJNICZAK, WŁADYSŁAW J.RODEWALD AND ZOFIA ZAWORSKA

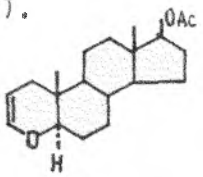
DEPARTMENT OF CHEMISTRY, WARSAW UNIVERSITY

The present communication concerns the synthesis of steroidal derivatives of hexacyclic triterpenes using the Diels-Alder reaction of active forms of o-quinodimethanes (o-quinone methides 2a and 2b, respevtively) with 4-oxa-5α -2-androsten-17β -acetate (3).



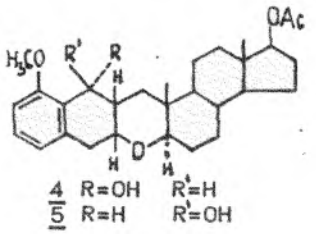
1a R=H
b R=Si

2a R=H
b R=Si

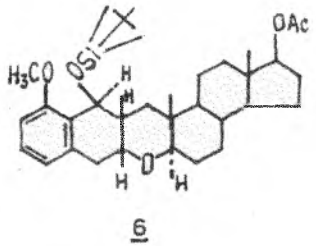


3

A mixture of compound 1a and the oxaandrostene derivative 3 was heated in sealed tube (130°) to furnish two endo adducts (isolated by column chromatography) crystalline 4 (m.p.93-95°) and oily 5 in ratio 4:1 in 30% yield. Starting, however, from 1b and 3only one adduct was isolated in 65% yield.



4 R=OH R'=H
5 R=H R'=OH



6

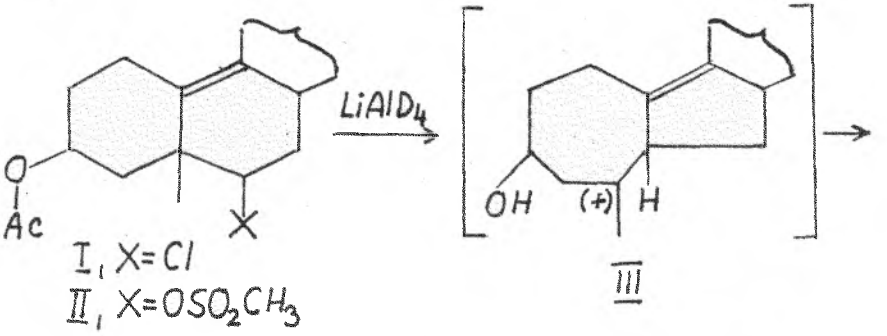
A selective deprotection of OSi≡ group in ether solution of $BF_3.Et_2O$ in adduct 6 afforded a product which was identical in all respect with compound 5. This fact as well as analytical and spectra data confirmed the structure of the obtained epimeric products 4 and 5 permitted as to suggest, that the additional rings are condensed with steroid 3 as cis - system.

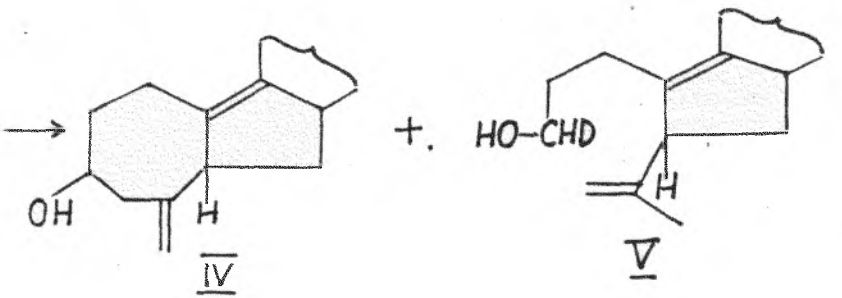
It should be added that the described reaction can find more general application in syntheses of steroids and heterosteroids functionalized with some additional rings and further investigations this problem are continued.

REARRANGEMENT AND FRAGMENTATION IN REACTIONS OF 5-METHYL-19-NOR-5β-CHOLEST-9-ENE DERIVATIVES

Alexander Kasal and Jaroslav Zajíček,
Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague,
Czechoslovakia.

Reaction of 6β-substituted derivatives I and II with lithium aluminium deuteride leads to the product of A-homo-B-nor-rearrangement III which then undergoes either elimination or fragmentation and reduction to yield compounds IV and V resp.





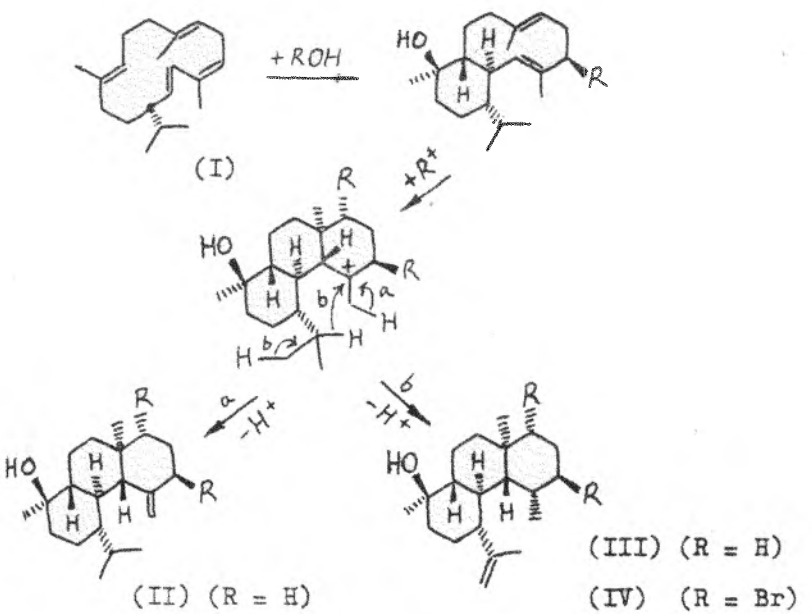
ELECTROPHILE CYCLIZATION OF CEMBRENE

V.A.Raldugin, S.A.Shewtsow, V.A.Pentegova

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

Reaction of cembrene (I) with aqueous formic acid in chloroform leads to complex mixture of hydrocarbons, formates and alkohols. The main oxygen-containing products are alkohols (II), (III) and its formates. Tricyclic product (IV) isolated as minor product from reaction of cembrene with N-bromsuccinimide in aqueous acetone.

Structure of these compounds was determined by X-ray analysis. Account for its stereochemistry it may propose the next route the formation of these products.



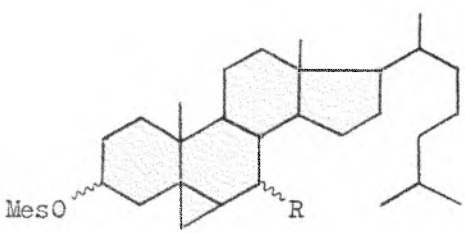
ACETOLYSIS OF 3-METHANESULPHONYLOXY-5,6-CYCLOPROPANO-CHOLESTANES WITH AN OXYGEN FUNCTION IN THE POSITION 7

L.Kohout[a], V.K.Sethi[b], J.Zajíček[a] and A.Kasal[a]

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

[b] Regional Research Laboratory, Jammu-Tawi, India

In one of our papers[1] on cyclopropano-steroids we studied the solvolysis of 5,6-cyclopropano-compounds with a methanesulphonyloxy group in the position 3 (I). Now we have synthetised similar compounds with oxygen functions in the position 7 (II) and studied the acetolysis of such compounds.



I, R = H

II, R = OR′

1. Kohout L., Fajkoš J.: Coll. Czech. Chem. Commun. 38, 913 (1973).

SYNTHESIS OF 24-FUNCTIONALIZED 19(10→9β)ABEO LANOSTANE DERIVATIVES

Witold Swoboda and Zdzisław Paryzek

Faculty of Chemistry, Adam Mickiewicz University
Poznań, Poland

The carbocationic rearrangements of 9,11-epoxy-7-oxo-lanostanes provides a good synthetic method leading to compounds with cucurbitane carbon skeleton. Having in mind the synthesis of natural cucurbitacins, the remaining problem is to retain a functional group in the side chain of the lanostane molecule, which makes possible further elaboration toward functionalities present in natural compounds.

The attempts will be described of the synthesis of synthons having the above mentioned feature. Few possibilities were examined, the most promising appears to be the introduction of 24-hydroxy group protected as a benzoate. It is resistant in all synthetic steps leading to 19(10→9β)abeo lanostanes, according to the general method reported by us previously.

OXIDATIVE SIDE-CHAIN DEGRADATION OF THE ERGOSTERYL-ACETATE-IRONTRICARBONYL-COMPLEX

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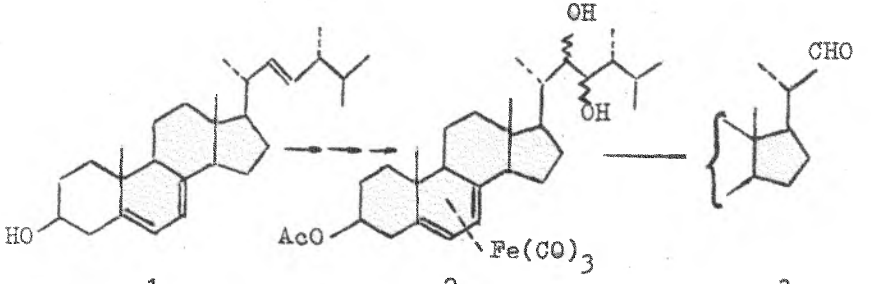
+) Institute for Plant Biochemistry, Academy of Sciences of the GDR, DDR-4020 Halle/Saale

++) VEB Jenapharm, Division of Research DDR-6900 Jena

Ergosterol (1) is a convenient starting material for the synthesis of other biologically interesting steroid compounds. Key reaction is the oxidative side-chain degradation after protection of the 5,7-diene system. We have shown, that the irontricarbonyl group is a suitable protecting group, which is stable against different oxidants. Reaction of the 22,23-diol of ergosterylacetate-irontricarbonyl-complex (2), obtained by the method of EVANS et al. /1/, with $Pb(OCOCH_3)_4$ or MnO_2 furnished the aldehyde 3 in good yields.



