"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

Sorm, F.

7

The synthesis of L-4-amino-3-isoxazolidinone, the unnatural stereoisomer of cycloserine and its antibiotic activity. J. Sauer, J. Beránek, J. Sicher, J. Škoda, V. F. Hess, and F. Sorm (Czech. Acad. Sci., Prague). *Experientia* 13, 291 (1957) (in English); cf. C.A. 51, 1468c.—L-Serine or D-serine (Me ester) was successively treated with NEt_3 and trityl chloride to give 1-(triphenylmethyl)-2-carbomethoxyethylenimine (I) (L, m. 123-5°, $[\alpha]^{20}_{D}$ −94.2° in $CHCl_3$; D, m. 123-4°, $[\alpha]^{20}_{D}$ 95.0° in $CHCl_3$). I was then treated with NH_2OH and $MeONa$ to yield 1-triphenylmethyl-3-hydroxycarbamoylethylenimine (II) (L, m. 164°, $[\alpha]^{20}_{D}$ −101.8° in $CHCl_3$; D, m. 163°, $[\alpha]^{20}_{D}$ 102.0° in $CHCl_3$). II was converted in HCl to α-amino-β-chloro-*N*-hydroxypropionamide (III) (L, m. 199-4°, $[\alpha]^{20}_{D}$ −14.1° in MeOH; D, m. 194-3°, $[\alpha]^{20}_{D}$ 14.2° in MeOH). III was then cyclized with Zerolit FF to 4-amino-3-isoxazolidinone (L, m. 153-4°, $[\alpha]^{20}_{D}$ −114.5° in H_2O; D, m. 152-3°, $[\alpha]^{20}_{D}$ 115° in H_2O). Tests with cultures of *Escherichia coli* indicate that DL-4-amino-3-isoxazolidine is substantially more antibiotic than either of the optically active forms. D. S. Farner

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

GRYUNBERGER, D. [Grünberger, D.]; SHORMOVA, Z. [Šormova, Z.]; SHORM, F. [Šorm, F.]

Effect of albomycin on oxidation processes and nucleic acid metabolism in Staphylococcus aureus and Escherichia coli [with summary in German]. Biokhimiia 22 no.1/2:148-153 Ja-F '57. (MLRA 10:7)

1. Biokhimicheskoye otdeleniye Khimicheskogo instituta Chekhoslovatskoy akademii nauk, Praga.

(MICROCOCCUS PYOGENES, effect of drugs on,
albomycin, on oxidation & nucleic acid metab. (Rus))
(ESCHERICHIA COLI, effect of drugs on
same)
(ANTIBIOTICS, effects,
albomycin on E.coli & Micrococcus pyogenes aureus
oxidation & nucleic acid metab. (Rus))
(NUCLEIC ACIDS, metabolism,
E.coli & Micrococcus pyogenes aureus, eff. of albomycin
(Rus))

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, F.; ROMANUK, M.

"Terpenes. LXXIII cis- and trans-bicylo (o, 3, 5) decane. In German."

p. 779 (Collection of Czechoslovak Chemical Communications, Sbornik,Chekhoslovatskikh Khimicheskikh Rabot) Vol. 22, no. 3, June 1957
Prague, Czechoslovakia

SO: Monthly Index of East European Accessions (EEAI) LC. Vol. 7, no. 4, April 1958

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, F.

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and Their Synthetic Analogs. G-3

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11420.

Author : Jarolim, V., Streibl, M., Dolejs, L., and Sorm, F.
Inst : Not given.
Title : On Terpenes. LXXV. Cis- and Trans-homocaryophyllenic Acid. LXXVI. Synthesis of 4,8,11,11-tetramethylricyclo-(0,2,7)-undecance (Caryophyllene).

Orig Pub: Sbornik Chekhoslov Khim Rabot, 22, No 4, 1266-1276; 1277-1282 (1957) (in English with a summary in Russian)

Abstract: See RzhKhim, 1957, 44661, 44662.

Card : 1/1

3

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and their Synthetic Analogs. G-3

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11467.

Author : Smrt, J., Beranek, J., Sicher, J., and Sorm, F.
Inst :
Title : Synthesis of 4-amin-3-isooxazolidone (Cycloserine)

Orig Pub: Chem Listy, 51, No 1, 112-122 (1957) (in Czech); Sbornik Chekhoslov Khim Rabot, 22, No 1, 262-273 (in English with a summary in Russian)

Abstract: The antibiotic cycloserine (I) (see RZhKhim, 1956, 16239) has been synthesized from the methyl ester of N-tritylserine (II) via the methyl ester of O-mesyl-N-tritylserine (III), 1-trityl-2-carbomethosyethyleneimine (IV), which on reaction with $NH_2OH.HCl$ gives

Card : 1/10

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and their Synthetic Analogs. G-3

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11467.

hydroamic acid (V); the latter adds HCl with the formation of the hydrochloride of α-amino-β-chloropropiohydroxamic acid (VI); strongly basic anion exchange resins cyclize VI to I. For comparison purposes 4-benzylamine- (IX) and 4-benzhydrylaminoisoxazolidone-3 (X) were synthesized from N-benzyl-2-carbomethoxyethyleneimine (VII) and N-benzhydryl-2-carbomethoxyethyleneimine (VIII) by the same method. 1-benzylethyleneimine-2-carbohydroxamic acid (XI) is synthesized by refluxing 87.5 gms of the methyl ester of 1,2-dibromopropionic acid [sic] in 550 ml C_6H_6 for 3 hrs with 71.4 gms triethylamine and 38.2 gms benzylamine, shaking the mixture with water for 12 hrs and allowing the mixture to stand with VII [TN: meaning appears garbled] for 48 hrs, obtained by eva-

Card : 2/10

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and their Synthetic Analogs. G-3

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11467.

0.5 liter CH_3OH with 12.5 gms Na_2CO_3 in 1 liter water, allowing to stand 4 days, and acidifying with 50 ml CH_3COOH in 200 ml alcohol; the yield is 73%, mp 139-141° (decomp; from CH_3OH). Hydrogenation and hydrolysis of the latter product give serine. The hydrogenation of 0.03 mol X in 100 ml alcohol and 1 ml CH_3COOH over PtO_2 by 800 ml H_2 gives 2.15 gms of the amide of N-benzhydrylserine, mp 142-144° (from alcohol). A mixture of 0.03 mol II, 50 ml dry pyridine, and 2.5 ml mesyl chloride is kept 24 hrs at 0.4°, diluted with 200 ml water and $CHCl_3$; III is extracted in 90% yield, mp 128° (from benzene-alcohol) 0.01 mol II in 50 ml dioxane is mixed with NH_2OH (prepared from 14 gms $NH_2OH.HCl$ in 100 ml abs

Card : 7/10

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and their Synthetic Analogs. G-3

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11467.

CH_3OH and 5.9 gms Na in 80 ml CH_3OH); after 3 days the reaction mixture is diluted with 100 ml water, and neutralized with CH_3COOH; further dilution results in the formation of a precipitate (33 gms) of N-tritylserinehydroxamic acid, mp 109° (CH_3OH); the product contains 1 molecule of combined CH_3OH. A mixture of 0.02 mol III, 20 ml C_6H_6, 1 ml CH_3CH, and 2.5 gms N-ethylpiperidine is refluxed 8 hrs, diluted with 15 ml $CHCl_3$, washed with water, and evaporated; the yield of IV is 80%, mp 130-131° (from benzene-cyclohexane). On standing for 3 days a mixture of 0.18 mol IV in 100 ml dioxane and 25.2 gms $NH_2OH.HCl$ and 12.4 gms Na in 150 ml CH_3OH

Card : 8/10

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11467.

gas; after 3 hrs VI is obtained by suction filtration, yield 66%, mp 191° (decomp; from CH_3OH-ether). Hydrogenation and hydrolysis of the latter product give XII. 0.06 mol VI in 100 ml water is passed for 10 min through a column containing 300 ml [sic] of amberlite IRA-4000 anion exchange resin (strongly basic), the column is washed with 1 liter water (1 hr), and the product is eluted at 0° with 20% CH_3COOH. The eluate is collected until the pH attains 5.8, and the solution (60 ml) is diluted with 450 ml alcohol; at -60° DL-I precipitates, yield 51%, mp 141-142.5o (from 80% alcohol).

Card ; 10/10

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and Their Synthetic Analogs. G-3

Abs Jour: Ref Zhur-Khim., No 13, 1958, 43491.

Author : Fajkos J., Sorm F.
Inst :
Title : On Steroids. XXVIII. Synthesis of Analogues of Progesterone and Desoxycorticosterone With the Side Chain in Position 16.

Orig Pub: Sb. chekhosl. khim rabot, 1957, 22, No 6, 1873-1886.

Abstract: See RZhKhim, 1958, 11432.

Card : 1/1

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and Their Synthetic Analogs. G-3

Abs Jour: Ref Zhur-Khim., No 13, 1958, 43474.

Author : Suchy M., Herout V., Sorm F.
Inst :
Title : On Terpenes. LXXVII. On the Nature of Arctiopicrin -- the Unsaturated Lactone from Arctum Mines Bernh.

Orig Pub: Sb. chekhosl. khim. rabot, 1957, 22, No 6, 1902-1908.

Abstract: See RZhKhim, 1957, 54490.

Card : 1/1

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

Solle, F.

"Academician R. Lukes at sixty." p. 399.

Institute of Applied Physics, (Czechoslovak Academy of Sciences.) Vol. 91, no. 3, Mar. 1957.

SO: Monthly Index of EAST European Accession (EEAI) LC, Vol. 7, No. 5 May 1958

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, FRANTISEK

CZECHOSLOVAKIA/Organic Chemistry - Synthetic Organic Chemistry. G-2

Abs Jour: Referat Zhur-Khimiya, No 5, 1958, 14358.

Author : Novak Jiri, Ratusky Josef, Snoberk Vladimir, Sorm Frantisek.
Inst :
Title : Reactions of Diazoketones. I. Interaction of Diazoacetone with Unsaturated Compounds.

Orig Pub: Chem. listy, 1957, 51, No 3, 479-492; Sb. chekhosl. khim. rabot, 1957, 22, No 6, 1836-1851.

Abstract: Diazoketones [diazoacetone (I)] react with unsaturated compounds to form derivatives of acetyl cyclopropane. Reaction with aromatic compounds RH results in ketones RCH_2COCH_3 (II); C_6H_6 reacts only in the presence of BF_3; the yield of phenylacetone is 4%. Vinyl esters and ethers usually yield a mixture of cyclopropane derivatives and ketones II. Acrylonitrile formes with I (1 hour, 100°. addition of Cu) a compound

Card : 1/5

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry - Synthetic Organic Chemistry. G-2

Abs Jour: Referat Zhur-Khimiya, No 5, 1958, 14358.

$C_9H_{11}O_2N_3$, BP 120°/0.3 mm, MP 95°, the structure of which was not investigated. Furan and sylvan are cleaved by I. To 15 g styrene and 1 g Cu are added at 100° 5 g styrene + 3 g I and mixture is heated for 2 hours; 1-acetyl-2-phenylcyclopropane (III) is distilled and subjected to chromatography on Al_2O_3, yield 42%, BP 73°/0.3 mm; semicarbazon (SC), MP 135°. III is hydrogenated, over Pd/C, to 1-phenylpentanone-4, BP 130°/17 mm, 64°/0.22 mm; SC, MP 128°; oxidation of III with a solution of Br_2 in aqueous NaOH yields 2-phenylcyclopropanecarboxyl-1 acid, MP 90-; amide, MP 188°. Similarly to III there is formed from I and omega-ethylstyrene, in cyclohexane at 85° in the presence of $CoSO_4$, 1-cetyl-2-phenyl-3-ethylcyclopropane, BP 78°/0.005 mm. Solution of 5 g I in cyclohexane is added to boiling suspension of 0.2 g anhydrous CuSO4 in cyclohexane, to get 38.7% of 7-acetyl-bicyclo-[4,1,0]-heptane, BP 83-86°/10 mm, n^{20} D 1.4805; SC, MP 175°;

Card : 2/5

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry - Synthetic Organic Chemistry. G-2

Abs Jour: Referat Zhur-Khimiya, No 5,1958, 14358.

only the acetate of 7-acetyl-bicyclo-[4,1,0]-heptanol-1, yield 12%, BP 72-76°/0.3 mm; SC, MP 184°. In the same manner from dihydropyran was obtained only 7-acetyl-2-oxabicyclo-[4,1,0]-heptane (IV), yield 54%, BP 80-83°/10 mm; MP 144 . IV was obtained also from the acid chloride of 2-oxabicyclo-[4,1,0]-heptane-7-carboxylic acid, MP 89-93°/15 mm (V--acid) and $(CH_3)_2Cd$ in C_6H_6, yield 68%. V was obtained from dihydropyran and $N_2CHCOOC_2H_5$ with subsequent saponification with NaOH, yield 86%, MP 104°. Indole reacts with I in cyclohexane with addition of Cu at 80°; by distillation of the mixture and chromatographic purification is isolated, with a yield of 25%, 3-indolylacetone (MP 116.5-118.5°; picrate, MP 116-117°), which is reduced with $LiAlH_4$ to 1-(3-indolyl)-propanol-2, yield 89%, BP 146-147°/0.35 mm, MP 37.5°. Coumarone and $CuSO_4$ give with I at 80° 6-acetyl-2-oxa-3,4-benzobicyclo-[3,1,0]-hexene-3, MP 63°, which is converted with NaOBr in aqueous dioxane to 2-oxa-3,4-benzobicyclo-

Card : 4/5

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Natural Substances and Their Synthetic Analogues. G-3

Abs Jour : RZhKhim., No 10, 1958, 32586

Author : Vlastimil Herout, Ladislav Dolejs, František Sorm
Inst : Not given
Title : Terpenes. LXXIX. Structure of Artabsine, Prochamazulenogenetic Substance from Bitter Absinth.