1 2 3

/1/ G. EVANS, B. F. G. JOHNSON, J. LEWIS, J. Organomet. Chem. 102, 507 (1975)

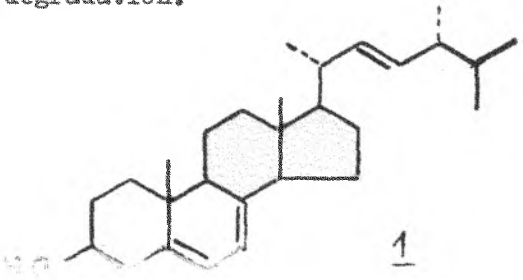
ON THE REACTIVITY OF 6- AND 22-DOUBLE BONDS IN PROTECTED ERGOSTEROL DERIVATIVES

B. Schönecker and U. Hauschild

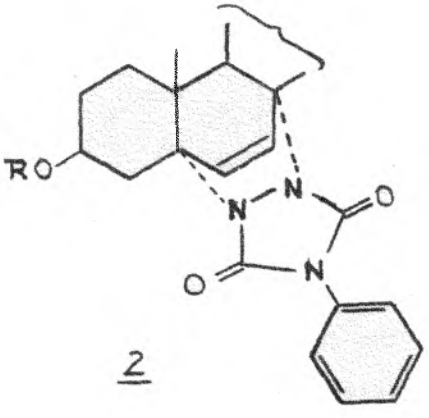
VEB Jenapharm, Division of Research, DDR-6900 Jena, GDR

The oxidative side chain degradation of ergosterol (1) is possible by functionalisation of the 22-double bond after protection of the 5,7-diene system with dienophiles. An attack on the 6-double bond is undesirable for the oxidation process.

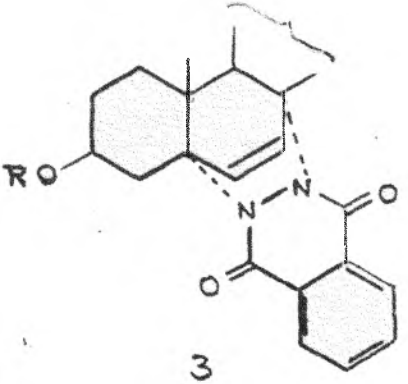
It is shown that the reactivity of the 6-double bond in the Diels-Alder adducts 2 and 3 against oxidants as OsO_4 and $KMnO_4$ depends on the structure of the protective group. This result is discussed in view of the oxidative side chain degradation.



1



2



3

UNUSUAL STABILIZATION OF AN ETHYNIL CARBONIUM ION

I. Vincze, M. Lőkös and Gy. Dombi*

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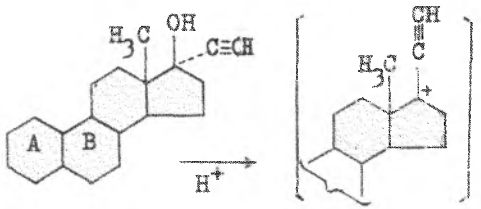
Szeged, Hungary

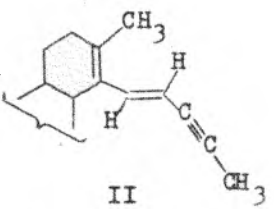
*Institute of Pharmaceutical Chemistry, University Medical
School, Szeged, Hungary

On the basis of literary data dehydration of 17α--ethynil-testosterone to 16-unsaturated compound is possible by formic acid.

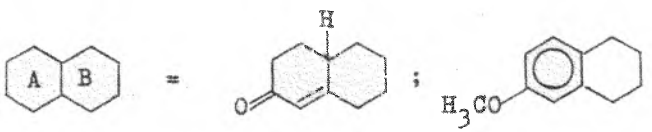
We found that 17α-ethynil-19-nor-testosterone as well as the corresponding estradiol derivative underwent a ring fission and rearrangement process resulting in II. The conjugated unsaturated product transforms easily to the III dimer.



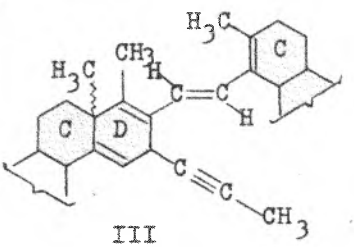
I



II



2 II $\xrightarrow{Al_2O_3}$



III

The structure of the products is given from spectroscopical evidences.

We propose a mechanism for the formation of II and III compounds.

Dehydration of ethynil-testosterone has been reinvestigated, too.

OXIDATION OF ENONE SYSTEM IN STEROIDS BY OXIDIZERS WITH REVERSIBLE RED-OX POTENTIAL

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Institute of Goods Science, Academy of Economics, Marchlewskiego 146/150, 60 967 Poznań, Poland.

Hitherto, reports on application of organic red-ox systems in the chemistry of steroids are still limited. The group of organic red-ox systems which can be recognized as thermodynamically reversible comprises, among others, tetrazolium salts, phenolindophenol salts and some flavins.

Here, we report results on the preparative use such oxidizing agents for obtaining keto or hydroxy derivatives of steroids containing enone systems at various positions. Pseudo-first-order constants were observed for this reactions. This oxidation appeared to be influenced to an unexpectedly large extent by functional groupings quite distant from the conjugated ketonic system.

The data indicate that reactivity of enone steroids is, in part, a function of their geometry in that steroid reactivity toward oxidizing agents with reversible red-ox potential increases with increasing planarity of the steroid molecule.

ELECTROCHEMICAL METHOXYLATION OF CITRONELLAL

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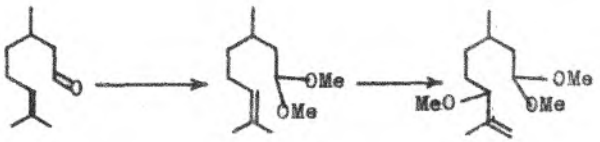
Institute of General Food Chemistry, Technical University
90-924 Łódź, Poland

The attemptes of the electrochemical methoxylation of citronellal /1/ were performed. The process was carried out* on a Pt-anode in methanol in the presence of sodium p-toluene sulfonate as a supporting electrolyte. The electrolysis was made to stop after the 1F/mol charge had delivered



1 2 3

Two main compounds were isolated: 3,7-dimethyl-1,1-dimethoxy--6-octene /2/in 50% and 3,7-dimethyl-1,1,6-trimethoxy-7-octene /3/ in 15% yield. Methoxylation of acetal 2 under similar conditions gave 3 in 62% yield.
It has been found that both transformation of 1 to 2 and 2 to 3 is of electrochemical character.

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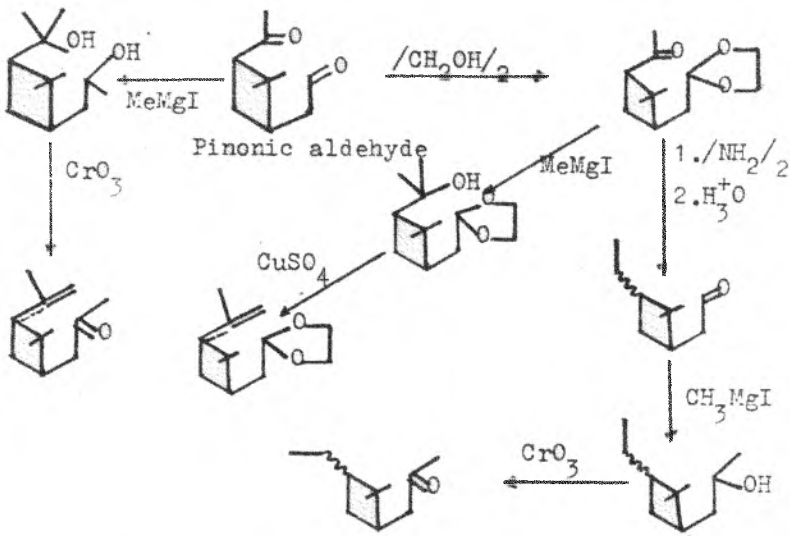
*J. Góra, K. Śmigielski, J. Kula, Zeszyty Naukowe Politechniki Łódzkiej, Chemia Spożywcza 39, 137 /1984/

CHEMICAL TRANSFORMATIONS OF PINONIC ALDEHYDE

. Podlejski, J. Kula

Institute of General Food Chemistry, Technical University Łódź, Poland

Pinonic aldehyde was obtained by ozonolysis of ∝-pinene Subsequently it was sujected to a series of reaction which are shown in the following scheme



The purity of the obtained compounds was verified by GLC and their structures were elucidated by IR, NMR and MS spectroscopies. Odcurproperties of some of these compounds were evaluated.

ISOMERISATION OF cis-3-SUBSTITUTED 2,2-DIMETHYLCYCLOPROPANE-ETHANOLS TO THE TETRAHYDROFURAN AND TETRAHYDROPYRAN DERIVATIVES

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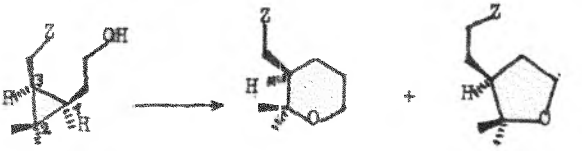
90-924 Łódź, Poland

Substrates 1 which were used in our investigation can be obtained by ozonolysis of 3-carene. 2-[2,2-Dimethyl-3-/2-oxopropyl/-cyclopropyl]ethanol (1a) when reacted with diluted solution of sulphuric acid at 90°C, gave 2,2-dimethyl-3-/2-oxopropyl/tetra-hydropyran (2a)* as the major product /THP-derivative/. However, 2-/2,2-dimethyl-3-propylcyclopropyl/ethanol (1b) under the same conditions, yielded 3-butyl-2,2-dimethyltetrahydrofuran (3b) as the major compound /THF-derivative/



1a 2a 3a /Z=$COCH_3$/
1b 2b 3b /Z=C_2H_5/

A mechanism for the formation of THP- and THF-derivatives involving a protonation of carbonyl group or cyclopropane ring followed by nucleophilic attack of the hydroxyl group on C-2 carbon atom, has been proposed.
Other examples of cyclization of cis-3-substituted cyclopropane-ethanols gave products according to the proposed mechanism.

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*J. Kula, Liebigs Ann. Chem. 1983, 890

CYCLIZATION OF LABDANE INTO ISOAGATHANE DITERPENOIDS IN SUPERACID MEDIUM

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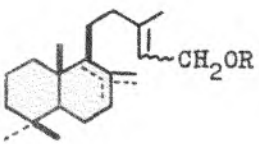
[a]Institute of Chemistry, the Moldavian SSR Academy of Sciences, Kishinev 277028, USSR

[b]Institute of Organic Chemistry of the Siberian Branch of the USSR Academy of Sciences, Novosibirsk, 630090, USSR

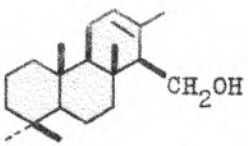
The high-yield structural- and stereoselective cyclization of labdanoids with a primary allylic hydroxile and acetate groups in the side chain into isoagathanic compounds was realised in the superacid medium (FSO_3H - SO_2FCl, -110°C).

Under given conditions the isomeric alcohols mixture (I) affords a mixture of the compounds (II)-(IV), and the acetates mixture (V) gives a mixture of isomeric hydroxyacetates (VI) and (VII).

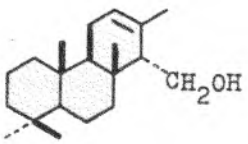
The structure and stereochemistry of obtained compounds were established on the basis of spectral and chemical data.



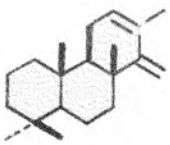
I R=H
V R=Ac



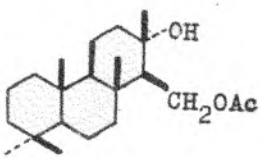
II



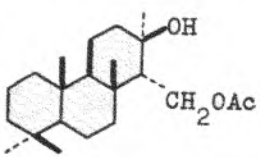
III



IV



VI

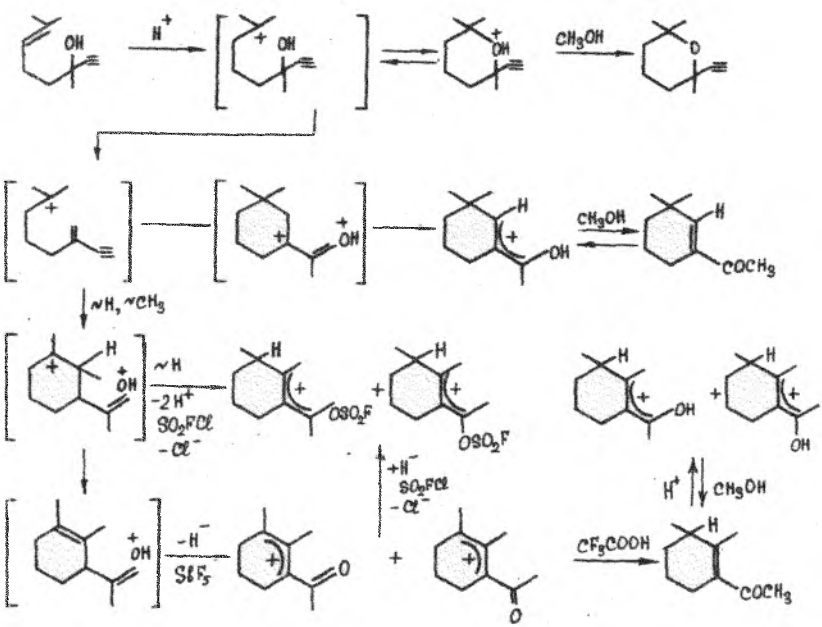


VII

MOLECULAR REARRANGEMENTS OF DEHYDROLINALOOL IN SUPERACIDS

O.A.Gavrilyuk, D.V.Korchagina, V.A.Barkhash
Institute of Organic Chemistry, Novosibirsk, USSR

Stable carbocations have been generated for the first time from dehydrolinalool in superacids (HSO_3F SO_2FCl, HSO_3F- SbF_5-SO_2FCl), and new molecular rearrangements of this compound, which were not possible in acid catalysis conditions, have been found. The mechanism of these rearrangements may be represented by the following scheme:

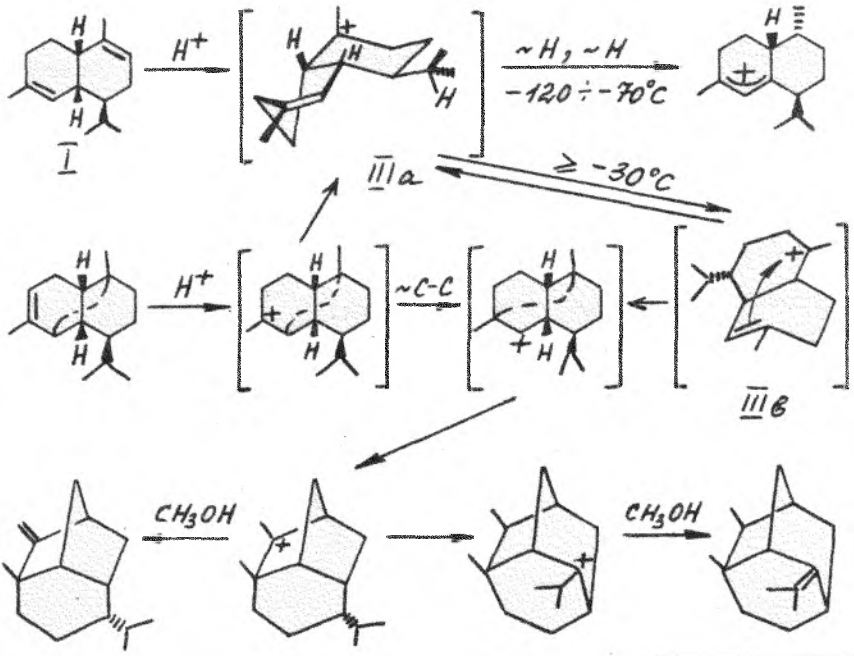


MOLECULAR REARRANGEMENT OF α-MUROLENE AND α-COPAENE TO GIVE TRICYCLIC COMPOUNDS

M.P.Polovinka, D.V.Korchagina, Zh.V.Dubovenko, V.A. Barkhash

Institute of Organic Chemistry, Novosibirsk, USSR

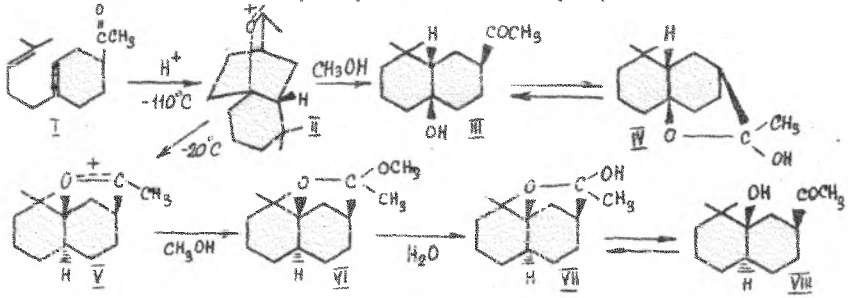
For the first time α-murolene (I) and α-copaene (II) were transformed in superacids to tricyclic compounds, which is in agreement with the schemes of biogenetic transformations of these substrates. Relation between the reaction routes giving bi- and tricyclic ions has been found to depend on the temperature of generation of stable ions, which may be caused by conformational changes in the initially formed ion (III).



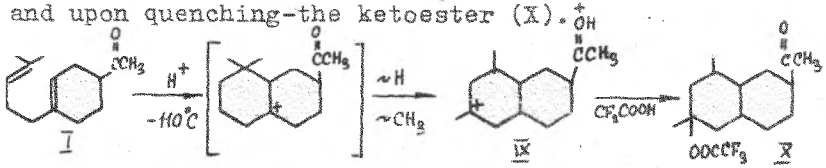
STABLE CARBOCATIONS AS INTERMEDIATES IN MOLECULAR REARRANGEMENT OF ISOLONE

O.A. Gavrilyuk, D.V. Korchagina, V.A. Barkhash
Institute of Organic Chemistry, Novosibirsk, USSR

The behavior of isolone(I) in long-life conditions of ions has been studied for the first time. In the HSO_3F-SO_2FCl mixture (-110°C), the carboxonium ion (II) was formed, and neutralisation of the acid solution gave a mixture of ketol (III) and lactol (IV).



Upon heating the salt of ion (II) up to -20°C, there occurred a rearrangement with formation of ion(V); neutralisation of the acid solution led to methyl ether(VI), which than was transformed to lactol(VII). In the HSO_3F -SbF_5 -SO_2FCl mixture other rearrangements of isolone took place which gave dication(IX), and upon quenching-the ketoester (X).