Orig Pub : Chem. listy, 1957, 51, No 3, 572-578; Sb. chekhosl. khim. rabot, 1957, 22, No 6, 1914-1920

Abstract : The authors attribute the probable structure of 4-oxyguaianodiene-2,4(10)-olide-8,12 to artabsine (I), the prochamazulenogenetic substance from bitter absinth (Artemisia absinthium L.) (see RZhKhim, 1955, 34562), based on the hydrogenation and oxidation products, their reactions and infra-red spectra. But the structure of 4-oxy-guaianodiene-1,3-olide-8,12 (RZhKhim, 1957, 37762) cannot

Card 1/4

34

CZECHOSLOVAKIA / Organic Chemistry. Natural Substances and Their Synthetic Analogues. G-3
APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R00165242001

Abs Jour : RZhKhim., No 10, 1958, No 32586

be completely excluded. 1.63 g of 1-oxyguaiaene-4(10)-olide-8,12 (dihydroartabsine) (II), melting point 133.5 to 134° (from isopropyl ether), $[\alpha]^{20}D$ = -130° (c = 1.71, all α-s in chloroform), was prepared by hydrogenation of 2.13 g of I in 10 mlit of alcohol on 0.17 g of PtO_2 and chromatography on 170 g of Al_2O_3 in C_6H_6. 110 mg of oxy-oxydolactone (III), melting point 160° (from alcohol - isopropyl ether), was produced by ozonization of 150 mg of II in 5 mlit of CH_3COOH (30 min. at 15°) and hydrogenation of the product on 50 mg of PtO_2. Ketooxidolactone (IV) $C_{15}H_{22}O_4$, melting point 145° (from isopropyl ether), yield 20 mg, was produced from the neutral fraction by oxidation of 33 mg of III by 50 mg of CrO_3 in 2 mlit of glacial CH_3COOH (12 hours) at 20°). 4 products were obtained by hydrogenation of 5.66 g of I in 10 mlit of glacial CH_3COOH on 692 mg of PtO_2 and

Card 2/4

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

Abs Jour : RZhKhim, No 10, 1958, No 32586

CrO_3 does not oxidize VI "a", "b" and "c" into CH_3COOH. 70 mg of guaiacene-1-olide-8,12 (VII), boiling point 128 to 129° under 1.2 mm was received by dehydrogenation of 100 mg of VI "a" with 150 mg of $SOCl_2$ in 1.5 mlit of pyridine (15 hours at 0° and 2 hours at 20°). 320 mg of trioxy-1,4-oxidoguaianolide-8-12, melting point 188° (from alcohol - isopropyl ether), was obtained from the neutral fraction by oxidation of 1 g of I with 1.5 g of $KMnO_4$ in the solution of 100 mlit of acetone, 4 mlit of water and 1 mlit of CH_3COOH (1.5 hour at 20°). HCOOH is formed at the oxidation of the product with $NaIO_4$ in water. The infrared spectra of IV, V, VI "a", "b" and "c" and VII are presented.

Card 4/4

Sorm, F.

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances andTheir Synthetic Analogs. G-3

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11432

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

Author : Fajkos, J. and Sorm, F.
Inst :
Title : On Steroids. XXVIII. Synthesis of Analogs of Progesterone and Desoxycorticosterone with the Side Chain in the 16-Position.

Orig Pub: Chem Listy, 51, No 3, 579-591 (1957) (in Czech)

Abstract: The following analogs of progesterone and desoxycorticosterone having the side chain in the 16-position have been synthesized: the action of CH_3MgBr on 3 β -acetoxy-16-cyanoandrostadiene-5,16 (II) which is selectively hydrogenated to 3β -hydroxy-16 β -

Card : 1/10

6

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and Their Synthetic Analogs. G-3

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11432.

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and their Synthetic Analogs. G-3

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11432.

(c = 1.77; alcohol). When a suspension of 0.3 gm XIII in 1.2 ml oxalyl chloride and 12 ml C_6H_6 is shaken for 15 min and evaporated under vacuum, 360 mg XV are obtained; the latter are dissolved in 6 ml C_6H_6 and poured at -10 to 0° into a solution of CH_2N_2 (from 5 gm nitrosomethylurea); after 1 hr the filtrate is evaporated and the XVI which is obtained (340 mg) is heated (1 hr, 90°) with 1.5 ml 5% CH_3COONa in CH_3COOH, the solution is evaporated, and the oily product is extracted with ehter; chromatography on Al_2O_3 gives 14% XVII (elution with petroleum ether : benzene = 1 : 2), mp 194-195° (from acetone), $[\alpha]^{20}_{C}$ + 36 ± 1° (c = 2.65). When 1 gm XX is refluxed for 1.5 hrs with 0.3 gm K_2CO_3 in 50 ml CH_3OH and 10 ml water, an 83% yield of 3 -hydroxy-17-

Card : 8/10

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and their Synthetic Analogs. G-3

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

Abs Jour: Referat Zhur-Khimiya, No 4, 1958, 11432.

cyanoandrostadiene-5,16 is obtained, mp 170-171° (from CH_3OH), $[\alpha]^{20}_{D}$ - 66 ± 1° (c = 3.18); the latter product is oxidized (as in the case of II to VIII) to 3-keto-17-cyanoandrostadiene-4,16 (XXVIII), yield 68%, mp 156-158° (from alcohol) $[\alpha]^{20}_{D}$ + 168 ± 2° (c = 2.08). When a mixture of 325 mg XXVIII, 2 ml ethylene glycol, 15 mg p-toluenesulfonic acid, and 10 ml C_6H_6 is refluxed for 20 hrs (removal of water), a 76% yield of 3-ethylenedihydroxy-17-cyanoandrostadiene-5,16 is obtained, mp 217-219° (from alcohol), $[\alpha]^{20}_{D}$ -45 ± 1° (c = 2.45) which is converted to XXI (as in the case of I to II, decomposition with a solution of NH_4Cl); after purification by chromatography on Al_2O_3 the yield

Card : 9/10

10

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring Substances and their Synthetic Analogs. G-3

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry - Theoretical and General Questions on Organic Chemistry. G.

Abs Jour : Ref Zhur - Khimiya, No 9, 1958, 28643

later becomes very marked. In the opinion of the authors methyl radicals are present in the reaction space both in the gas phase and on the furface of the Si or at the surface of the contact mass (CM). The radicals in the gas phase combine to form silicon-free reaction products while the radicals localized on the surface of the Si or on the CM form the methylchlorosilanes proper. The gradual decrease in the yield of methylchlorosilanes continues until the radicals present in the gas phase are exhausted. The sharp decrease in yield begins when the NO which is added begins to react also with the radicals localized on the surface of the CM. The reactions of the methyl radicals in the gas phase are discussed, in particular, the reactions with $CHCl_3$ and H_2, thermal decomposition,

Card 2/3

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry - Theoretical and General Questions on Organic Chemistry. G.

Abs Jour : Ref Zhur - Khimiya, No 9, 1958, 28643

and disproportionation reactions. The theoretical conclusions are compared with the experimental data on the composition of the reaction products (see RZhKhim, 1957, 68912).

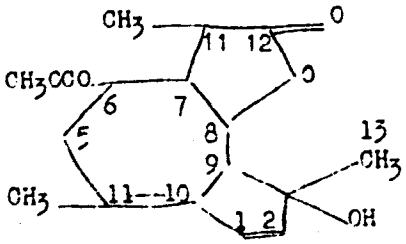
Card 3/3

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Natural Substances and Their Synthetic analogues. G-3

Abs Jour : RZhKhim., No 10, 1958, No 32587

ducts, 6-acetoxyguaianolides-8,12 (IIa and IIb) with melting points 115.5° and 123°, were produced by hydrogenation of I on Pt (from PtO_2) in glacial CH_3COOH, this indicates that the oxy group in I is bonded with the carbon atom next to a binary bond. 1-oxy-6-acetoxygaianolide-8,12 (tetrahydromatricine) (III) together with a little amount of dihydromatricine (IV) was produced by hydrogenation of I on PtO_2 in alcohol. IIa when saponified with K_2CO_3 in CH_3OH produces the corresponding 6-oxiguaianolide-8,12(V).



Card 2/8

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Natural Substances and Their Synthetic Analogues. G-3

Abs Jour : RZhKhim., No 10, 1958, No 32587

tetrol (XII) was detected only in a small amount in mother liquors (by paper chromatography). XII was synthetized by reducing with $LiAlH_4$ at an elevated temperature in N-ethylpyridine. XI produces X when dehydrogenated with Se, while XII produces a mixture of X with linderazulene (XIII) under the same conditions. The formation of XIII together with X from XII is a proof that the position of the acetoxyl group is at C(6). III is stable with respect to CrO_2 in glacial CH_3COOH in the cold, while VI produces 1-oxy-6-ketoguaienolide-8,12 (XIV) under the same conditions, which is a proof that the free oxy group in I is a tertiary group. Ketoguaienone-1(9)-olide-8,12 (XV) was synthetized by the dehydrogenation of XIV with BF_3 esterate or HCOOH, its binary bond is not conjugate either with the lactone carbonyl, or the ketone carbonyl, which is shown by the infrared and

Card 4/8

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Natural Substances and Their Synthetic Analogues. G-3

Abs Jour : RZhKhim., No 10, 1958, No 32587

ultraviolet spectra. XII does not change even after a 70 hour action of HIO_4. The above presented formula was attributed based on a discussion of ultraviolet and infrared spectra and all the experimental results. IIa and IIb, melting point 115.5°, $[\alpha]^{20}_D$ = -6.5° (c = 10.1; all α-s in chloroform); melting point 123°, $[\alpha]^{20}_D$ = -9.0° (c = 4.3). III, melting point 183 to 184°, $[\alpha]^{20}_D$ = +12.5° (c = 6.8); IV, melting point 166.6 to 168°, $[\alpha]^{20}_D$ = -20.5° (c = 11.1), was separated from mother liquors after the crystallization of III. IV can be converted into III by hydrogenation on PtO_2 in glacial CH_3COOH. V, melting point 157° (from diisopropyl ether - petroleum ether), was obtained from 289 mg of IIa and aqueous-methanol solution of K_2CO_3 (48 hours of seasoning), yield 221 mg. Similarly, 0.85 g of VI, melting point 138.5 to 140° (from diisopropyl ether - acetone), $[\alpha]^{20}_D$ = +33.0° (c = 0.91), was received from 1.1 g of III.

Card 5/7

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

= 0.92), was prepared of III by reducing it with $LiAlH_4$ in ether. The reduction of 300 mg of III with 1.2 g of $LiAlH_4$ in boiling N-ethylpiperidine (4 hours) resulted in XII, yield 245 mg, melting point 138 to 139° (from diisopropyl ether - acetone), $[\alpha]^{20}D$ = -11.9° (c = 0.84). A mixture of X and XIII (1 : 1), melting point 103 to 105° (from alcohol), is obtained by the dehydrogenation of XII with Se; trinitrobenzolate, melting point 150 to 152°. The latter was proved by paper chromatography, R_f for X is 0.75 (at the application of 45%-ual H_3PO_4) and R_f for XIII is 0.30. XIV, melting point 187.5 to 189° (from diisopropyl ether - acetone), was synthetized of 300 mg of VI and 83 mg of CrO_3 in glacial CH_3COOH (40 hours, 0°), yield 268 mg. XV, melting point 100 to 101° (from diisoptopyl ether), was prepared of 300 mg of XIV and 5 mlit of BF_3 esterate (15 min. seasoning), yield

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

226 mg. A method of descending paper chromatography in the system diisopropyl ether - water was developed for the study of the degradation reaction course. The development was carried out with a saturated solution of $SbCl_3$ in $CHCl_3$, to which 20% of $SCCl_2$ was added. The spots were seen best after the chromatogram was heated to from 90 to 100°. The values of R_f are: I - 0.64, III - 0.63, VI - 0.25, XI - 0.29, XII - 0.23, XIV - 0.52, and XV - 0.74.

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

ARNOLD, Zdenek 1st SOBM, Frantisek

1

2/3

from aq. soln.; *H*, m. 185-90° (from pyridine), 35% (*picrate*, m. 141.5-2.5°); *Me*, m. 178-80° (from $(CH_2Cl)_2$), 20% (*picrate*, m. 127-8°); *Et*, m. 169.5-71.5° (from pyridine), 30% (*picrate*, m. 68-9°); C_4H_9 (*picrate*, m. 113.5-14.5°); *Ph*, m. 236° (from dioxane-MeOH), 26.5° (*picrate*, m. 114.5-15.5°) (all picrates from EtOH). Depending on the method of isolation, derivs. were prepd. as follows. Passing a slow stream of $COCl_2$ into 3.65 g. $HCONMe_2$ until all solidified, adding dropwise 4.35 ml. $PrCH(OEt)_2$, heating the mixt. slowly to 75°, keeping 15 min. at 75°, decompg. with ice, and adding 8.2 g. AcONa and 12.5 ml. 4*N* $PhNH_2.HCl$ gave 4.7 g. cryst. ppt. of *PhNHCH:CEtCH:NPh.HCl* m. 200-7° (from EtOH). A similar procedure with $MeCH(OEt)_2$ combined with pptn. of the product with 85% $HClO_4$ gave 74% brown ppt. of *$Me_2NCH:CH-CH:NPh.HClO_4$*, m. 158.5° (from EtOH). When 3.65 g. $PrCH(OEt)_2$ was treated with excess $COCl_2$ and the products worked up as described, the mother liquors after sepn. of II (R' = Et) yielded, on extn. with ligroine and distn., 2 g. yellowish liquid, b_{15} 102-5°, n_D^{20} 1.4753, apparently *EtOCH:CEtCHO* (III), besides 1.3 g. $Me_2C:CEtCHO$. III shaken with 30% aq. $NHMe_2$ gave I (R = Et). III was also obtained in 1.3-g. yield by boiling 1.8 g. Na salt of $EtCH(CHO)_2$ 9 hrs. in 20 ml. EtOH with excess of EtBr. The I heated to 70° with 50% NaOH and the resulting solns. evapd. almost to dryness *in vacuo* gave in 90% yield Na salts of dialdehydes which were pptd. with EtOH-Me_2CO, dried and converted to the following free $R''CH(CHO)_2$ (R'' shown) by addn. of *N* HCl in Et_2O or 5*N* aq. HCl with cooling and sublimation of the evapn. residue: *H*, m. 73-4°)

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

Arnold, Zdenek and Sorm, Frantisek

Me, m. 88–9.5° (from C_6H_6); *Et*, m. 69–70°; *Pr*, m. 58.5°; iso-*Pr*, m. 62–3°; *Bu*, m. 54–5°; C_5H_{11}, m. 55°; *Ph*, m. 92–3°; *PhCH*$_2$, m. 136–7° [from $(CH_2Cl)_2$]. Reaction mechanisms are discussed. L. J. Urbánek

3/3

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour : Ref. Zhur. - Khimiya, No. 15, 1958, No. 50339

Author : Ratusky, Josef; Sorm, Frantisek
Inst : -
Title : Reactions of Diazoketones. II Reactions of WO-diazoacid Esters With Indole and N-methyl-pyrrole.