A REGIOSELECTIVE REDUCTION OF 2-EXO-UNSATURATED BONDS IN 2-METHYLENE DERIVATIVES OF TESTOSTERONE

Microbiological models of metabolism in mammals.

J.Dmochowska-Gładysz, T.Kołek, B.Osipowicz, A.Siewiński
Agricultural University, Wrocław, Poland.

The transformations of four derivatives of testosterone with additional double bond : Δ^1/1/ ; Δ^6/2/ and exo C-2 /3 and 4/ were carried out by means of Aphanocladium album. The following results were obtained : /Fig 1/

17β-Hydroxy-1,4-androstadien-3-one/1/
17β-Hydroxy-4,6-androstadien-3-one/2/
→ Aph. album did not undergo transformation

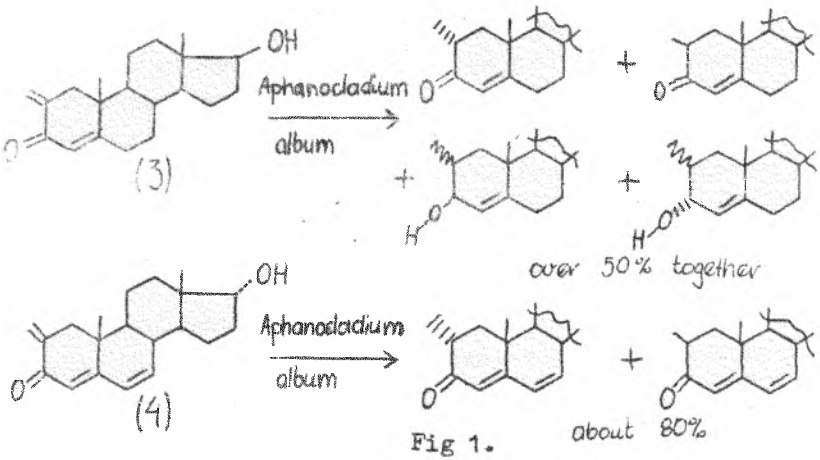


Fig 1.

-the substrates 1 and 2 did not undergo transformation
-in the next substrates 3 and 4 a regiospecific reduction of the exo-unsaturated bond at C-2 took place exclusively; both possible isomers at C-2 were formed
-the unstereospecific reduction of carbonyl group at C-3 in the substrate 3 was also observed.

THE MECHANISM OF ISOMERIZATION OF CARDENOLIDES

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Academy of Sciences of GDR,
Central Institute of Molecular Biology,
1115 Berlin-Buch, GDR

The action of KOH in EtOH/H_2O on digitoxigenin leads to the formation of 14,21-epoxy-20(22)-dihydro-digitoxigenin. This reaction and analogous ones are named "isomerization" of cardenolides and are known for more than 60 years. The different mechanisms proposed for this reaction are not sufficient to explain the experimental facts detected in the meantime by different investigators. However, this is reached by the following reaction sequence:
a) Deprotonation of 21-CH_2 of the lactone ring of cardenolides (1) leads to the 23-oxyfuryl anion (2).
b) Reprotonation of 2 takes place, in agreement with the HSAB principle, mainly at C21 leading to 1, but to a small extent at C22, too, leading to a 20 (21)-cardenolide (3).
c) Protonation of 3 at C20 leads to a cation (4) with the positive charge at C21 and O21. d) Electrophilic attack of 14ß-OH at C21 followed by deprotonation of 14ß-OH leads to the 14,21-epoxy-cardanolide (5), the isomerization product.
That means, isomerization needs a sequence of various reactions with different pH-dependence:
Step a) needs a strong base such as alcoholate, whereas steps b) and c) need sufficient protons, e.g., from H_2O. But higher concentration of H_2O blocks step a). The whole reaction sequence, i.e. the isomerization, is possible therefore, only in a relatively narrow pH-range as is realized, e.g., by KOH in a proper mixture of EtOH and H_2O. In the equilibrium between 1, 2, and 3 the last one is formed in small amounts only but is permanently formed from 1 to the extent as it is consumed in steps c) and d). According to this mechanism isomerization can be avoided by avoiding deprotonation at C21 or equilibrium pH-range.

NOVEL ANDROSTANE GLYCOSIDES

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Academy of Sciences of the G.D.R., Central Institute of Molecular Biology, 1115 Berlin-Buch, G.D.R.

M.M. Kabat, A. Kurek, M. Masnyk, and J. Wicha
Polish Academy of Sciences, Institute of Organic Chemistry, 01-224 Warszawa, Poland

The preparation of the 3ß-O-glycosides of various androstane compounds has been studied in an attempt to improve the Koenigs-Knorr method. In the presence of silver carbonate, finely deposited on celite, 17ß-substituted 5ß,14ß-androstane-3ß,14-diols react at room temperature in benzene with an O-acylglycosyl bromide to the O-acylated glycosides which, after mild removal of the protecting groups, give the glycosides in high yield with little or no side reactions. In the absence of a substituent at C17 the glycosidation leads in a small extent to the 14-anhydro compound.

The presence of a 4(5)-double bond in the aglycon prevents the formation of a glycoside because dehydration takes place to the 3,5-diene. To solve this problem modified reaction conditions has been studied to get glycosidation of an androst-4-ene derivative.

The target compounds has served as the key compounds for the elucidation of the structure-activity relationships in cardiac glycosides particularly for the definition of the lead structure, i.e. the substructure that meets the minimal receptor recognition requirement, cannot be functionally replaced by other structures and endows, in connection with suitable substituents, highest selectivity and potency in interacting with the receptor (Na^+/K^+-transporting ATPase).

SYNTHESIS AND NMR-STUDY OF STEROIDAL 2'-DEOXY-GLUCOSIDES

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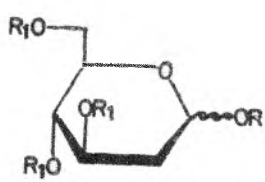
*Institute of Chemisty, Faculty of Sciences, University of Novi Sad, Veljka Vlahovića 2, 21000 Novi Sad, Yugoslavia

**Department of Organic Chemistry, L. Kossuth University, Debrecen, Hungary H-4010

In order to obtain some new sterol' glycosides with enhanced water solubility and/or potential biological activity, 2'-deoxy-glucosides (general formula I) have been synthesized.

The mentioned derivatives have been obtained, in a high yield, by an action of 2-deoxy-3,4,6-tri-O-acetyl-glucopyranosyl chloride on cholesterol, β-sitosterol and stigmasterol, in nitro-methane, in presence of $Hg(CN)_2$ as a catalyst. The formed mixtures of isomeric 2'-deoxy-glucosides were separated by column chromatography on silica gel, while the structures and configurations of the synthesized 2'-deoxy-glucosides (I) were determined on the basis of their specific optical rotations, as well as by interpreting the corresponding two-dimensional homo- and heterocorrelation ^{1}H- and ^{13}C-NMR--spectra.



R = Cholesteryl
β-Sitosteryl
Stigmasteryl

R_1 = Acetyl or H

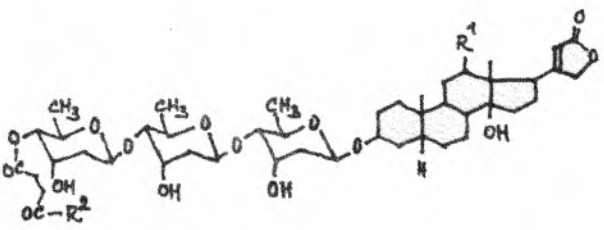
SUCCINATE CONJUGATES OF DIGITOXIN AND DIGOXIN

Pavel Drašar, Vladimír Pouzar, Ivan Černý, Miroslav Havel, and František Tureček*

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

*J.Heyrovský Institute of Physical Chemistry and Electrochemistry, Máchova 7, 121 38 Prague, Czechoslovakia

Digitoxin and digoxin 4‴-hemisuccinates (3-carboxypropanoates 1 and 2 were prepared by an indirect method, using dicyclohexylcarbodiimide-induced condensation of the cardioglycoside with 4-(2,2,2-trichloroethoxy)-4-oxobutanoic acid followed by removal of the 2,2,2-trichloroethyl group with zinc in acetic acid medium. In case of digoxin derivatives difficulties with acid-labile 14-hydroxy group arose, and alternative method, using 2-trimethylsilyl group removable by tetrabutylammonium fluoride in tetrahydrofuran, was developed. The hemisuccinates 1 and 2 were condensed with L-tyrosine methyl ester in tetrahydrofuran, using N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline as the coupling reagent. Structure of the products was proved by ^{1}H and ^{13}C NMR spectra. The obtained conjugates 3 and 4 are designed after radioiodination as a part of the RIA system for cardioglycoside analyses.



	R^1	R^2
1	H	OH
2	OH	
3	H	L-Tyr Me est.
4	OH	

PREPARATION OF DIGITOXIGENIN 3-(β-D-GLUCOPYRANOSIDE) BY DIGITALIS LANATA CELLS

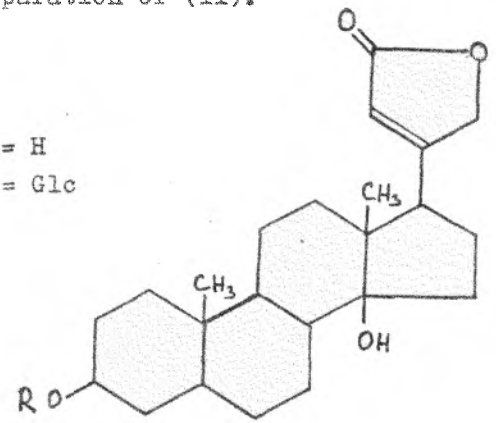
T. Vaněk[1], T. Macek[1], H. Barešová[2], J. Harmatha[1]

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

[2]Institute of Experimental Botany, Czechoslovak Academy of Sciences, 166 30 Prague, Czechoslovakia

The glucosylation of digitoxigenin (I) producing digitoxigenin 3-(β-D-glucopyranoside) (II) was performed with relatively high yield using cells of Digitalis lanata, strain DIG 32. Cells cultivated on medium of Murashige and Skoog, supplemented with 2,4-dichlorophenoxyacetic acid and kinetin gave 36% yield of product (II) after one week of incubation in shaked flasks (dark, 27°C). The biotransformation rate was obtained at the cell concentration 100g of fresh weight per liter and digitoxigenin concentration 100 mg per liter of nutrient medium. The conversion yield is comparable with the yield of chemical methods of preparation of (II).

I R = H
II R = Glc



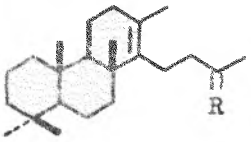
SYNTHESIS OF Δ^{12}- AND $\Delta^{13(14)}$-ISO-20-DEOXOLUTEONES

P.F.Vlad and N.D.Ungur

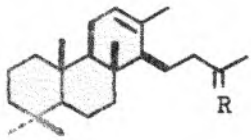
Institute of Chemistry, the Moldavian SSR Academy of Sciences, Kishinev 277028, USSR

The synthesis of Δ^{12}- and $\Delta^{13(14)}$-iso-20-deoxoluteones (I)-(III) from 13Z- and 13E-bicyclogeranylgeranylacetones (IV) and (V) was realised.

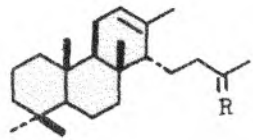
The ketones (IV) and (V) were reduced into the corresponding alcohols (VI) and (VII) which were acetilated into acetates (VIII) and (IX) and the latter were cyclized by fluorsulfuric acid in the tricyclic compounds (X)-(XII). Saponification of the esters (X)-(XII) followed by oxidation of the reaction products (XIII)-(XV) with the pyridine chromate leads to ketones (I)-(III).



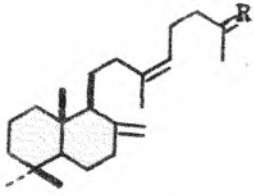
I,X,XIII



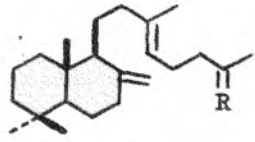
II,XI,XIV



III,XII,XV



IV,VI,VIII



V,VII,IX

I-V R=O; VIII-XII R=H,OAc; VI,VII,XIII-XV R=H,OH

SYNTHESIS OF 21,27-BISNOR-DEMISSIDINE AND 21,27-BISNOR--SOLANIDINE. CONFIRMATION OF THE STRUCTURE OF 21,27-BISNOR-DEMISSIDINE BY X-RAY ANALYSIS

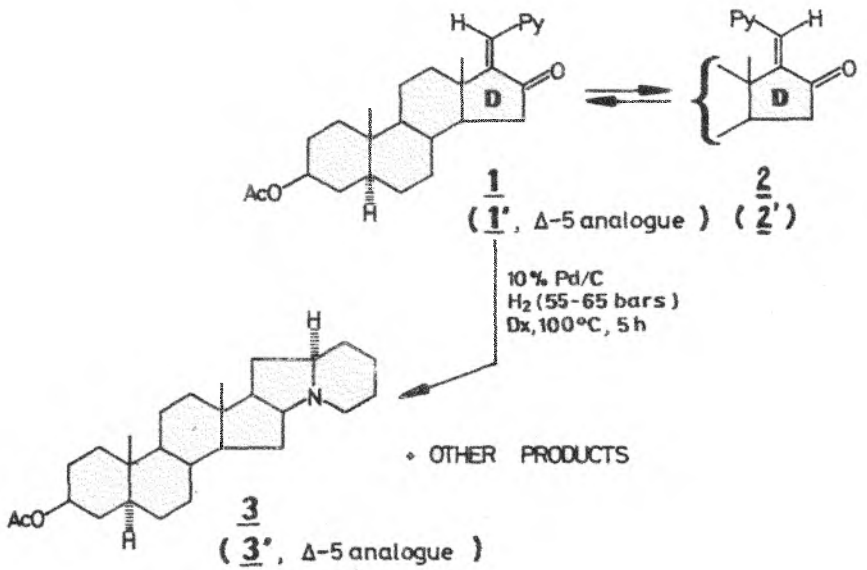
K. Gaši, M. Kindjer and D. Miljković

Institute of Chemistry, Faculty of Sciences, Novi Sad, Yugoslavia

S. Stanković

Institute of Physics, Faculty of Sciences, Novi Sad, Yugoslavia

3β-Acetoxy-17-picolinylidene-5α-androstan-16-one (both geometrical isomers, 1 and 2), as well as their Δ-5 analogues (1' and 2') were synthesized from epiandrosterone- and dehydroepiandrosterone acetates in four steps. The reductive cyclization reaction of 1 (1') and or 2 (2') was successfully carried out under the conditions of catalytic hydrogenation (Scheme 1). The structure of 3β-acetoxy-21,27-bisnor--5α-solanidane (3) was confirmed by X-ray structural analysis.



Scheme 1.

FORMATION OF DEOXYCHOLIC ACID LACTONES

K. Kuhajda[1], J. Hranisavljević[2] and D. Miljković[1]

1. Institute of Chemistry, Faculty of Sciences, Novi Sad, Yugoslavia

2. Institute of General and Physical Chemistry, Belgrade, Yugoslavia

Deoxycholic acid (1) was firstly converted to 3α-acetoxy--12α-hydroxy-5β-cholanic acid (2), in a yield of 60%, by treating 1 with AcOH in presence of catalytic amound of $HClO_4$ (room temperature, 4 hours). By treating the compound 2 with dichloroethylphosphate and Et_3N in $MeCl_2$ at room temperature during 96 hours, 3α-acetoxy-12αhydroxy-5β-cholanic acid lactone (3) was obtained in a very satisfactory yield (60%). This surprisingly clean and smooth formation of the eight-membered lactone (3) can be explained by steric proximity of the C-24 carboxyl function and 12α-hydroxy group and by using proper experimental conditions. Mild treatment of 3 with $NaOCH_3$ in benzen afforded 3α-hydroxy-lactone 4 (withaut affecting the lactone ring).

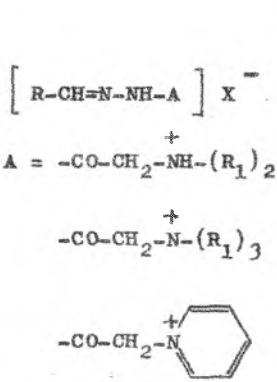
The structure of 2, 3 and 4 were unambigously proved by spectroscopic data (^{1}H-NMR; ^{13}C-NMR; and M-spectra) and by satisfactory elemental microanalyses.

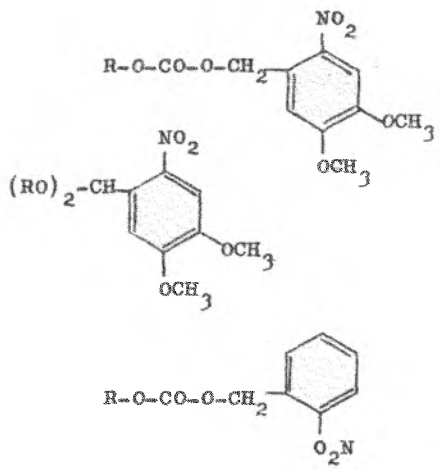
SYNTHESIS OF SOME PROPHEROMONES

Souček M., Streinz L., Vrkoč J. and Romaňuk M.

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

Some propheromone derivatives of active aldehydes and alcohols (R) were prepared using Girard reagents, 2-nitrobenzylalcohol, 4,5-dimethoxy-2-nitrobenzylalcohol or 4,5-dimethoxy-2-nitrobenzaldehyde as a derivatizing agents. All compounds possessed sufficient degree of purity. When tested under laboratory conditions, both corresponding Girard and 2-nitroderivatives were found to answer the purpose, the former liberating active components even after 120 days of the experiment, the latter getting decomposed by UV light. All the compounds will be trialed during the next season.





SYNTHESIS AND DETERMINATION OF THE ENANTIOMERIC PURITY OF (R)- AND (S)-3-METHYL-1,2,3-BUTANETRIOL-1-(4-METHYLBENZENESULFONATE)

E. Schrötter, A. Hauser, H. Hamann and H. Schick
Central Institute of Organic Chemistry of the Academy of Sciences of the GDR, Berlin,
German Democratic Republic

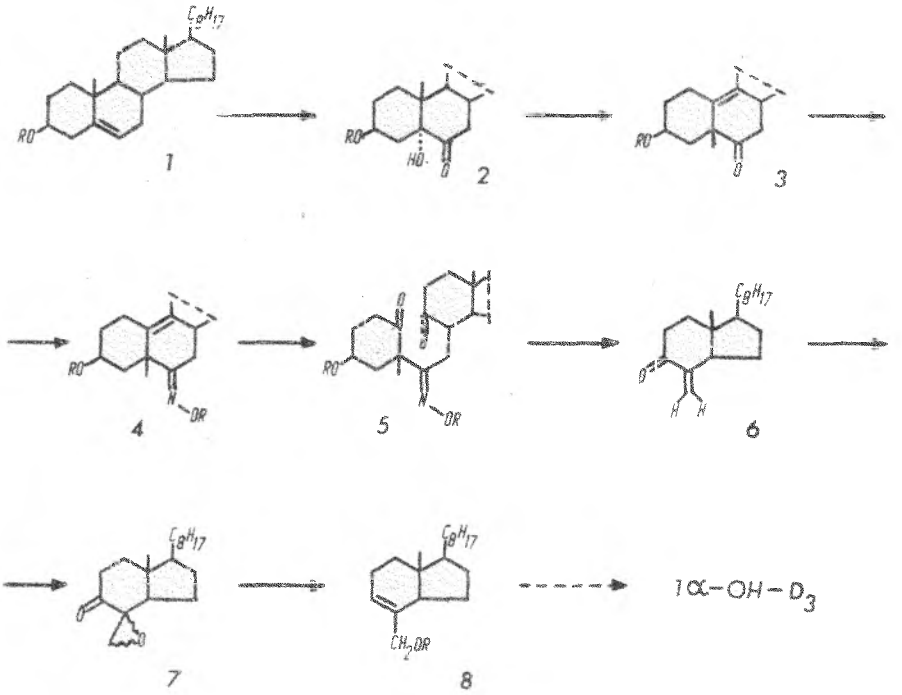
The enantiomeric 3-methyl-1,2,3-butane-triol-1-(4-methylbenzenesulfonates), chiral building blocks for vitamins (1) and carotinoids (2), were resynthesized because different physical constants are reported in the literature (1,2). The data of the (S)-enantiomer were corrected. A new reaction path to the (S)-enantiomer shortened by four steps was described. The optical purity of both enantiomers, estimated by ^{1}H-NMR with the aid of a chiral shift reagent, was better than 94 %.