Orig Pub : Chem. Listy, 1957, 51, #6, 1091-1100.

Abstract : Ethyl (1a) and methyl (1b) diazopyroacetate, as well as ethyl γ-diazoacetoacetate (11) and δ-diazolevullinate (III) were synthesized. The reactions of these compounds with indole (IV) and with methyl pyrrole (V), in presence of Cu, were studied. In both cases substitution of H by an ester radical takes place with elimi-

Card 1/7

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA / Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour : Ref. Zhur. - Khimiya, No. 15, 1958, No. 50339

nation of N_2, examples in (IV) in the 3rd position, and in (V) in the 2nd position. The structure of diazo compounds (DC) was proven by reactions with hydrogen halides, CH_3COOH and by Wolf's rearrangement. DC were synthesized by stirring an ether solution of CH_2N_2 with a corresponding ester chloride for 30 min., at -5 to -8° Listed below are: % yield, M.P. in °C, or B.P. °C/mm and derivative: Ia, 90.2, 73-74, ethoxyallyl chloride; Ib, 90, 103-105, methoxyallylchloride; II, 77, 70/0.05, $C_2H_5OCOCH_2$-COCl; III 82, 75/0.01, $C_2H_5OCOCH_2CH_2COCl$. Reaction with IV was accomplished by introducing DC into a solution of IV in the presence of Cu (85-95°C, 5-10 min.). From a solution of I in

Card 2/7

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour : Ref. Zhur. - Khimiya, No. 15, 1958, No. 50339

over Al_2O_3. Upon boiling of the latter (1 hour) with a 30% KOH 3-indolyl acetate, M.P. 165° was formed. III in cyclohexane led to ethyl δ-3 (indolyl)-levullinate, 85% yield. Oxication with O_2 yielded indole carboxylic-3 acid, detected by chromatography on paper. Reactions of V are analogous, but take from 0.5 - 2 hours (the extent of reaction being determined by the quantity of liberated N_2). I without a solvent yielded ethyl 2- (N-methyl pyroyl) pyroacetoacetate, 39% yield B.P. 110°/0.25mm which yielded with a 3N NaOH 2-(N-methylpyroyl) pyroacetate, M.P. 112°. From II in cyclohexane may be obtained ethyl δ-(2-N-methyl pyroyl)-acetoacetate, 23.2% yield, B.P. 90°/0.5 mm. Heating of the latter for 15

Card 4/7

CZECHOSLOVAKIA / Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour : Ref. Zhur. - Khimiya, No. 15, 1958, No. 50339

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

min. resulted in the formation of 2-N-methyl-pyroylacetone, (semicarbazone), M.P. 166°. III in C_6H_6 yielded ethyl δ-2-N-methylpyoryl levullinate, 65.8% yield, B.P. 114°/0.2 mm. In order to prove the structure of DC the following compounds were synthesized: methyl ethyl chloropyroacetate from Ib and HCl (g) in CH_3OH, 94.5% yield, B. P. 78°/13 mm which with a 35% HCl (acid) gave chloropyroacetic acid, M.P. 57°; ethyl bromopyroacetate, B.P. 87°/9 mm, obtained by shaking Ia in ether with a 40% HBr. At the same time bromopyroacetic acid, M.P. 75° was formed. By analogy, II and HCl (g) yielded ethyl δ-chloroacetoacetate, 66.5% yield, B.P. 95°/10 mm, n^{20} D 1,4550 (tear gas), while II

Card 5/7

CZECHOSLOVAKIA / Organic Chemistry. Synthetic Organic Chemistry. G

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour : Ref. Zhur. - Khimiya, No. 15, 1958, No. 50339

δ-acetoxyacetoacetate 86% yield, B.P. 70°/0.1 mm, and ethyl -acetoxylevullinate, 84% yield B.P. 71°/0.0005 mm. Heating of alcoholic solutions of DC with $AgNO_3$ yielded complex esters. Listed below are esters and % (yields): $CH_2(COOCH_3)_2$ (from Ib), 66.5; ethyl succinate (from II), 67; ethyl glutanate (from III), 90.5; Communication I see Ref. Zhur. Khim., 1958, 14358. -- T. Kovaz

Card 7/7

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

Proteins. XL. Comparison of weakly basic peptides from partial hydrolyzates of chymotrypsinogen and trypsin. Jiří Vaněček, Bedřich Meluzín, and František Šorm (Czechoslov. akad. věd, Prague). *Chem. listy* 51, 1567-76(1957); cf. *C.A.* 51, 12188a.—Partial hydrolysis of chymotrypsinogen (I) and trypsin diisopropyl phosphate (II) (carried out by treating 5 g. of the protein with 150 ml. concd. HCl at 37° 6 days, dilg. with H_2O to 180 ml., evapg. to dryness *in vacuo* at 35°, and removing the residual HCl by repeated evapn. with H_2O), and combined electrophoresis at pH 7 in a 5-chamber app., descending paper electrophoresis at pH 5.6, and paper chromatography yielded a series of peptides, most of which are common both for I and II. The following peptides were identified from I and II, resp: alanylhistidine (I, II), histidyl-3-sulfoalanine (I, II), phenylalanylhistidine (I), histidylphenylalanine (I), tyrosylhistidine (II), prolylhistidine (II), lysylglutamic acid (I, II), lysylglutamylisoleucine (I, II), lysylserine (I, II), lysylleucine (I, II), lysyl-3-sulfoalanine (I, II), 3-sulfoalanylglutamic acid (I, II), 3-sulfoalanylthreonine (I), 3-sulfoalanylvaline (I), 3-sulfoalanylserine (II). M. Hudlický

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Synthetic Organic Chemistry. G-2

Abs Jour: Ref Zhur-Khimiya, No 23, 1958, 77633.

Author : Novak, J. and Sorm, F.
Inst : Not given.
Title : Reactions of Diazoketones. III. The Reaction of Diazoacetone with Furan and With Its Homologs. A New Simple Synthesis of Octa-3,5-diene-2,7-dione.

Orig Pub: Chem Listy, 51, No 9, 1693-1698 (1957) (in Czech).

Abstract: In the course of their investigation of the feasibility of the utilization of diazoacetone (I) in the synthesis of other compounds, the authors have reacted I with furan (II) and with its homologs using 1 : 1 mol ratios. The reaction is accompanied by the evolution of N_2 and the opening of the ring of II. With II, 2, 4-heptadiene-6-one-al

Card 1/4

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Synthetic Organic Chemistry. G-2

Abs Jour: Ref Zhur-Khimiya, No 23, 1958, 77633.

Abstract: of NaBrO in the cold gives trans, trans-muconic acid (VII), yield 70%, mp 303° (from water). VII is also obtained by the direct oxidation of III with NaBrO. The Hydrogenation of III over PtO_2 in alcohol gives 6-heptanone-1-al, bp 98-102°/ 15mm; hydrogenation over Raney Ni (120 atm) gives 1,6-heptanediol, bp 80°/0.3mm. The reaction of I with IIa is carried out by adding the mixture of reactants to a boiling suspension of Cu in IIa; the yield of IV is 39%, mp 127° (from CH_3OH). V is obtained by a similar procedure from I and IIb, yield 38%, bp 93-96°/0.3mm, mp 38°. The ethyl ester of diazoacetic acid under similar conditions

Card 3/4

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64585.

(absorption line at 1737 cm^{-1}). Oxidation of formylacoranone (III) gives dicarboxylic acid (IV). Catalytic reduction of (I) leads to the keto-alcohol (V), produced by the dehydrogenation of acorenone (VI) with CO-groups in the 5-member ring. Upon dehydrogenation with S, (VI) yields a product whose UV-spectrum reveals lines at 1714 cm^{-1} (CO-group in 6-member ring) and 1514 cm^{-1} (aromatic system). In this fashion, dehydrogenation is accompanied by the enlargement of the 5-member ring, from which it follows that one of the C atoms, common to the 5- and 6-member rings, appear to be quaternary. Upon dehydrogenation of (IV), there are produced 1-methyl-4-ethylbenzol (VII), 1-methyl-4-isobutylbenzol (VIII), propionic acid (IX), and isovaleric acid (X).

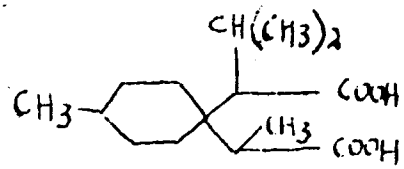
Card : 2/10

36

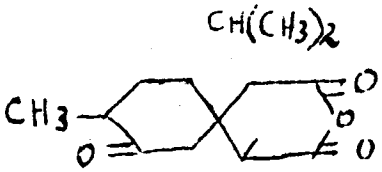
APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64585.



(IV)



(XI)

Monobenzilidene-derived (I) yields, upon ozonification, the keto-anhydride (XI). Upon pyrolisis of the Ba salts of dicarboxylic acid (XII), derived from (XI), there are separated (IX), (X) and two ketones, $C_9H_{16}O$ (XIII) and $C_{11}H_{20}O$ (XIV), whose carbon skeleton has

Card : 3/10

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64585.

Herout, Collect. czechoslow. chem. Commun., 1949, 14, 723) give, upon dehydration with phthallic anhydride (260-280°, 1 hour) (VI), yield 2.84 g. b.p. 147-151°/13 mm. Dehydrogenation of 1.65 g. of (VI) with S (0.63 g) (3 hours, 220-230°), and chromatographing the product on Al_2O_3, gave 0.55 g. of a substance (b.p. 140-160°) temp. bath/13 mm. From (I) (2.7 g) by means of ethanedithiol (2.65 g) and ethered BF_3 (3 ml), there was produced the monothicethyleneketal of (I) (Ia), m.p. 77-78.5°, $[\alpha]^{20}D$ + 111.6° (w. 4.42); from the mother solution, by way of chromatographing on Al_2O_3 (washed with C_6H_6) there was separated. the bithioethyleneketal of (I), m.p. 95-97° (in petr. ether) $[\alpha]^{20}D \pm 0$ (w. 2.3).

Card : 5/10

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64585.

From 4.6 g. of (Ia), boiled with elemental Ni in dioxane (10 hours), (II) was produced, yield 2.9 g., b.p. 151-154°/15 mm, $[\alpha]^{20}D$ + 47.0° (w.2.2, chloroform, $n^{20}D$ 1.4857, d_4^{20} 0.9539. By the action of CH_3ONa (from 1.4 g. Na) and $HCOOC_2H_5$ on (II) (2.7) in C_6H_6 (20° ml) (20°, 40 hours, atmosphere N_2), (V) is synthesized, yield 2.6 g., b.p. 110-114°/0.04 mm, 142-147°/2.5 mm, $[\alpha]^{20}D$ + 29.6° (w 3.17). To a solution of (III) (5.7 g) and KOH (11.4 g) in CH_3OH (225 ml) is added 30% H_2O_2 (225 ml); after boiling for 50 minutes, 5.2 g of (IV) are precipitated (not crystalline); dimethylether (IV), b.p. 120-126/0.05 mm. Upon dehydrogenation with 5% Pd/C (310-330°, 3-9 hours), (IV) gives a mixture of (VII) and (VIII), b.p. 70-95° (temp. bath)/

Card : 6/10

38

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and G

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64585.

over 5% Pd/SrCO; (1.5 g.) and distillation in a column yields (XIII) (4.3 g), b.p. 73-78°/10mm; semicarbazone, m.p. 152-154° (in 70% al.); (XIV), yield 2.7 g., b.p. 97-102°/10 mm; semicarbazone, m.p. 172° (in 90% al.). (XIII) (1.03 g) is reduced by $LiAlH_4$ (0.55 g) in ether (20 ml) (boiled for 10 minutes), the products of the reaction (b.p. 93-95°/14 mm., 0.94 g.) being dehydrogenated by heating with phthallic anhydride (40 minutes, 270-280°). Chromatographing on Al_2O_3, a product is separated (b.p. 80-90°, (bath temp.)/62 mm,0.57 g) which can be dehydrogenated with 0.37 g of S (8 hours, 220-250°) and chromatographed on Al_2O_3 to produce (VII) yield 0.17 g., b.p. 70-80° (bath temp.)/35 mm, n^{20} D 1.4953, d 0.8585. Similarly, (XIV) (1 g) canbe reduced to a product

Card : 8/10

39

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64585.

with a b.p. of 108-113°/13 mm (0.95 g), which upon dehydration gives a product with b.p. 107-117° (bath temp) 57 mm (0.62 g); dehydrogenation of this product gives (VIII), b.p. 80-90° (bath temp.)/13 mm, 0.17, n^{20} D 1.4880, d_4^{20} 0.8523. By comparison, (X) is synthesized out of 4-methylcyclohexanone (2.2 g) boiled with isobutyl lithium (out of 1.9 g Li and 18 ml isobutyl chloride) in petr. ether for 1 hour, giving 1-methyl-4-isobutylcyclohexanone-4, yield 2.85 g, b.p. 90-101°/11 mm. Dehydration of 2.62 g. of this latter with 85% HCOOH (100°, 1 hour) gives 2.05 g of a hydrocarbon with b.p. 64-69°/12 mm., the dehydrogenation of which (1 g) with the aid of 0.47 g S (200-250°, 8 hours), produces (VIII). The reduction of 20 g (XV) with $LiAlH_4$

Card : 9/10

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64586.

benzyl alcohol there is derived a product (350 mg), $n^{20}D$ 1.5030, d_4^{20} 0.9505. The latter by being hydrolized in alcohol in the presence of an alcohol solution of KOH and 5% Pd/$SrCO_3$ (1 g), distilled (118-125°/20 mm), dehydrogenated with 50 mg /omission transl/ (180-220°, 4 hours), chromatographed on Al_2O_3 in gasoline and cleaned by picrate, m.p. 92° (in alc.) this product is converted into 1,7-dimethyl-4-isopropyl-naphtalene (120 mg), m.p. 60° (in alc.); styphnate, m.p. 124° (in alc.). Oxidizing (II) (2 g) with $HIO_4.2H_2O$ (4.4 g) in 0.5 l water (20°, 2 days) produced HCOOH. The saponification of (I) (2 g) with a 5% methanol solution of KOH (20°, 1 hour) produced laserol (III), yield 79%, m.p. 190° (in ethyl acetate). The oxidation of (III) (1 g) with

Card : 2/7

41

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64586.

CrO_3 in pyridine (20°, 24 hours) produced laserone, m.p. 180-181° (in ethylacetate). From 0.5 g (III), by the action of $ClCOOC_2H_5$ (1 ml) in dioxane (5 ml) and pyridine (0.8 ml) (20°, 4 hours), and by boiling for 30 minutes in 2% HCl (13 ml), there was derived mono-O-carboethoxyl laserol, m.p. 144°, (in acetone). This latter, (0.7 g) was oxidized with CrO_3 (1 g) in pyridine (20 ml) (30°, 24 hours) to mono-O-carbethoxy-diketone $C_{19}H_{23}O_7$, m.p. 98-99° (in ether-gasoline). The dehydration of (I) (1 g) with $SOCl_2$ (12 ml) in pyridine (15°, 10 minutes) gave unsaturated hydroxyketodiether $C_{25}H_{36}O_6$ (IV), yield 0.7 g, m.p. 110°. Hydrogenation of (IV) (169 mg) over Pt (from PtO_2) in glacial CH_3COOH, and chromatographing the products of the reaction on Al_2O_3

Card : 3/7

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64586.

on nitr. Al_2O_3 in gasoline gave a dimethyl ether ketodicarboxylic acid $C_{17}H_{22}O_5$, yield 150 mg. Dehydration of tetrahydroxylaserpitine (XI) (2g) (see reference above) with $SOCl_2$ (10 ml) in pyridine (30 ml) at 15° and chromatographing the results of the reaction on nitr. Al_2O_3 gave an unsaturated hydroxyketodiether $C_{25}H_{40}O_6$ (XII), b.p. 134-142°/0.3 mm, yield 1.8 g. This latter can be reduced with $LiAlH_4$ (like V) to give VII, m.p. 183-184°. Dehydration of (XI) (2.5 g) with SOCl (5 ml) at 80° in pyridine yields an unsaturated ketodiether $C_{25}H_{38}O_5$, yield 1.7 g., m.p. 75° (in alc.). This latter, upon reduction with $LiAlH_4$, gives (IX), yield 0.65 g. (XI) could not be oxidized by

Card : 6/7

43

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogs. G

Abs Jour: Ref. Zhur-Khimiya, No 19, 1958, 64586.

CrO_3 in glacial CH_3COOH or pyridine. Added are the UV-spectrum data of (III), (IV), (VIII) and (XII).

Card : 7/7

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Products and Their Synthetic Analogues. G-3

Abs Jour: Ref Zhur-Khim., No 24, 1958, 81783

Author : Cerny V., Labler L., Sorm F.
Inst :
Title : The Steroids XXXIV. The Structure of Holarrhedine

Orig Pub: Chem. listy, 1957, 51, No 12, 2351-2355.

Abstract: The authors have suggested a structural formula 3α, 20α-diamino-18-oxy-Δ⁵-pregnen for holarrhydine (I) based on the results of thermal splitting and leading to the products which were identical with the products of the splitting of holarrhymine (II), based on the difference of corresponding desoxitetramethyl derivatives of I

Card : 1/4

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Natural Products and Their Synthetic Analogues G-3

Abs Jour: Ref Zhur-Khim., No 24, 1958, 81783.

and II, and on the difference of the molecular rotation between I and II, which corresponds to the difference between 3α-amino-Δ⁵-steroid and 3β-epimer. N, N, N', N'-tetramethyl holarrhymine (III) was allowed to stand in aqueous acetic acid and CrO_3 for 12 hours, and 3β, 20α-bis-dimethylamino-Δ⁵-pregnenal-18 $C_{25}H_{42}ON_2$ separated, m.p. 141-143° C., [α]D + 8°, which by heating for 3 hours with $N_2H_4 \cdot H_2O$ and KOH in triethylene glycol to 200-215° C. produced 3β, 20α-bis-dimethylamino-Δ⁵-pregnen, m.p. 140-141° C., [α]D -40°. In the same way from N, N, N', N'-tetramethyl-I (IV) was obtained 3α, 20α-bis-dimethylamino-Δ⁵-pregnenal-18, m.p. 164-165° C., [α]D + 12°,

Card : 2/4

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

Distr: 4E2c(1)

A contribution to the structure of absinthin and anabsinthin. L. Novotný, V. Herout, and F. Sorm (Czechoslovak Acad. Sci., Prague). *Chem. & Ind.* (London) 1958, 465-6. —The mol. wt. of cryst. anhyd. absinthin (I), m. 179-80° (decompn.), detd. by the isothermal distn. method in Me_2CO, is 520 ± 50, thus I is a dimeric guaianolide, $C_{30}H_{40}O_8$, contg. 2 OH groups/mol. Anabsinthin (II) has the same mol. wt. and mol. formula. The infrared spectrum of I shows absorption bands due to a γ-lactone carbonyl group (1768 cm.$^{-1}$), a double bond (1662 cm.$^{-1}$), and an OH group (3530 cm.$^{-1}$). Hydrogenation of I with PtO_2-HOAc did not proceed readily, but gave *tetrahydro*-I (III), $C_{30}H_{44}O_8$, m. 252°, and II, proving the presence of 2 double bonds in I. The OH groups in III are tertiary, since they could be neither oxidized with CrO_3 nor acetylated. Reduction of I with $LiAlH_4$ gave I *dilactol* (IV), $C_{30}H_{46}O_8$, m. 195°; use of $LiAlH_4$ in *N*-ethylpiperidine gave a glassy product, probably a *tetrol* (V), formed by subsequent etherification of 2 OH groups. Dehydrogenation of IV with Se gave *chamazulene*, *guaiazulene*, and *artemazulene* (VI) (*trinitrobenzene adduct* m. 191°); similar dehydrogenation of V gave the above azulenes and *12-hydroxyguaiazulene* (*trinitrobenzene adduct*, m. 148°) as the principal product. Infrared bands due to double bonds and OH groups are absent in the spectrum of II, which does not take up H even under forcing conditions. Reduction of II with $LiAlH_4$ in Et_2O gave a *product*, $C_{30}H_{48}O_8$, m. 211°, probably a pentol, which on dehydrogenation with Se gave VI in fair yield. Oxidation of I and II with concd. HNO_3 gave a mixt. which chromatographed on Dowex-2 gave $HO_2CCH_2CH.CHMe.CO.O.CHCO_2H$ (VII), m. about 165°, and liquid $HO_2CCH_2CH(CO_2H)CHMeCO_2H$ (VIII), identified as its *tri-Me ester*. The infrared spectrum of the *di-Me ester* of VII has bands at 1744 cm.$^{-1}$ (ester group) and 1792 cm.$^{-1}$ (γ-lactone). VII and VIII also were obtained from artabsin (IX) by a similar procedure. Treatment of both I and II in alk. soln. with HCHO gave *1,3,4-trimethyl-7-ethylazulene* and with AcH gave *1,4-dimethyl-3,7-diethylazulene*. It is assumed that I is formed by diene addn. of an unknown precursor contg. a cyclopentadiene group and an OH group in the 10-position of guaianolide (isomer of IX). The structure of I is proposed as shown, which permits the stereochem. formation of II from I by the probable addn. of 1 of the OH groups to the double bond, affording the oxide ring. Rip G. Rice

6
2-May
1

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

KEILOVA, Helena, (Chemicky ustav CSAV, Praha 19, Na cvicisti 2.) SORM, Frantisek, (Chemicky ustav CSAV, Praha 19, Na cvicisti 2.)

A contribution to the study of resistance to Crocker's tumour. Neoplasma, Bratisl. 5 no.1:26-33 1958.

1. Institute of Chemistry, Czechoslovak Academy of Sciences, Prague.
(NEOPLASMS, exper.
Crocker's tumor, ligation & transpl. time in relation to immunity)

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

WINKLER, Alojz; UJHAZY, Viliam; KNOTZOVA, Kornelia; SORM, Frantisek

The level of 6-azouracile in the serum of rats. Neoplasms, Bratisl. 5 no.2:97-100 1958.

1. Oncological Research Institute, Bratislava. Chemical Institute of the Czechoslovak Academy of Sciences, Praha. Authors' address: Dr. A. Winkler and co-workers, Bratislava, ul. Cs. armady 17; akademik F. Sorm, Praha, Chemicky ustav CXAV.

(URACIL, antag.
6-azouracil, retention in blood in rabbits)
(CYTOTOXIC DRUGS, in blood,
6-azouracil, retention in rabbits)

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

EXCERPTA MEDICA Sec 2 Vol 12/5 Physiology May 59

2022. THE ANTI-TUMOUR ACTIVITY OF 6-AZAURACIL RIBOSIDE - Šorm F. and Keilová H. Inst. of Chem., Czechoslovak Acad. of Sci., Prague - EXPERIENTIA (Basel) 1958, 14/6 (215) Tables 1

6-Azauracil riboside is 6 times as active as 6-azauracil against the s.c. form of Ehrlich ascites tumour. Fischer - Buenos Aires (II, 5, 16)

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

Country : CZECHOSLOVAKIA G
Category : Organic Chemistry. Natural Substances and Their Synthetic Analogs
Abs. Jour : Ref Zhur - Khim., No 5, 1959, No. 15499

Author : Sykora, V.; Herout, V.; Pliva, J.; Sorm, F.
Institut. : -
Title : Terpenes. LXXXII. Structure of Acoron

Orig Pub. : Collect. czechosl. chem. commun., 1958, 23, No 6, 1072-1082
Abstract : No abstract.
See Ref Zhur-Khim, 1958, 64585.

Card: 1/1

G - 78

Sorm, F.

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Organic Synthesis. G-2

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31331

Author : Novak, J., Sorm, F.
Inst : -
Title : Reactions of Diazoketones. III. Interaction of Diazoacetone with Furan and Its Homologues. New Simple Synthesis of Octa--3,5-Dienedione-2.7.

Orig Pub : Collect. czechosl. chem. commun., 1958, 23, No 6, 1126-1132

Abstract : See Ref Zhur-Khimiya, 1958, 77633.

Card : 1/1

138

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, F

CZECHOSLOVAKIA / Organic Chemistry--Natural compounds and their synthetic analogs G-3

Abs Jour: Ref Zhur-Khimiya, No 8, 1959, 27578

Author : Motl, O., Herout, V., and Sorm, F.; Motl, O., Sykora, V., Herout, V., and Sorm, F.

Inst : Not given

Title : On Terpenes. LXXXV. The Structure of 'Juniper Camphor', Another Alcohol of the Selinane-Type from Juniper Oil. LXXXVI. The Structure of Two Crystalline Cadinols.

Orig Pub: Collection Czechoslov Chem Commun, 23, No 7, 1293-1296 and 1297-1306 (1958) (in English with a Russian summary)

Abstract: See RZhKhim, 1959, 8394, 8395.

Card 1/1

117

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, F.; [illegible], M.; [illegible], V.

"Terpenes. [illegible]. Composition of cosuts oil (from Saussurea lappa Clarke)."
(In English)

COLLECTION OF CZECHOSLOVAK CHEMICAL COMMUNICATIONS, Praha, Czechoslovakia,
Vol. 23, no. 12, Dec. 1958

Monthly list of EAST EUROPEAN ACCESSIONS, (EEAI), LC, Vol. [illegible], No. 7, July 1959, Unclas.

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, F.; [illegible], M.

"Terpenes. XC. Synthesis of 1, 7-dimethyl-4-isopropylcyclodecane (germacrane). (In English)

COLLECTION OF CZECHOSLOVAK CHEMICAL COMMUNICATIONS, Praha, Czechoslovakia, Vol. 23, no. 12, Dec. 1958

Monthly List of EAST EUROPEAN [illegible] (EEAI), LC, Vol. 8, No. 7, July 1959, Unclas.

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

[illegible], F.; [illegible], V.

"Mechanism of the cancerostatic action of 6-azauracil and its riboside."
(In English)

COLLECTION OF CZECHOSLOVAK CHEMICAL COMMUNICATIONS, Praha, Czechoslovakia, Vol. 23, no. 12, Dec. 1958

Monthly list of EAST EUROPEAN ACCESSIONS (EEAI), LC, Vol. 8, No. 7, July 1959, Unclas.

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, F.

CZECHOSLOVAKIA / Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour: Ref Zhur-Khimiya, No 3, 1959, 8394.

Author : Motl, Otakar., Herout, Vlastimil, Sorm, Frantisek.

Inst : Not given.

Title : On Terpenes. LXXXV. Structure of "Juniper Camphor", a New Alcohol of Selinan-Type, from Essential Oil of Juniper.

Orig Pub: Chem. listy, 1958, 52, No 1, 116-119.