1) H. TAKAYAMA, S. YAMADA and M. OHMORI,
Europ. Pat. 45 524
2) R. DUMONT and H. PFANDER,
Helv. Chim. Acta 66, 814 (1983)

THE EASY DEGRADATION OF CHOLESTEROL TO 8-METHYLENE--DES-A,B-CHOLEST-9-ONE

Jacek W. Morzycki, Jarosław Jurek and Władysław J. Rodewald

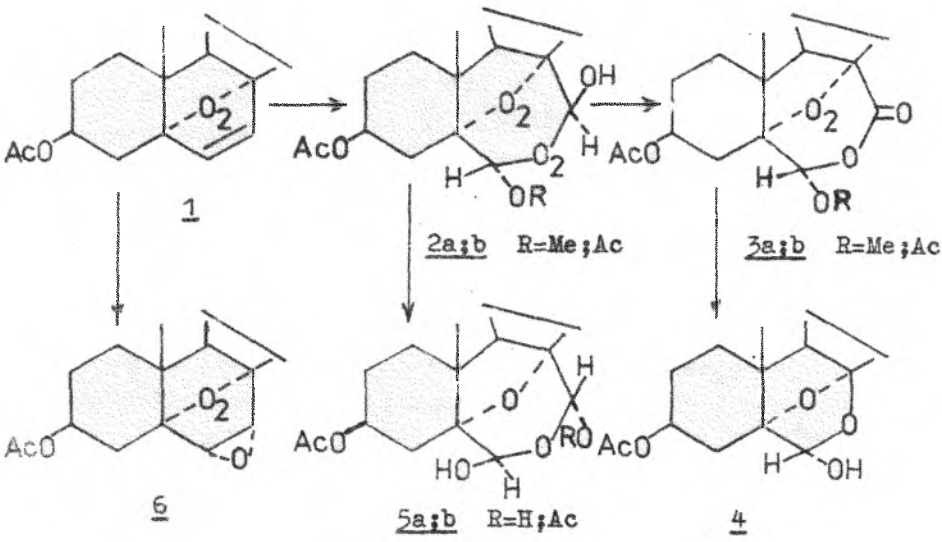
Department of Chemistry, University of Warsaw



The simple and convenient route to CD fragment 6 useful for the synthesis of vitamin D_3 relatives is presented. The crucial step consists in compound 5 fragmentation to the α-methylene ketone 6. The mechanism of this reaction is discussed. The conversion of compound 6 to the allylic alcohol 8, the intermediate in Lythgoe's synthesis of 1α-OH-D_3, is to show it may serve as a precursor of vitamin D_3 relatives.

REARRANGEMENTS OF RING B POLYOXYGENATED STEROIDS

Wojciech J. Szczepek and Jerzy Gumułka
Department of Chemistry, University of Warsaw
02093 Warszawa, Pasteura 1, Poland



We have recently shown that ozonolysis of 7-dehydrocholesterol acetate peroxide 1 and spontaneous decomposition of primary products gave compound 4 and corresponding 5,8-seco-6,7-dinor-5,8-dione.

Ozonolysis of 1 in the presence of methanol or acetic acid and chromatography on SiO_2 gives methoxy- or acetoxy-product (2a or 2b), respectively. Both compounds (2a and 2b) undergo rearrangement to give the methoxy-lactone 3a or acetoxy-lactone 3b. The labile lactones afford compound 4 as the final stable product.

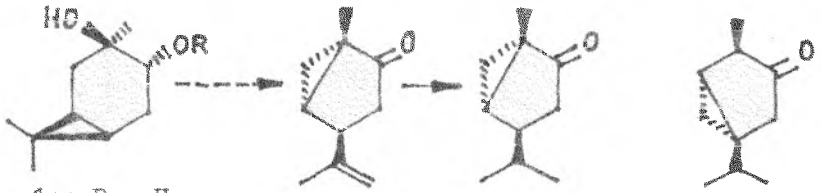
The rearrangement of epidioxy-epoxide 6 will be also presented.

SYNTHESIS OF /+/-4-TRANS-ISOPROPYL-1-METHYLBICYCLO-[3.1.0]HEXAN-2-ONE FROM /+/-3-CARENE

Mirosław Walkowicz and Sławomir Janicki

Institute of Organic and Physical Chemistry,
Technical University, Wrocław

Interesting pharmacological properties of /-/-isothujone /4/, described in literature, prompted us to elaborate a simple synthesis of /+/-4-trans-isopropyl--1-methylbicyclo[3.1.0]hexan-2-one /3/. Ketone 3 has the same and identically sterically situated alkyl substituents as 4 but differs from it in position of the cyclopropane ring.



1a: R = H
1b: R = Ac

2 3 4

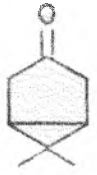
Synthesis of ketone 3, described by Kropp in 1966, is rather troublesome, e.g. 3β,4α-caranediol /1a/ was synthesized via epoxide. We utilized simple hydroxylation of /+/-3-carene for obtaining this diol. Some modifications of procedure of dehydration of acetate 1b, with application of smaller amounts of reagents /$POCl_3$ and pyridine/ and of lower temperature, allowed us to reach yields higher by ca.20%. Crude dehydration products after hydrolysis to unsaturated alcohols /mixture of alcoholic precursor of ketone 2 and carenol/ were oxidized with excess of CrO_3 in acetone affording practically only ketone 2. Hydrogenation of 2 by the use of a selective catalyst yielded bicyclic saturated ketone 3 in high yield.

UTILISATION OF 6,6-DIMETHYLBICYCLO[3.1.0]HEXAN-3-ONE FOR SYNTHESIS OF TRANS-CHRYSANTHEMIC ACID

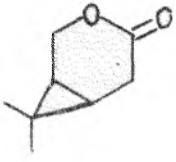
Stanisław Lochyński, Bogdan Jarosz, Mirosław Walkowicz and Krzysztof Piątkowski

Institute of Organic and Physical Chemistry, Technical University, Wrocław

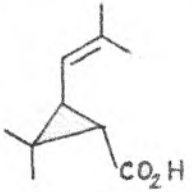
3-Acetyl-6,6-dimethylbicyclo[3.1.0]hexane can be obtained in high yield from readily accessible bromohydroxycarane. This ketone was transformed, via acetate and alcohol, in 6,6-dimethylbicyclo[3.1.0]hexan-3-one /1/.



1



2



3

The Baeyer-Villiger reaction of ketone 1 afforded lactone 2 which yielded monocyclic diol by the Grignard reaction. Oxidation of the primary hydroxy group in this compound led to corresponding hydroxy acid which was then cyclized to dihydrochrysanthemolactone. Its hydrolysis with simultaneous dehydration resulted in the formation of trans-chrysanthemic acid /3/.

UREIDOGERANYL ETHERS AS INSECT GROWTH REGULATORS

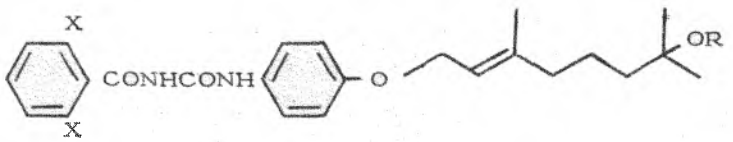
R.Balicki[x],W.Biernacki[x],M.Kozłowska[x], J.Nawrot[xx],W.Sobótka[x], B.Styczyńska[xxx]

[x]Institute of Organic Chemistry,Polish Academy of Sciences, Warsaw, Poland ;

[xx]Institute for Plant Protection,Poznań,Poland ;

[xxx]State Institute of Hygiene, Warsaw,Poland.

A series of 4 - [N'- (2",6"- dihalogenobenzoyl)-ureido] - 1 - (7' - alkoxygeranyl)-phenylene ethers (I) has been obtained and bioassayed on selected insect species. Since the ether molecule I includes both the isoprenyl unit , which also occurs in several insect hormonomimetics like sesquiterpenoid juvenoids , and the disubstituted urea moiety characteristic for insect chitin inhibitors we expected to find new morphogenetic properties within this group of compounds.