Abstract: It is demonstrated that the so-called "juniper camphor" isolated from Juniperus Communis L., is 1.10-dimethyl-7-isopropylidene-decalol-1($\Delta^{7(11)}$-selinenol-4) (I). Hydrogenation of I gives selicanol-4 (II), which on dehydration with $SOCl_2$ in pyridine is converted to a mixture of hydro-

Card 1/3

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour: Ref Zhur-Khimiya, No 3, 1959, 8335.

Author : Motl, Otakar, Sykora, Vladimir., Horcut Vlastimil., Sorm Frantisek.

Inst : Not given.

Title : On Terpenes. LXXXVI. On the Structure of Two Crystalline Cadinols.

Orig Pub: Chem. listy, 1958, 52, No 2, 316-324.

Abstract: It was ascertained (on the basis of comparison of infrared spectra and physical constants) that two alcohols isolated from essential oil of juniper, are Δ^4-cadinonol-10 (I) and $\Delta^{1(10)}$-cadinonol-4 (II). I is identical with the cadinol previously isolated (Platter P.A., Markus R., Helv. chim. acta, 1942, 25, 1674) from essential

Card 1/9

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour: Ref Zhur-Khimiya, No 3, 1959, 8395.

Abstract: hydrocarbon mixture gave 4-isopropyl-6-methyl-decelone (IX). On the basis of the course of these reactions it can be considered that the hydroxy-group of I is equatorial, which is in accord with the ready ester-formation by the hydroxyl group. On dehydration-dehydrogenation with S, II is converted to cadalin. Hydrogenation of II gave cadinol-4 (X), which yielded on dehydration a hydrocarbon from which was synthesized, by ozonization, a diketo-alcohol (XI). Under ordinary conditions II is not esterified, which indicates an axial position of OH. Since relative configuration of cadinene dihydrobromide had been determined previously, (see RZhKhim, 1958, 76438), the authors attribute to I and II the

Card 3/9

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour: Ref Zhur-Khimiya, No 3, 1959, 8395.

Abstract: Slovak origin, by fractionation of sesquiterpene alcohols in a column having an efficiency of 30 theoretical plates, followed by crystallization of the fraction of BP 123-125°/2mm. I, MP 74.5°, $[\alpha]^{20}_D$ - 47° (c 2.00; chloroform), was obtained, a) from essential oil of juniper mother-liquor (following separation of II), over the p-nitrobenzoate, MP 138°, $[\alpha]^{20}_D$ - 67.4°; b) from essential oil of citronella, by distillation in a glass bubbler-cap column (34 theoretical plates) from the fraction of BP 134-139°/2 mm, after chromatography on Al_2O_3 (activity III-IV) and purification over the p-nitrobenzoate. Into a solution of 311 mg I in a mixture of 20 ml dioxane and 5 ml water,

Card 5/9

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA / Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour: Ref Zhur-Khimiya, No 3, 1959, 8395.

Abstract: -cadinandiol-5,10, yield 0.4 g, MP 209-210°. Dehydration of the latter (0.3 g) by heating with 4 ml CH_3COOH and 2 drops 70% $HClO_4$ (30 minutes at 100°) and dehydrogenation of the product with 0.11 g S (3 hours at 210-250°) followed by chromatography on alkaline Al_2O_3, give cadalin; picrate, MP 113°. Reduction of 1.5 g Vb with $LiAlH_4$ gives VI, yield 1.3 g, MP 214-216°. Oxidation of 0.85 g VI with CrO_3 in CH_3COOH gives VII, MP 109-109.5° (from petroleum ether). Reaction of 430 mg VII with CH_3MgI in ether, dehydration of the product (0.44 g) in CH_3COOH 4.4 ml with 2 drops of $HClO_4$ (1 hour, 100°), and chromatography on Al_2O_3, followed by dehydrogen-

Card 7/9

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

G

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs.

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38774.

Author : Holub, M., Herout, V., and Sorm, F.
Inst :
Title : Chemistry of the Terpenes. LXXXVII. Proof of the Structure of Laserpitine.

Orig Pub: Chem Listy, 52, No 3, 498-504 (1958) (in Czech); Collection Czechoslov Chem. Commun, 23, No 7, 1307-1313 (1958) (in English with a Russian summary)

Abstract: The formula proposed earlier by the authors for Laserpitine [I, R = $CH_2CH=C(CH_3)CO$] (RZhKhim, 1958, 64586) is confirmed by the proof of the structure of dihydrolaserol [spelling uncertain] (II) and of the triol (III) [see insert below]. The oxi-

Card : 1/6

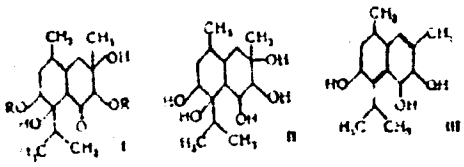
G

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs.

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38774.

dation of II by $KMnO_4$ gives a mixture of acids from which β, γ-dimethyl-δ-keto-γ-carboxycaprylic acid (IV), 1-isopropyl-3-methyl-1-hydroxycyclopentane-2,4-dicarboxylic acid (V), methyl succinic acid (VI), betamethylglutaric acid (VII), and β-methyl-β'-carboxydipinic acid (VIII) have been separated. The oxidation of III by



G-44

Card : 2/6

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38774.

$KMnO_4$ at 10° gives CH_3COOH, $(CH_3)_2CHCOOH$, VI, and beta-methyl-alpha-carboxyglutaric acid (IX). When III was oxidized at 60° only VI could be identified among the reaction products. An emulsion of 10 gms II in 250 ml 5% H_2SO_4 is treated with $KMnO_4$ at 6° until the color no longer disappears, the MnO_2 formed is decomposed by passing SO_2 into the solution, and the latter is extracted with ether. The volatile components are removed by steam distillation, the neutral substances are separated by extraction with ether, leaving 1.25 gms of nonvolatile acids (fraction a). On further extraction [ether] an additional 0.3 gms of nonvolatile acids is obtained (fraction b).

Card : 3/6

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38774.

CH_3COOH). The triethyl ester of IX, bp 100-103°/1.5-1.7 mm, $n^{20}D$ 1.4384, has been synthesized for comparison purposes by condensing 16 gms $CH_2(COOC_2H_5)_2$ and 11.4 gms $CH_2CH=CHCOOC_2H_5$ with C_2H_5ONa; saponification of the condensation product (refluxing with 5% alcoholic KOH) yields IX, mp 131-132°. The condensation of 15.7 gms of the triethyl ester of beta-methyl-alpha-carboxyglutaric acid with 20.0 gms $BrCH_2COOC_2H_5$ in the presence of Na in abs ether gives the tetraethyl ester of β-methyl-β',β',-dicarboxydipinic acid (XI acid), yield 62.5%, bp 153-155°/0.3 mm, $n^{20}D$ 1.4490, d^{20}_4 1.1090, [R]D [sic] 87.2 (calculated 86.9); saponification of the latter product gives

Card : 5/6

Synthetic Analogs.

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38774.

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

XI, mp 110-111° (from conc HCl). When XI is heated for 20 min at 145°/20 mm, VIII is obtained, mp 153-154° (from conc HCl). Data on the UV spectra of IVa and X and on the IR spectra of the methyl ester of V and of X are given. For Communication LXXXVI see RZhKhim, 1959, 8395. -- L. Novotny.

Card : 6/6

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

stanol-3 α-one-17 acetate (II) is produced by bromination of I in CCl_4 at -5°, yield 80 percent, melt. p. 187-188° (from alc.), $[\alpha]^{20}D = +55°$ (c = 1.59). The solution of II in $CHCl_3$ is allowed to stand with methanol solution of HBr for 20 hours, and 16 α-bromoandrostanol-3 α-one-17 (III) is separated, yield 69 percent, melt. p. 205-207°, $[\alpha]^{20}D = +53°$ (c = 3.05); II is obtained again by acetylation of III. 16 β-bromoandrostanediol-3α-,17β triacetate is formed, with a simultaneous epimerization at $C_{(16)}$, by the reduction of II with $NaBH_4$ (at 5° in alcohol, 20 hours); the yield

Card : 2/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

by boiling IV with methanol solution of KOH (48 hours), yield 70 percent, melt. p. 181-182° (from acetone-petr. ether), $[\alpha]^{20}D = +94°$ (c = 2.42; alc.), which confirms the 16 β configuration of Br. The configuration of OH at $C_{(17)}$ in IV and V was established by hydrogenation of V (5 percent Pd / $CaCO_3$ in alcohol) into the known androstanediol-3 α, 17β diacetate, melt. p. 161-162° (from CH_3OH), $[\alpha]^{20}D = +119.4°$ (c = 1.23). Oxidation of IV with CrO_3 in CH_3COOH (20°, 20 hours) produces 16 β-bromoandrostanol-3 α-one-17 acetate, melt. p. 103-105° (from CH_3OH), $[\alpha]^{20}D = +107°$ (c = 1.49), which when

Card : 4/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

hours. The oily product obtained, when acetylated with $(CH_3CO)_2$ in pyridine, produces 16 α-bromoandrostanediol-3 α, 17 β diacetate (II), melt. p. 171-172° (from CH_3OH), $[\alpha]^{20}D = -29°$ (c = 2.07). The 16 α configuration of Br in IX is confrimed by dehydrobromination (boiling with methanol KOH for 72 hours) into 16 β, 17 β -epoxyandrostanol-3 α, yield 82 percent, melt. p. 190-191° (after crystallization from CH_3OH and sublimation at 180° / 0.1 mm), $[\alpha]^{20}D = +35.5°$ (c = 1.69); acetate, melt. p. 185-188° (from CH_3OH), $[\alpha]^{20}D = +289$ (c = 1.85). By the saponi-

Card : 6/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

203° (from CH_3OH), $[\alpha]^{20}D$ = +113° (c = = 2.39) is obtained, which when oxidized with CrO_3 in CH_3COOH, produce VIII, yield 50 percent. Analogous conversions were carried out with dehydroepiandrosterous acetate. $\Delta^{5,16}$-androstadienediol-3 β -17 diacetate is obtained from the latter (similarlyto I), yield 48 percent, melt. p. 147-148° (from benz.-petr. ether), $[\alpha]^{20}D$ = -49.7° (c = = 3.82); when brominated in CCl_4 at -10°, this discetate produces Δ 5-16 α-bromo-androstenol-3 β -one-17 acetate (XII), yield 77 percent, melt. p. 181-183° (from alc.), $[\alpha]^{20}D$ = -23.7° (c = 3.77). By the

Card : 8/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

$[\alpha]^{20}D = +9^{\circ}$ (c = 2.22). By the saponification of XV, Δ^{5}-16β-bromo-androstenediol-3β,17β is obtained, melt. p. 175-176° (from CH_3OH), $[\alpha]^{20}D = -41.5^{\circ}$ (c = 187). The dehydrobromination of VY (methanol solution of KOH), 20°, 48 hours) results in dehydroepiandrosterone (XVI), yield 67 percent, melt. p. 147-148° (from CH_3OH), $[\alpha]^{20}D = +2.8^{\circ}$ (c = 1.75), which confirms the 16β-configuration of Br. By the oxidation of VI with CrO_3 in pyridine, Δ^{5}-16β-bromoandrostenol-3β-one-17 acetate (XVII) is produced, yield 69 percent, melt. p. 173-174° (from CH_3OH),

Card : 10/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

separated from this mixture after acetylation with $(CH_3CO)_2O$ in pyridine and cristallization from CH_3OH. XX: yield 38 percent, melt. p. 186-188°, $[\alpha]^{20}D$ = -94° (c = 2.56); XXI: yield 15 percent, melt p. 203-205°, $[\alpha]^{20}D$ = -64° (c = 1.34). The dehydrobromination of XXI results in XVI, yield 62 percent, and from XX Δ^{5}-16β,17β-epoxyandrostenol-3β is formed, melt. p. 143-144° (from CH_3OH), [ ]^{20}D = -25° (c = 1.84); acetate, melt. p. 168-169° (from CH_3OH), $[\alpha]^{20}D$ = -68.5° (c = 1.11). XIV and XIX diketones were used to obtain epimeric 16-bromotestosterones. The reduction

Card : 12/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

of XIV with $LiAlH_4$ at 0° produces crude Δ^4-16 α -bromoandrostenediol-3 β ,17 β (XXII), which is oxidized in $CHCl_3$ with freshly prepared MnO_2 (20°, 18 hours) into Δ^4-16 α -bromoandrostenol-17 β -one-3 (XXIII), yield 21 percent, melt. p. 172-174° (from chlorof.-petr. ether), $[\alpha]^{20}D$ = +53.8° (c = 2.6); acetate, melt. p. 216-217° (from CH_3OH), $[\alpha]^{20}D$ = +29.8° (c = 1.41). Δ^4-16 β -bromoandrostenol-17 β -one-3 (XXV) is synthesized analogously to XXIII from XIX through the crude 16-epimer of XXII (XXIV), yield 26 percent, melt. p. 187-189° (from acetone), $[\alpha]^{20}D$ = +73° (c = 2.14°);

Card : 13/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

acetate, melt. p. 158-159° (from CH_3OH), $[\alpha]^{20}D = +126°$ (c = 2.41). The configuration of Br in XXIII and XXV is confirmed by their oxydation with CrO_3 in pyridine into XIV, yield 65 percent, and XIX, yield 67 percent respectively. The dehydrobromination of XXII (boiling with methanol KOH for 48 hours) resulted in a product, the infrared spectrum of which did not show the CO group; on the contrary, the product of dehydrobromination of XXIV contained the CO group, which confirms the configuration of OH in the initial compounds. XXV was synthesyzed also in another way. XVIII formate,

Card : 14/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

melt. p. 190-191° (from CH_3OH), $[\alpha]^{20}D$ = =+45.5 percent (c = 1.82) was obtained by heating XVIII in 87 percent HCOOH; Δ^5-16β-bromodiol-3β,17β 3-formate (XXIV) is separated from the latter with $LiAlH[OC(CH_3)_3]_3$ (at 0°, 10 min), yield 97 percent, melt. p. 174-175° (from benz.), $[\alpha]^{20}D$ = -59° (c = 2.42). XXVI can also be synthesized with a 30 percent yield by partial formylation of XIX, heating with 87 percent HCOOH for 15 min. Acetylation of XXVI with $(CH_3CO)_2O$ in pyridine results in 3-formate-17-acetate of Δ^5-16β-bromoandrostenediol-3β,17β, yield 81 percent, melt.