I

X = Cl , F

R = Me, Et

High mortality of stored-product pest Tribolium confusum Duv. larvae and substantial changes in female Musca domestica L. adults development were observed after exposure of the insects to some of the ethers I

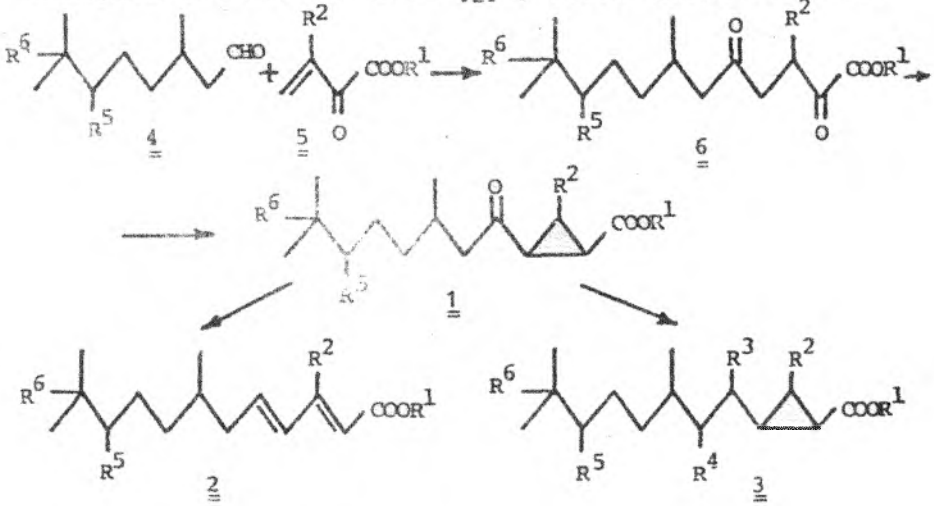
NEW JUVENILE HORMONE ANALOGS. SYNTHESIS OF ALKENOIC ACID DERIVATIVES WITH CYCLOPROPANE RING

Gábor Baán[a], Péter Vinczer[a], Lajos Novák[b], Csaba Szántay[a,b]

[a]Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, Hungary

[b]Institute for Organic Chemistry, Technical University of Budapest, H-1111 Budapest, Hungary

We elaborated a simple synthesis of derivatives of dodecanoic acid with cyclopropane ring [1] using "umpol" reaction in the key step. These compounds [1] were suitable key intermediates for the preparation of known [2] (Hydroprene, Methoprene e.t.c.) and novel [3] juvenile hormone analogs.



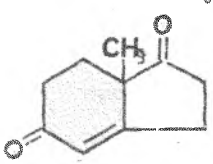
Compounds 1 were synthesized *via* alkyl 2,5-dioxododecanoates [6] prepared from natural dihydrocitronellal [4] with nucleophilic acylation and they were transformed into new alkenoic acid type juvenoids [3] having an "internal" cyclopropane ring close to the carboxylic acid group.

Intermediates 1 were also converted into known alkyl 2(E), 4(E)-dodecadienoates (Hydroprene, Methoprene).

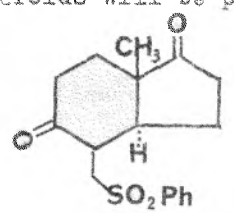
UTILIZATION OF ENEDIONE (I) FOR TOTAL SYNTHESIS OF 6α-METHYL-STEROIDS

Andrzej Robert Daniewski and Emilia Piotrowska
Institute of Organic Chemistry, Polish Academy of Sciences
01-224 Warsaw, ul. Kasprzaka 44/52, Poland.

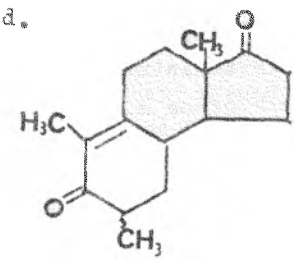
The chiral enedione (I) was transformed into tricyclic compound (III) through Wiechert's sulphone (II). Conversion of III into 6α-methyl-steroids will be presented.



I



II

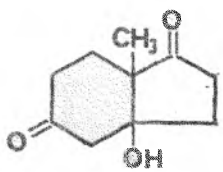


III

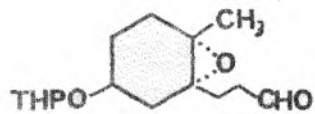
SIMPLE WAY TO CHIRAL SYNTHON USED IN van TAMELEN[1] BIOMIMETIC SYNTHESIS OF STEROIDS

Andrzej Robert Daniewski and Jarosław Kiegiel
Institute of Organic Chemistry, Polish Academy of Sciences
01-224 Warsaw, ul. Kasprzaka 44/52, Poland.

The five steps synthesis of chiral epoxide (II) starting from easily avilable dione (I) will be presented.



I



II

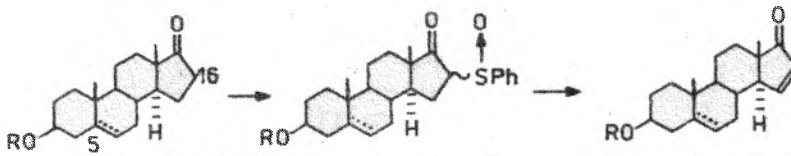
1. E. E. van Tamelen and J. R. Hwu, J. Am. Chem. Soc., 105 2490 (1983).

AN IMPROVED PROCEDURE FOR PREPARATION OF ANDROST-15-EN-17-ONE DERIVATIVES

G.Groszek, A.Kurek, M.M.Kabat, M.Masnyk, J.Wicha

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

The sulfinylation[1] of representative 17-oksoandrostane derivatives 1a - 1d with methyl benzenesulfinate and pyrolysis of 16β - phenylsulfinyl-17-ketones 2a, 2e and 2f leading shortly and inexpensivly to α,β -unsaturated ketones 3a, 3b and 3c is discribed/ overall yield 40-56%/. This method is also applicable for large scale preparations.



1a R= CH_3,5α-H
b R= THP,5-ene
c R= THP,5β-H
d R= H ,5β-H

2a R= CH_3,5α-H
b R= THP,5-ene
c R= THP,5β-H
d R= S/O/Ph,5β-H
e R= H ,5-ene
f R= H ,5β-H

3a R= CH_3,5α-H
b R= H ,5-ene
c R= H ,5β-H

THP = 

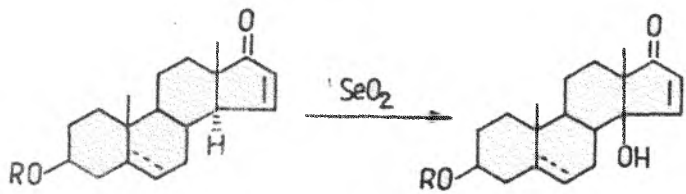
1. H.J.Monterio, J.P. DeSouza, Tetrahedron Letters, 1975, 921: R.M.Coates, H.D.Piegott, Synthesis, 1975, 319.

A NEW METHOD FOR PREPARATION OF 14β-HYDROXY-ANDROST-15-EN-17-ONES

G. Groszek, M.M. Kabat, M. Masnyk, J. Wicha

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

In the course of our studies on synthesis of cardenolides a one-step procedure for preparation of 14β-hydroxyandrost-15-en-17-ones was developed.
Treatment of androst-15-en-17-ones with selenium dioxide in dioxane - water (4:1) solution under reflux temperature for 6 - 8 hr. gives directly corresponding 14β-hydroxy derivatives.



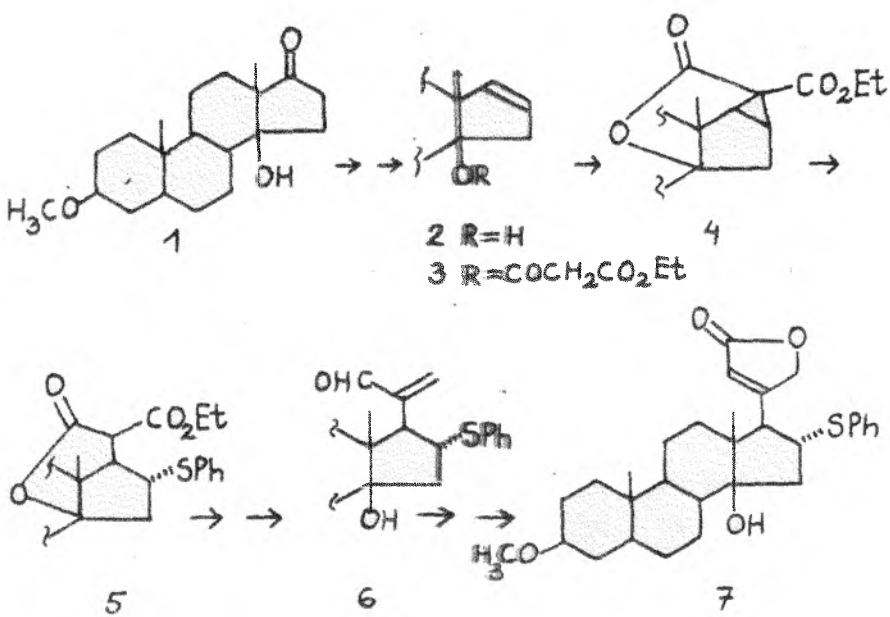
Starting material	Yield
R = CH_3, 5α-H	60%
R = Ac , 5β-H	52%
R = H , 5β-H	56%
R = Ac , 5-ene	47%

Previously described methods for preparation of the title compounds from androst-15-en-17-ones involved at least two steps and were less efficient.

A SYNTHESIS OF CARDENOLIDES FROM 14β-HYDROXY-17-OXOANDROSTANE DERIVATIVES

Alicja Kurek and Jerzy Wicha
Institute of Organic Chemistry of the Polish Academy of Sciences, 01-224 Warsaw, Kasprzaka 44, Poland

Synthesis of the cardenolide7 from 14β-hydroxyandrostan--17-one derivative 1 is described. The major transformations are shown in the scheme. Attempted synthesis of the bufadienolide starting from the intermediate 5 will be presented.