Card : 15/16

165

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogues. G-3

Abs Jour : Ref Zhur-Khimiya, No 9, 1959, 31508

p. 200-201° (from chlrof.-CH_3OH), $[\alpha]^{20}D$ = = +5.2° (c = 2.58). The latter produces XXV acetate by the oxidation with Al isopropylate in toluene in the presence of cyclohexanone, and the XXV acetate produces XXV by saponification. Data concerning the ultraviolet spectra of XIV, XIX, XXIII and XXV are presented. All the $[\alpha]$Ds were determined in $CHCl_3$, the exceptions are mentioned. See Ref Zhur-Khimiya, 1958, 81783, for report XXXIV. -- Antonin Enr.

Card : 16/16

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

Author : Farkas, J., Kourim, P., Sorm, F.
Inst : -
Title : The Relationship between Chemical Structure and Insecticidal Activity of Pyrethroid Compounds. II. Analogues of Chrysanthemic Acid Containing Atoms of Chlorine in the Side Chain.

Orig Pub : Chem. listy, 1958, 52, No 4, 688-694

Abstract : For the purpose of investigating the relationship between the insecticidal activity and structure, cis-(Ia) and trans-2-(ββ -

Card : 1/9

H-90

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

dichlorvinyl)-3,3-dimethylcyclopropane carbonic acids (Ib), and also ester of Ib and 2-allyl-3-methyl-4-oxy-2-cyclopentenone (allylretrolon) (II) were synthesized. By the addition of CCl_4 to 3-methylbutane-1 in the presence of benzoyl peroxide (23 hours in an autoclave at 90-95°) a 38 percent yield of 1,1,1,3-tetrachlor--4-methylpentane (III) of 80-82°/10 mm boiling point and 1.4860 $n^{20}D$ was obtained. In the dehydrochlorination of alcohol solution of III with 1 mol of KOH (48 hours at 0°), 1,1,1-trichlor-4-methyl-

Card : 2/9

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

pentene-2 (IV) of 78-83°/30 mm and of 1.4800 $n^{20}D$ is being formed. In the presence of 2 mols of KOH (48 hours at 20°) III yields a mixture containing 90 percent of IV (or also 1,1,3-trichlor-4-methylpentene-1) and 10 percent of 1,1-dichlor-3--ethoxy-4-methylpentene-1. The acetylation of 1,1,1-trichlor-2-oxy-4-methylpentene 3 (Ref Zhur-Khimiya, 1957, 37259) while heating with acetic anhydride in C_5H_5N (3 hours up to 100°) results in the 86 percent yield of 1,1,1-trichlor-2 acetoxy-4--methylpentene-3 (V) of 98°/10 mm boiling

Card : 3/9

H-91

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

point and 1,4795 $n^{20}D$. Analogically, from a mixture of 1,1,1-trichlor-2-oxy-4-methylpentene-3 and -pentene-4, obtained through condensation of chloral and iso-butylene in accordance with Callonge and Perro (Ref Zhur-Khimiya, 1955, 26089; 1957, 54285) forms a mixture of V and 1,1,1-trichlor-2--acetoxy-4-methylpentene-4 (VI) with 89 percent yield. By introducing an ether solution of V drop by drop (in the course of 3 hours) to the suspension of Zn dust in the boiling mixture of ether and CH_3COOH, 76 percent yield of 1,1-dichlor-4-methylpenta-

Card : 4/9

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

diene-1,3 (VII) of 165-170°/720 mm boiling point, 1.5199 $n^{20}D$, $\lg \varepsilon_{max}$ of 4.87 at 253 mμ is derived. Analogically, by conducting the reduction of a mixture of V and VI, 62 percent yield of a mixture containing VII and its unconjugated isomer (of 145-150°/720 mm boiling point of a mixture 1.4798 $n^{20}D$) is obtained, which, isomerized by heating for 1 hour with n-toluene sulfonic acid up to 150°, results in 81 percent yield of VII. When mixture of 0.3 mols of VII and 0.2 mols of diazoacetic ester are added drop by drop in the

Card : 5/9

H-92

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

course of 4 hours to 0.5 g of Cu-dust, heated to 110°, followed by filtering-out the catalyst and subjecting the filtrate to fractional distillation, 17.52 g of a mixture containing ethyl esters of Ia and Ib acids is obtained, having 119-120°/15 mm boiling point and 1.4883 $n^{20}D$. Purest sample of the mixture [with 130-135°/15 mm boiling point (bath temperature) and 1.4907 $n^{20}D$] is obtained after hydrolysis and esterification of the Ia and Ib mixtures (La Forge, F. B., Berthl, W. F., J. org. Chem., 1947, 12, 199). The purified mixture of esters (15.16 g) is

Card : 6/9

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

heated for 4 hours at 100° in 80 ml CH_3COOH and 15 ml of 20 percent HCl (acid), followed by pouring into water, extraction with petroleum ether, fractionation, yielding 10.5 g of viscous oil that has 100-110° /0.2 boiling point, which after mixing with 10 ml of n-hexane produces 7.46 g of Ia and Ib mixture of 60-65° melting point. By agitating 2.8 g of the preceeding mixture in 20 ml of hexane, 0.85 g of Ib having 95-96.5° melting point (from hexane) are obtained. From mother liquors obtained after the separation of Ib, upon extended standing at -30°, 0.15 g

Card : 7/9

H-93

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

of Ia having 88-89° melting point (from Hexane) are derived. By heating 0.277 g Ib with 1 ml $SOCl_2$ in 3 ml of n-hexane (1 hour on a steam bath), followed by dissolving of raw chloranhydride in 5 ml C_6H_6, addition of 0.2 g II, and 12 hours standing of the mixture, 0.2 g of a complex ester of Ib acid with II are obtained with the boiling point of 140-150/0.2 mm and $n^{20}D$ of 1.5274. In conducting comparison tests of insecticidal activities of Ib ester and II as against that of alletrine (on ordinary house flies), it has been established that substitution of methyl

Card : 8/9

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24569

groups in the side chain of the chrysanthemic acid with chlorine atoms does not lead to changes in the insecticidal activity of a compound.

Card : 9/9

H-94

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

Author : Farkas, J., Kourim, P., Sorm, F.
Inst : -
Title : The Relationship between Chemical Structure and Industrial Activity of the Pyrethroid Compounds. II. Analogues of Chrysanthemic Acid Containing Aryl Group.

Orig Pub : Chem. listy, 1958, 52, No 4, 695-706

Abstract : By the condensation of diazoacetic ester with the substituted derivation of styrol, 2-arylcyclopropane carbonic acids and the esters with alletrolon (I) are obtained.

Card : 1/12

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

In the comparison of insecticidal activities of these esters with those of alletrene, it was established that the substitution of iso-butylene in the chrysanthemic acid (II) for a phenyl group does not lead to the lowering of its activity. However, its activity is lowered when the phenyl group is being substituted. The presence of hemin CH_3-groups in the cyclopropane ring of II is essential from the standpoint of insecticidal activity. The most effective of all the esters obtained are (±)-trans-2-phenyl-33-dimethylcyclopropanecarbonic acid

Card : 2/12

H-95

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

ester (trans-III) or its pravoratory antipodes (trans- (+) -III) with I. The absolute configuration of trans-III has been proved. The following aromatic carbinols $R_1R_2R_3 \cdot COH$ are obtained (using usual methods) from an aldehyde, ketone, or compound ester and aryl, or alkyl-MgBr, or the corresponding MgCl derivatives. Presented are: R_1, R_2, R_3, boiling point in °C/mm, $n^{20}D$, yield in percent. They are: H, C_2H_5, C_6H_6 (IV), 110/15, 1.5262, 66; CH_3, CH_3, benzyl, 95/8, 1.5169, 74; C_2H_5, C_2H_5, benzyl, 125/15, 1.5165, 64; CH_3, CH_3, o-xylyl;

Card : 3/12

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

113/8, 1.5186, 71; CH_3CH_3, m-xylyl, 119/20, 1.5144, 71; CH_3, CH_3, n-xylyl IV, 102/8 (melting point 90-41° [sic]), 1.5129, 73 3,5-dinitrobenzoate IV, melting point of 133-134°); CH_3, CH_3, n-chlorbenzyl (V), 129/11 (34° melting point), -, 73 (3,5--dinitrobenzoate V, melting point 126-127°); CH_3, CH_3, 2,4-dichlorobenzyl, 135/10, 1.5451, 71 (3,5-dinitrobenzoate, melting point 116°). The following derivatives of styrol $R_1 \cdot C_6H_4 \cdot CH = C(R_2)(R_3)$ were obtained in the 3 hours of boiling of the corresponding alcohol with 30 percent excess of acetic anhydride and 1

Card : 4/12

H-96

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 29570

percent H_2SO_4 (Method A), or from the corresponding alcohol in the contact with Al_2O_3 at 300-320° (Method B). Presented below are R_1, R_2, R_3, boiling point in °C/ /mm, $n^{20}D$, synthesis method, yield in percent. They are: H, H, CH_3 (VI), 71/15, 1.5485, A. 52; H, CH_3, CH_3, 78/16, 1.5387, A, 82; H, C_2H_5, C_2H_5 (VII) 101/15, 1.5189, A, 86; o-CH_3, CH_3, CH_3, 87/18, 1.5283, A, 84; m-CH_3, CH_3, CH_3, 92/17, 1.5312, A, 84; n-CH_3, CH_3, CH_3, 97/22, 1.5332, A, 88 (B, 66); n-Cl, CH_3, CH_3, 102/11, 1.5521, A, 74; 2,4-Cl_2, CH_3, CH_3, 123/15, 1.5593, A, 89.

Card : 5/12

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

H-18

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides.

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

VI ($n^{20}D$ = 1.5490) also obtained with 80 percent yield from allylbenzene by heating it with 1 percent tert-butylate K up to 150°, but VII ($n^{20}D$ = 1.5314) with 55 percent yield by heating (1 hour) 1-methyl-3-methallylbenzene with 1 percent n-toluenesulfonic acid at 160° temperature. 2-arylcyclopropanecarbonic acids $R_1C_6H_4CHC(R_2)(R_3)CHCOOH$ were synthesized when a mixture of 0.2-0.3 mols of corresponding styrol derivative and 0.1 mols of diazoacetic ester were added drop by drop to 0.1 mols of styrol derivative and 1 g Cu dust in the course of 6 hours at 120-125°

Card : 6/12

H-97

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

with the subsequent heating for 1/2 hour at 150°. The mixture of corresponding ethyl esters, isolated by vacuum distillation, is saponified by boiling for 3 hours with 20 percent water-alcohol solution of KOH (50 percent excess). From the mixture of stereo-isomeric acids, after the addition of petroleum ether, the corresponding cis-acid in crystalline form (notations of cis- and trans- refer to corresponding positions of $R_1 \cdot C_6H_4$ and COOH groups) is usually separated. The non-crystallizing mixtures are converted (by means of 3 hour heating with $SOCl_2$) into C_6H_6

Card : 7/12

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

H-18

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Posticides.

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

with the corresponding chloranhydrides, or else by the interaction of these chloranhydrides with NH_3 solution in $CHCl_3$ at 0°, into the corresponding amides. All the cis-acids were recrystallized from C_6H_6 + petroleum ether, all the trans-acids from petroleum ether. The following arylcyclopropane acids were obtained (given below are R_1, R_2, R_3, yield in percent of the isomeric acids, melting point in °C of trans- and cis-isomers, boiling point in °C/mm of chloranhydrides of cis- and trans- acids): H, H, H VIII, 59, 104, 92, -, -, (melting points of amides cis-VIII

Card : 8/12

H-98

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

and trans-VIII are 88-89° and 189°, melting point of toluidido cis-VIII is 174°); H, H, CH_3 (IX), 50, 114, 77.5, -, -; H, CH_3, CH_3 (III), 63, 134, 102, -, 122/11 (melting points of amides cis- and trans-III are 98-99° and 141°); 2-CH_3, CH_3, CH_3(X), 40, -, 126, -, 144/16; 3-CH_3, CH_3 (XI), 62, -, boiling point 135°/0.1 mm, -, 122/5 (melting point of toluidido trans-XI is 145-147°); 4-CH_3, CH_3, CH_3 (XII), 62, 142, 134, -, 105/0.4; 4-Cl, CH_3, CH_3 (XIII), 46, -, 140-141, -, 120/0.2; 2,4-Cl_2, CH_3, CH_3, 46, 174 (?), 96 (?), -, -; H, C_2H_5, C_2H_5 (XIV),

Card : 9/12

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

58, -, 98, -, -. When a mixture of solutions of 9.5 g of trans-III in 50 ml of ether and 4.2 g (-) ephedrin in 10 ml of ether are kept at 0° for 3 hours, 5.85 g (-)-ephedrin salt of trans-(+)-III of 169° melting point (from ethylacetate), $[\alpha]^{20}D$ of +0.51° (with 3.13, in C_2H_5OH) are derived. From mother liquors after addition of 4.9 g (-)-ephedrin and after keeping at 0° for 5 hours, (-)-ephedrin salt of trans-(-)-III of 130-131° melting point (from ethylacetate), $[\alpha]^{20}D$ - 38.8° (with 2.64 in C_2H_5OH) is obtained. And from the decom-

Card : 10/12

H-99

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Pesticides. H-18

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

position of salts with 4 percent HCl (acid), were obtained free trans-(+)-III of 84-85° melting point, $[\alpha]^{20}D$ + 31.9° (with 4.93 in C_2H_5OH) and trans-(-)-III of 84-85.5° melting point, $[\alpha]^{20}D$ - 32.2° (with 4.85, in C_2H_5OH). Esters of the proceeding acids and I are obtained with yields of approximately 50 percent in a mixture of C_6H_6 + C_5H_5N from I and chloranhydride of corresponding acid when keeping a mixture for 1 hour at 0° and 12 hours at approximately 20°. After the usual treatment of a solution in C_6H_6, the raw ester is purified

Card : 11/12

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

H-18

CZECHOSLOVAKIA/Chemical Technology. Chemical Products and Their Applications. Posticides.