BIOLOGICAL ACTIVITY OF SOME ANDROSTANE DERIVATIVES

H.Velgová [a], L.Stárka [b]

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

[b]Endocrinological Research Institute, 116 94 Prague 1, Czechoslovakia

3β,7-Diacetoxy-6,7-seco-5-androsten-17-one[1] was converted into 17β-hydroxy-5-methyl-6-oxa-5β-androstan-3-one and 17β-hydroxy-6,7-seco-4-androsten-3-one. Neither of the substances was found active in tests for antiandrogens. Previously this kind of biological activity was found in 4,5-seco analogues of testosterone[2].

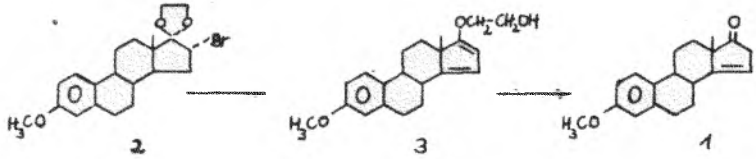
[1] H.Velgová, V.Černý: Coll.Czech.Chem.Commun. 41, 2630 (1976).

[2] L.Stárka, R.Hampl, A.Kasal, L.Kohout: J.Steroid Biochem. 17, 331 (1982).

PREPARATION OF 3-METHOXY-ESTRA-1,3,5(10),14-TETRAEN-17-ONE UNDER CONSIDERATION OF INDUSTRIAL ASPECTS

H.Kasch and K.Ponsold
Central Institute of Microbiology and Experimental Therapy,
Academy of Sciences of the GDR , Jena

3-Methoxy-estra-1,3,5(10),14-tetraen-17-one 1 is interesting in synthesis of heart active and other biologically active substances. In literature the best method for the preparation of 1 is the reaction of 16α-bromo-17,17-ethylendioxy-estra-1,3,5(10)-triene 2 with potassium-tert.-butoxide in DMSO followed by acid isomerisation and ketal cleavage /1/.
In this connection we studied the dehydrobromination of 2. On one hand we tried to optimize the synthesis and on the other we wanted to substitute relatively expensive reagents such as potassium-tert.-butoxide by KOH or methanolic KOH.
We found that one product, the enolether 3 , which was formed as a byproduct during dehydrobromination and normally was neclected could be used for synthesis of 1 in the same reaction sequence as for Δ^{15}-ketal.



2 3 1

The influence of temperature and basicity of different reagents such as potassium-tert.-butoxide, KOH, KOEt, KOMe, NaOMe and potassium-iso-propoxide in different solvents like xylene, DMSO, DMF and DMA on the substitution- and elimination- reactions is discussed as well as the isomerisation of the 15-double bond into 14-position.
Although the cheap KOH or methanolic KOH was used in the dehydrobromination step the overall yield of 1 could be increased from 80 % to 90 % /2/.

/1/ J.H.Fried , US 3.372.175 ; CA 69 ,(1968) , 87 365 u
/2/ H.Kasch, K.Ponsold , DD 213 633

INSECT ANTIFEEDANT ACTIVITY OF AZADIRACHTIN AND FOUR PRIEURIANIN TYPE LIMONOIDS

Zev Lidert, David A. H. Taylor, Muthuvelu Thirugnanam and Keith Wing

Rohm and Haas Company, Research Laboratories, Spring House, PA 19477, USA

Abstract.

Plants of Meliaceae family have been used in folk medicine and to control insect pests. Limonoid azadirachtin is a well-known insect antifeedant isolated from seeds of a Meliaceae tree Azadirachta indica (neem tree), commonly occuring in many tropical arieas. The mode of action of azadirachtin is still not clearly understood, but the gross, measurable effects are feeding, growth and ecdysis inhibition.

We wish to report antifeedant activities of four structurally interrelated limonoids of prieurianin class using azadirachtin as a standard. These limonoids were prieurianin acetate, prieurianin, rohitiuka-7 and rohitiukin isolated from Trichilia prieuriana, Trichilia dregeana and Aphanamixis polystacha of Meliaceae family. Test insects were tobacco budworm (Heliothis virescens F.), southern army worm (Spodoptera eridania Cramer) and mexican bean beatle (Epilachna varivestis Mulsant). Prieurianin acetate was remarkably active at a level comparable to that of azadirachtin.

Our results indicate great activity variations with seemingly negligible structural changes within the same structural framework. Particularly surprising is inactivity of rohitiukin.

PHYTOECDYSTEROIDS OF SILENE GENUS.

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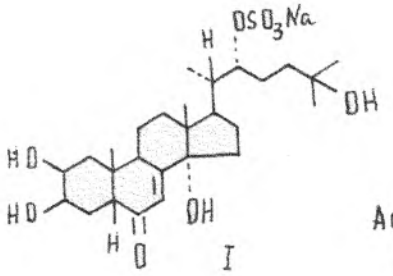
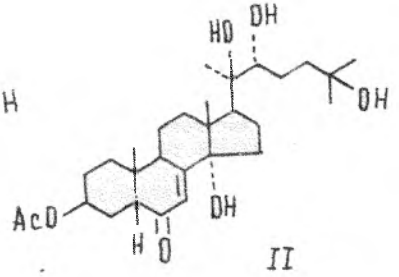
22-Sulfat-α-ecdysone(I) and 2-deoxyecdysterone-3-acetate(II) from Silene brachuica Boiss. and Silene praemixta M. Pop. respectively (family Coryophyllaceae),have been isolated besides glycoside formes of ecdysterone and integristerone A reported earlier/I/.

From Silene nutans L. ecdysterone,polypodine B and two new phytoecdysteroides 22-deoxyecdysterone(III) and nusilsteron (IY) were isolated HPLC.



I



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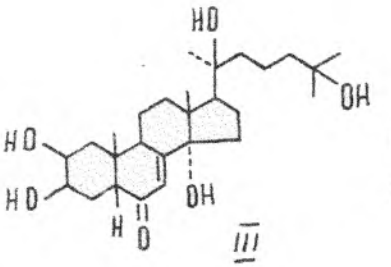
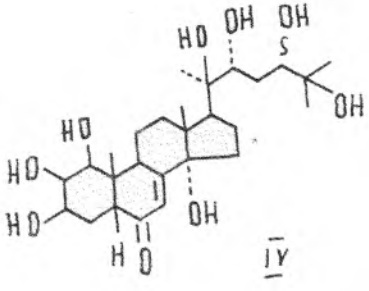


III



IY

/I/. N.K.Abubakirov. Khimija prirod.soedin.685-702 (I98I).

NEW WITHASTEROIDES FROM PHYSALIS GENUS

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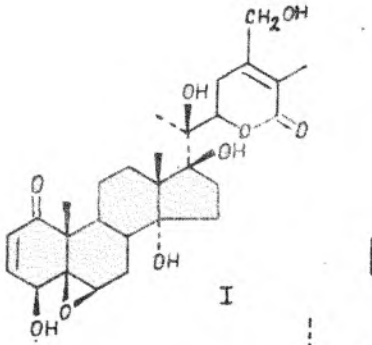
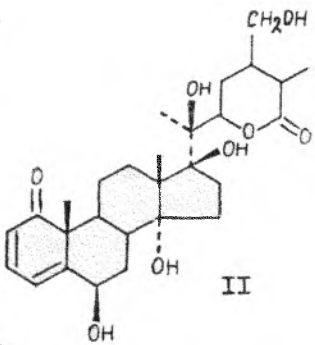
Four new withasteroides have been isolated from 3 species of Physalis genus. The structures of visconolide (I) and 28-hydroxywithaperuvin C (II) (from Ph.viscosa), ixocarpanolide (III) (from Ph.ixocarpa) and 14α-hydroxy-ixocarpanolide (IV) (from Ph.angulata) have been elucidated on the basis of spectral data, including ^{1}H and ^{13}C NMR- spectra, and some chemical transformations.



I



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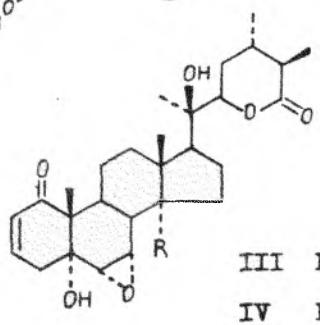

III R = H

IV R = OH

SESQUITERPENIC ESTERS OF CAROTANE TYPE FROM FERULA AKITSCHKENSIS

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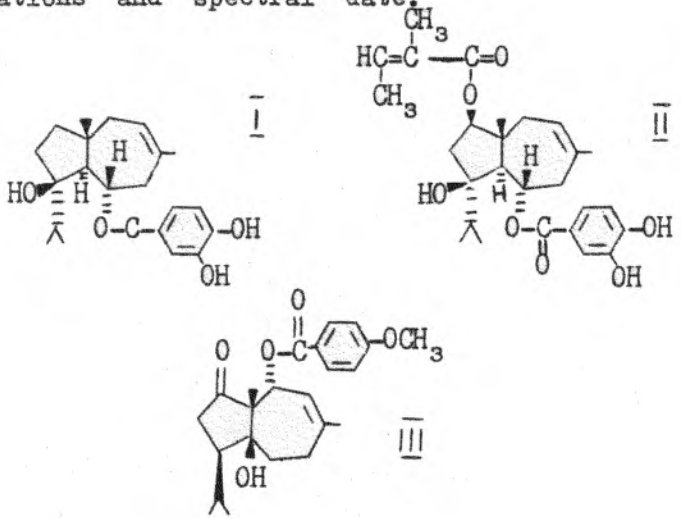
The sesquiterpenic esters akiferidine (I), akiferidinine (II) and akifericine (III) have been isolated from the Ferula akitschkensis.

The structure and stereochemistry of substances have been proved on the basis of chemical transformations and spectral date.



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