Abs Jour : Ref Zhur-Khimiya, No 7, 1959, 24570

with Al_2O_3 and volatile fractions are removed by heating to 78°/0/1 mm for 8 hours, or by fractionation at 180-190°/0/1 mm. The following esters were synthesized (given below are initial acid and $n^{20}D$ of ester): trans-VIII, 1.5517; trans-IX, 1.5450; trans-III, 1.5382; trans-(+)-III, 1.5371; trans-(-)-III, 1.5378; cis-III, 1.5401; X, 1.5369; XI, 1.5362; trans-XII, 1.5365; XIII, 1.5452; XIV, 1.5355. For Part I, see preceeding abstract.

Card : 12/12

H-100

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, F.

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38775.

Author : Ognyanov, I., Ivanov, D., Arnout, V., Horak, M., Pliva, J., and Sorm, F.

Inst :

Title : Chemistry of the Terpenes. LXXXVII. Structure of Germacrone, the Crystalline Component of Bulgarian Medicinal Volatile Oil.

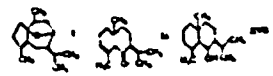
Orig Pub: Chem Listy, 52, No 6, 1163-1173 (1958) (in Czech)

Abstract: The authors have shown that the principal component of Bulgarian medicinal essential oil (Germanium macrorhizum L.), previously designated germacrol, does not have the oxide structure (I) [see inset below], as

Card : 1/12

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38775.



CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38775.

previously assumed, but that of the ketone (Ia). The authors propose the name Germacrone for Ia. The structure of Ia has been proved spectroscopically and by chemical reactions. The hydrogenation of I in glacial CH_3COOH over a Pt (from PtO_2) catalyst gives a liquid product (II) which on reduction with LiH_4 gives hexahydrogermacrol (III). The oxidation of II with CrO_3 in glacial CH_3COOH gives hexahydrogermacrone (IV). IV like Ia does not form a semicarbazone and 2,4-dinitrophenylhydrazone derivative. The reduction of I by aluminum isopropylate or by $LiAlH_4$ gives germacrol (V) which on dehydration yields a hydrocarbon (VI). The dehydrogenation of V

Card : 3/12

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38775.

or of VI with S gives guaiazulene (VII). The hydrogenation of VI in glacial CH_3COOH over Pt (from PtO_2) with 4 moles of H_2 gives elemane (VIII); the hydrogenation of V under the same conditions gives selinene (IX). The hydrogenation of I over Pt (from PtO_2) in alcohol gives α, β-unsaturated tetrahydrogermacrone (X). The reduction of X by $LiAlH_4$ gives tetrahydrogermacrol (XI) which on hydrogenation in glacial CH_3COOH over Pt (from PtO_2) gives the saturated hydrocarbon germacrane (XII) and III. The IR spectrum of XII differs from the spectra of saturated sesquiterpenic hydrocarbons and resembles the spectra of hurulane and farnesane (see RZhKhim, 1953, 8544). The dehydra-

Card : 4/12

G-48

tion of III gives a hydrocarbon (XIII). The ozonation of X yields 1 mol of acetone, while the ozonation of I gives 1.5-1.6 mol of acetone. The oxidation of I by $KMnO_4$ in acetone gives $(COOH)_2$ and levulinic acid. The action of C_6H_5OHn on I in the cold gives crystalline isogermacrone (XIV). The hydrogenation of XIV in glacial CH_3COOH over Pt (from PtO_2) gives IV; when the hydrogenation is carried out in alcohol, tetrahydrogermacrone (XV) is obtained. The acid isomerization of I yields a liquid ketone (XVI) which on hydrogenation over Pt (from PtO_2) in glacial CH_3COOH with subsequent reduction by $LiAlH$ gives selinanone (XVII) [sic: nomenclature]; oxidation of the

Card : 5/12

latter product yields selinanone (XVIII) [sic]. The dehydration of XVII followed by hydrogenation of the product obtained gives IX. Ia, bp 56-57° (from CH_3OH), $[\alpha]_D^{20}$ D 0° (chloroform). The hydrogenation of I (278 mg) in glacial CH_3COOH over 30 mg of freshly reduced PtO_2 gives II, bp 134-135°, n_D^{18} D 1.4774, d_4^{18} 0.9162. The reduction of 2 gm II by $LiAlH_4$ in ether followed by chromatography on Al_2O_3 (active towards I-II) [sic] gives III, yield 1.8 gm, bp 108.5-109.5°/0.05mm. The oxidation of 2 gm II with an excess of CrO_3 in glacial CH_3COOH for 20 min at about 20° followed by chromatography on Al_2O_3 (active towards I-II) gives IV, bp 131-136°/7 mm, n_D^{13} D 1.4770, d_4^{13} 0.9225. The

Card : 6/12

G-49

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38775.

duction of 2 gm I by aluminum isopropylate (from 1.0 gm Al) gives (after chromatography) 1.3 gm V, bp 108-110°/0.15 mm. The reduction of 0.6 gm I by $LiAlH_4$ gives V, bp 128°/0.8 mm, $n^{15}D$ 1.5297. When 3 gm V and 7 ml of 100% HCOOH are heated quickly to boiling, VI is obtained, yield 1.5 gm, bp 124.5-127°/11 mm, $n^{24}D$ 1.5250, d^{24}_4 0.9115. When 0.4 gm V is heated to boiling and chromatographed on Al_2O_3 (active towards I-II) 0.25 gm VI is obtained. When 1 gm V (or VI) and 0.25 gm S are heated for 30 min at 180°, followed by chromatography on Al_2O_3 (active towards II), 0.25 gm of VII is obtained, trinitrobenzoate derivative mp 151-152°.

Card : 7/12

The hydrogenation of 312 mg VI in 5 ml glacial CH_3COOH or freshly reduced PtO_2 gives VIII, bp 124°/14 mm, $n^{24}D$ 1.4581, d^{24}_4 0.8538. The hydrogenation of 330 mg V under the same conditions as described in the last case, followed by chromatography on Al_2O_3 (active towards I-II) gives IX, bp 129-132°/14 mm, $n^{15}D$ 1.4817, d^{15}_4 0.8939. The hydrogenation of 3 gm I over Pt (from PtO_2) in alcohol (7 days) with 4 mols of H_2, followed by chromatography on Al_2O_3, gives X, yield 2.6 gm, bp 108°/0.8 mm, $n^{18}D$ 1.5038, d^{18}_4 0.9549. The reduction of 0.90 gm X by $LiAlH_4$ (0.15 gm) gives XI, bp 123-125°/2.5 mm. The hydrogenation of 500 mg XI in glacial CH_3COOH over Pt (from PtO_2) followed

Card : 8/12

0-50

by chromatography of the product obtained on Al_2O_3 (active towards I-II) and elution with petroleum ether, gives XII, yield 320 mg, bp 132-135°/22 mm, $n^{20}D$ 1.4717, d^{20}_4 0.8538; elution with alcohol gives 130 mg of III. The dehydration of 900 mg III with 1.0 gm $KHSO_4$ at 180-200° (30 min) gives XIII, yield 750 mg, bp 114-115°/7 mm, $n^{15}D$ 1.4799, d^{15}_4 0.8594; the hydrogenation of the latter product (230 mg) over Pt (from 30 mg PtO_2) in glacial CH_3COOH, gives XII, bp 115-117°/8 mm, $n^{21}D$ 1.4704, d^{21}_4 0.8562. When 15 gm I are treated with C_6H_5OMe (from 2 gm Na and 30 ml alc, 12 hrs) gives XIV, yield 9.5 gm bp 131-134°/1mm, mp 50-52°, 2,4-dinitrophenylhydrazone

Card : 9/12

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs.

G

Ref Jour: Ref Zhur-Khim., No 11, 1959, 38775.

mp 183-183.5°. The hydrogenation of XIV (700 mg) in glacial CH_3COOH by the same procedure as that used for I, followed by oxidation of the reaction product by CrO_3 in glacial CH_3COOH and purification by chromatography on Al_2O_3 (active towards I-II) gives IV, bp 120-121°/3 mm, $n^{17.5}D$ 1.4760, $d^{17.5}$ 0.9222. The hydrogenation of XIV (500 mg) over Pt (from PtO_2) in alcohol (or procedure used for I), followed by reduction of the reaction product by $LiAlH_4$ in ether and chromatography on Al_2O_3 (active towards I-II) gives 30 mg XIII, bp 130-132°/20 mm, $n^{19}D$ 1.4720, $d^{3.5}$ 0.8576. When 2 gms XIV are reduced by $LiAlH_4$ (0.4 gm) in ether solution, XV

Card : 10/12

0-52

is obtained, bp 129-131°/1.1 mm, mp 64-65° (from alcohol). When a mixture of 10 gms I, 5 ml H_2SO_4 and 20 ml alcohol is heated to 60°, XVI is obtained, yield 7.75 gms, bp 130.5-138.5°/2.5 mm, $n^{4.5}D$ 1.5270, $d^{4.5}$ 0.9840; XVI forms two 2,4-dinitrophenylhydrazone derivatives melting at 195-196° and 184-185°. The hydrogenation of 2 gms XVI over Pt (from 50 mg PtO_2) in glacial CH_3OH gives XVII, yield 1 gm, mp 107.5-108.5° (from hie). The oxidation of 150 mg XVII by CrO_3 in glacial CH_3COOH, followed by chromatography of the product on Al_2O_3 (active towards I-II), gives XVIII, $n^{20}D$ 1.4694, d^{20} 0.9643. The dehydration of 300 mg XVII by heating in 5 ml 100% HCOOH

Card : 11/12

for 5 min to boiling, followed by chromatography of the reaction products on Al_2O_3 (active towards I-II) (from petroleum ether, 150 mg, bp 109.5°/9 mm) (sic), and hydrogenation over Pt (from PtO_2) in glacial CH_3COOH gives IX, bp 110-112°/1.5 mm, $n^{4}D$ 1.4840, d^{4} 0.8912. The UV spectra of Ia and X are given together with the IR spectra of Ia, II, IV, X, XII, XVIII, and IR absorption curves for Ia, IX, and XII. — L. Novotny.

Card : 12/12

0-52

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38777.

Author : Suchy, M. and Sorm, F.
Inst :
Title : Chemistry of the Terpenes. XC. Synthesis of 1,7-dimethyl-4-isopropyl-cyclodecane (Germacrane)

Orig Pub: Chem Listy, 52, No 6, 1180-1185 (1958) (in Czech); Collection Czechoslov Chem Commun, 23, No 12, 2175-2180 (1958) (in English with a Russian summary)

Abstract: The authors have synthesized 1,7-dimethyl-4-isopropyl-cyclodecane (I) which was found to be identical with germacrane, obtained by the complete reduction of germacrone. The condensation of $CHCH_2COOH_2$ with

Card : 1/7

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38777.

$(CH_3)_2CHCHO$ gives the diamide of α, α'-dicyanoβ-isopropylglutaric acid (II), which on saponification and decarboxylation gives beta-isopropylglutaric acid (III). The diethyl ester of III on reduction with $LiAlH_4$ gives 3-isopropylpentane-1,5-diol (IV) from which 3-isopropyl-1,5-diiodopentane (V) is obtained. The condensation of V with $CH_3CH(COOC_2H_5)_2$ gives an ester which on saponification yields α, α'-dimethyl-α, α'-dicarboxy-δ-isopropylazelaic acid (VI); decarboxylation of VI gives α, α'-dimethyl-δ-isopropylazelaic acid (VII). The hemiester of VII (VIII) [sic] is converted to the acyl chloride (IX) which by the Arndt-Eistert reaction gives the dimethyl ester of α, β'-

Card : 2/7

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38777.

dimethyl- δ -isopropylsebacic acid (X). The acyloin condensation of X gives the hydroxyketone (XI). The reduction of XI according to Clemmensen gives a mixture from which I is isolated after hydrogenation of the hydrocarbon fraction. The ketone fraction is similarly converted to pure I via the ethylenethioketal and desulfurization with Raney Ni. The IR spectra of synthetic and natural I (the curves are given) are identical. 94 gms $CHCl_2CONH_2$ in 50 ml water are treated dropwise with a mixture of 35 gms $(CH_3)_2CHCHO$ and 4 gms piperidine and the solution is stirred for 6 hrs at 13°; II is obtained, mp 152°. The hydrolysis of

Card : 3/7

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38777.

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

II by boiling with 250 ml conc HCl gives III, mp 102°. The action of HCl (gas) on III in alcohol gives 36.2 gms of the diethyl ester of III, bp 148-150°/15 mm. Reduction of the latter with $LiAlH_4$ under the usual conditions gives IV, bp 147-148°/15 mm. When 35 gms IV and 300 gms triphenoxyphosphonium methyl iodide, added in small portions, are heated 4 hrs to 60° and the resulting product mixture is subjected to chromatography on Al_2O_3 (active towards IV), 57.1 gms of V are obtained, bp 138-142°/2 mm. 11 gms V are added to a mixture of 11 gms $CH_3CH(COOC_2H_5)_2$ and 1.4 gm NaH in 70 ml toluene, the solution is heated for 1 hr at 110°, the tetraethyl ester is separated,

Card : 4/7

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. 0

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38777.

saponified with methanolic KOH (10 gms per 100 ml), the resulting solution is refluxed and treated [sic], giving VI, mp 176-177° (decomp; from water). The decarboxylation of 25.1 gms VI at 160°/15 mm gives 16.7 gms VII, bp 180-182°/0.1 mm. 16.7 gms VII in 300 ml ether are treated with 1 mol of an ether solution of CH_2N_2 and the resulting solution is cooled (with stirring); 8.1 gms VIII are obtained, bp 145-146°/0.3 mm. 8.1 gms VIII in C_6H_6 react with $SOCl_2$ to give 8.7 gms IX which is added dropwise with cooling to -15° to an ether solution of CH_2N_2 (prepared from 20 gms nitrosomethylurea). The diazoketone which is obtained is decomposed (5 por-

Card : 5/7

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

CZECHOSLOVAKIA/Organic Chemistry. Natural Compounds and Their Synthetic Analogs. G

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38777.

pure I, bp 126°/10 mm, $n^{20}D$ 1.4713, d_4^{20} 0.8596. 0.35 gms B of bp 149°/10 mm [semicarbazone mp 165° (from alc)] is condensed with 0.5 ml $(CH_2SH)_2$ and 1 ml $BF_3 \cdot (C_2H_5)_2O$ to give the ethylenethioketal which on desulfurization with 5 gms of Raney Ni in 20 ml dioxane (24 hrs), chromatography of the hydrocarbon on Al_2O_3, and hydrogenation over Pt (from PtO_2) gives I, $n^{20}D$ 1.4729, d_4^{20} 0.8571. -- L. Novotny.

Card : 7/7

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

COUNTRY : Czechoslovakia G-3
CATEGORY :

ABS. JOUR. : RZKhim., No. 16 1959, No. 57216

AUTHOR :
INST. :
TITLE :

ORIG. PUB. :

ABSTRACT : of IV followed by oxidation with dil HNO_3 to D(+)-isopropylsuccinic acid (V). I does not isomerize when refluxed for 45 min with 10% NaOH in alcohol. When (-)-cadinanedihydrochloride is heated with CH_3COONa in CH_3COOH followed by chromatography on alkaline Al_2O_3 followed by fractionation in a column with 70 theoretical plates packed with Diksone [sic], IV is obtained, bp 124°/9 mm, $n^{20}D$ 1.5059, d_4^{20} 0.9239. 9.5 gms IV are added over 2 hrs to

CARD: 2/6

158

CARD: 3/6

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

[illegible] : [illegible]

CATEG. :

ABS. JOUR. : RZKhim., No. 16 1959, No. 57216

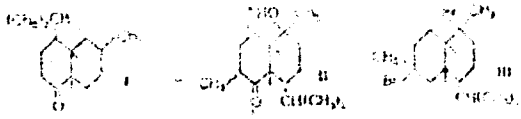
AUTHOR :

INST. :

TITLE :

ORIG. PUB. :

ABSTRACT : benzene), $[\alpha]^{20}D$ + 20.4° (c = 1.96: water). Further elution of the paper moistened with 1% H_2SO_4 yields an additional 112 mg of V. Better



CARD: 4/6

154

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

COUNTRY : Czechoslovakia

CATEGORY :

ABS. JOUR. : RZKhim., No. 16 1959, No. 57216

AUTHOR :

INST. :

TITLE :

ORIG. PUB. :

ABSTRACT : yields of V are obtained by the ozonation of 7.8 gms IV in 80 ml CH_3COOH and the decomposition of the ozonides at 100° with a mixture of 45 ml water and 2.2 ml 30% H_2O_2. The residue after the evaporation of the solution is oxidized (1 hr, 110-120°) with 50% HNO_3 and V_2O_5; after the usual treatment, 2.03 gms of the anhydride of V are obtained which on heating with water give V (yield 18%); the latter is purified by paper chromatography. The reaction dispersion

CARD: 5/6

160

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SORM, F.

COUNTRY : Czechoslovakia 7-3
CATEGORY : Organic Chemistry. Natural Compounds and their Synthetic Homologues
ABS. JOUR. : RZKhim., No. 20 1959, No. 71529

AUTHOR : Schwarz, Vladimir; Cerny, Vaclav; Sorm, Frantisek
INST. : Not given.
TITLE : Steroids. XXXVII. Preparation of Methyl-3β, 17α-diacetoxybisnoralluocholanate and Its 20-Epimer. A New Method for the Synthesis of *
ORIG. PUB. : Chem. Listy, 1958, 52, #8, 1633-1641.

ABSTRACT : A new method for the formation of a side chain in bisnor steroid acids was described. The method consists of a reaction of CH_3CHN_2 with a corresponding 17-carbonate chloroanhydride with a subsequent regrouping of the resulting diazoketone. Upon the reaction of Na-3β-acetoxy-Δ5-etionate (I) with $(COCl)_2$ in C_6H_6 in the presence of pyridine (2 hours, 20°), I-chloroanhydride was formed (99% yield). Its solution in C_6H_6 (no purification) was added at -20° into an ether solution of CH_3CHN_2. The mixture was left

CARD: 1/8

* Side Chains in Bisnor Steroid Acids

34

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

COUNTRY : Czechoslovakia G-3
CATEGORY :

ABS. JOUR. : RZKhim., No. 20 1959, No. 71589

AUTHOR :
INST. :
TITLE :

ORIG. PUB. :

ABSTRACT : #4, 11431), a mixture of three substances was obtained. Upon repeated chromatography on Al_2O_3 the mixture yielded 604 mg of methyl 3β-acetoxy-Δ5-bisnorcholenate (III), m.p. 136-137°, $[\alpha]^{22}D$ - 62 ± 0.5° (from 1.8). Upon reacting 3β-acetoxyallo ethionic acid (IV) with $SOCl_2$ (0°, followed by 16 hours at 20°) IV-chloroanhydride, (97% yield) was obtained. The reaction of the latter with CH_2CHN_2 (by the above-described method) yielded 17β-(α-diazopropionyl)-androstanol-3β-acetate (V), 85% yield, m.p. 141-143° (dec), $[\alpha]^{19}D$ - 16.6 ± 3° (from 1.3).

CARD: 3/8

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

G-3

CONTRIB. : Czechoslovakia
CATEGORY :

ACC. JOUR. : RZKHIM., No. 20 1959, No. 71589

AUTHOR :
INST. :
TITLE :

ORIG. SUB. :

ABSTRACT : a corresponding chloroanhydride (93% yield) by means of the above-described method. The latter, reacted with CH_2CHN_2, gave an impure 17α-diazopropionyl)-androstandiol 3α,16α-acetate-benzoate (VII), 91% yield. Rearrangement of VII at the above conditions, followed by saponification, esterification, acetylation and chromatographic separation over Al_2O_3, led to the formation of methyl 3α,16α-diacetoxybisnorallocholanate (VIII), 19% yield, m.p. 143-144° (from CH_3OH), $[\alpha]^{20}$ - 68 ± 1.5° (from 1.9). After the elimination of VIII from the mother liquor

CARD:
5/8

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

COUNTRY : Czechoslovakia G-3
CATEGORY :

ABS. JOUR. : RZKhim., No. 20 1959, No. 71589

AUTHOR :
INST. :
TITLE :

ORIG. PUB. :

ABSTRACT : dithiol (2 hours, 0°C,) and introduction of dry HCl led to the formation of methyl-3-ethylsnedithiobisnorallocholanate (XI), 90% yield, m.p. 168-169° (precipitation with hot CH_3OH from a hot solution of $CHCl_3$), $[\alpha]^{21}D$ + 20 ± 2° (from 1.1). Upon boiling ~~of~~ XI for 5 hours, with sponge Ni in alcohol, IX was obtained, 79% yield, m.p. 100°, $[\alpha]^{20}D$ + 10 ± 0.5° (from 2.4). In a similar manner 50 mg of VIII was saponified by shaking it for 16 hours with 4 ml CH_3OH, containing 60 mg K_2CO_3. 7% thus obtained unpurified dioxy compound was oxidized with 30 mg CrO_3 in

CARD: 7/8

31

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

COUNTRY : Czechoslovakia G-3
CATEGORY :

ABS. JOUR. : RZKhim., No. 20 1959, No. 71589

AUTHOR :
INST. :
TITLE :

ORIG. PUB. :

ABSTRACT : 2 ml CH_3COOH (16 hours, 20°). The resulting diketone was condensed with ethanedithiol (at the above-described conditions) and after boiling with sponge Ni and Al_2O_3 chromatography was transformed into 12 mg of IX. All $[\alpha]D$ were determined in $CHCl_3$. Article XXVIII RZKhim, 1959, #15, 53547.

-- S. Ananchenko

CARD: 8/8

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

[illegible] : Czechoslovakia

[illegible] :

[illegible] JOUR. : [illegible]Chim., No. 22 1359, No. [illegible]719

[illegible] :

[illegible] :

[illegible] :

[illegible] JUB. :

[illegible] : 40 ml CH_3OH. Following filtration of the solution, the filtrate is treated with 3.5 gms NaOH in 7 ml water and 20 gms Zn-dust, the solution is stirred for 1 hr at 25°, and filtered after 14 hrs; the filtrate is concentrated under vacuum at 45° to 400 ml, diluted with 200 ml water, and extracted with C_6H_6. After extraction with NaOH (3 60-ml portions of 15% solution) and the usual treatment, the benzene layer yields 6.7 gms of neutral fraction. This fraction is dissolved

[illegible]: 2/8

133-134

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

3-5

COUNTRY : Czechoslovakia
CATEGORY :

ABS. JOUR. : RZKhim., No. 22 1959, No. 76719

AUTHOR :
INST. :
TITLE :

ORIG. PUB. :

ABSTRACT : semicarbazone of the acetate of Δ^5-B-norandrostenol-3 β-one-17 (I), mp 264-266°. A solution of 0.25 gm I in 5 ml CH_3COOH and 0.7 ml of 30% CH_2O are heated for 1 hr at 65°, and the solution is poured into water and extracted with ether; 0.19 gm of the acetate of Δ^5-B-norandrostenol-3 β-one-17 (II ketol, mp 135-136° (from CH_3OH)) is obtained, $[\alpha]^{20}D$ -52±5° (c = 3.1). A solution of 0.1 gm of the acetate of II in 5 ml CH_3OH is refluxed for 1 hr in a stream of N_2 with

CARD: 4/8

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

3-5

COUNTRY : Czechoslovakia
CATEGORY :

ABS. JOUR. : RZKhim., No. 22 1959, No. 78719

AUTHOR :
INST. :
TITLE :

ORIG. PUB. :

ABSTRACT : with ether. The acid fraction is recovered from the ether extract by extraction with 4 gms Na_2CO_3 in 150 ml water; the addition of dil HCl to the latter extract gives 3.9 gms of 3β-acetoxy-5,17-diketo-5,6-Seco[Sequo?]-6-androstanic acid (IV), mp 162-163° (from ether), $[\alpha]^{20}D$ +70±3° (c = 3.7). The ether layer gives 2.9 gms of the acetate of Δ^5-androstenol-3-dione-7,17, mp 185-186° (from CH_3OH), $[\alpha]^{20}D$ -74±3° c = 2.3; in alc). A mixture of 3.5 gms IV, 9 ml pyridine,

CARD: 6/8

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

[illegible] : Czechoslovakia

[illegible] :

ABS. JOUR. : RZKhim., No. 22 1959, No. 75719

[illegible] :

[illegible] :

[illegible] :

[illegible] :

[illegible] : $NaHCO_3$ is shaken for 48 hrs, after which the usual treatment gives 0.1[illegible] gm of the methyl ester of 3 β-hydroxy-5,17-diketo-5,6-seco[sequo?]-6-androstenic acid, mp 131-132° (from CH_3OH), $[\alpha]^{20}_D$ -100±3° (c = 2.6). The IR spectra of II prepared by both of the procedures described above are given. For Communication XXXVII see RZhKhim, 1959, No 20, 71569.

A. Emr

CARD: 8/8

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"

"APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4

SOKM, I.

32/8-52(82)-10-21/39

AUTHORS: Romaňuk, M., Herout, V. and Šorm, F.

TITLE: Plant Substances. VII. (O rostlinných látkách VII) The Structure of Aplotaxene from Costus Oil (Struktura aplotaxenu z kostusové silice)

PERIODICAL: Chemické Listy, 1958, Vol. 52(82), Nr 10, pp 1965 - 1968 (Czechoslovakia)

ABSTRACT: The authors investigated the constitution of aplotaxene which is an unsaturated hydrocarbon, and ascribed to it the structure of n-heptadeca-1,8,11,14-tetraene. This hydrocarbon was previously described by Semmler and Feldstein (Ref.2), who found that the physical constants of the octahydro derivative of aplotaxene correspond to those of n-heptadecane, and gave the formula $C_{17}H_{28}$. The physical constants of the investigated aplotaxene were practically identical with those given in previous publications (Ref.2). Strong absorption bands at 910, 991 and 1645 cm^{-1} were observed in the infra-red spectrum which appertained to the vinyl group and at 720 cm^{-1} corresponding to the cis-configuration of the substituents. However, in the ultra-violet spectrum there was no

Card 1/3

3

...ication that conjugated double bonds were present. In this way, all double bonds in aplotaxene were isolated. The position of the double bonds was determined by the ozonisation of aplotaxene and by analysing the oxidation products. Formaldehyde, acid aldehyde and propionaldehyde were separated in the form of their 2,4-dinitrophenylhydrozones, by paper chromatography. The presence of the propionaldehyde was also verified on the basis of its melting point. Only malonic and premelic acids could be identified by chromatography in the ozonisation products. Both acids were also obtained in the crystalline state. Three possible structural formulae are suggested (Ia, Ib and Ic). The structure formula Ib was given to this compound: $CH_2=CH-(CH_2)_5-CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH_3$, on the basis of results obtained during the partial hydrogenation of aplotaxene, ozonisation and fractional distillation and oxidation. Regarding the biogenesis, the authors suggest that aplotaxene is formed by the decarboxylation of the unsaturated C_{18} monocarboxylic acid.

Card 2/3

Details on the course of the distillation of various fractions are given in Tables 1 and 2. The co-operation of Dr. M. Horák, Candidate of Chemical Sciences, Miss H. Sedláková and K. Blabolil is acknowledged. There are 2 Tables and 5 References: 4 Czech and 1 German.

ASSOCIATION: Oddělení přírodních látek, Chemický ústav, Československá akademie věd, Praha (Department for Natural Substances, Chemical Institute, Czechoslovak Academy of Sciences, Prague.

PRESENTED: 7th March, 1958

Card 3/3

APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420016-4"