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On terpenes. Pt. 154 Coll Cz Chem 28 no.7:1715-1719 Jl '63.

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

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KREPINSKY,J.; ROMANUK,M.; HEROUT,V.; SORM.V.

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

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1. I. interni klinika (prednosta: prof. MUDr. F. Cernik); Urologicka klinika (prednosta: doc. MUDr. Jozef Svab); Patologicko-anatomicky ustav (prednosta: DrSc. prof. MUDr. A. Fingerland) Karlova universita v Hradci Kralove.

VRKOC, J.; JONAS, J.; HEROUT, V.; SORM, F.

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

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On terpenes. Pts. 167,168. Coll Cz Chem 29 no.9:2182-2193 S '64.

1. Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague. 2. Member, Advisory Board, "Collection of Czechoslovak Chemical Communications" (for Herout). 3. Chairman, Advisory Board, "Collection of Czechoslovak Chemical Communications" (for Sorm).

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1. Ortopedicka klinika lekarske fakulty Karlovy University v Hradci Kralove (prednosta prof. dr. J. Vavrda) a Ustav patologicke anatomie lekarske fakulty Karlovy University v Hradci Kralove (prednosta prof. dr. A. Fingerland, DrSc.).

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1. Ortopedicka klinika (prednosta: prof.dr. J. Vavrda). Ustav patologicke anatomie (prednosta: prof. dr. A. Fingerland, DrSc.) lekarske fakulty Karlovy University v Hradni Kralove.

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1. Institute of Organic Chemistry and Biochemistry of the Czechoslovak Academy of Sciences, Prague. Submitted December 29,1963. 2. Present address: Moskovskiy institut tonkoy khimicheskoy tekhnologii M.V.Lomonosova, Moscow (for Zvorkova).

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1. Orthopaedic Clinic, Medical Faculty, Charles University, Hradec Kralove (Czechoslovakia) (Director: Prof. Jaroslav Vavrda, M.D.) and Institute of Pathology, Medical Faculty, Charles University (Director: Prof. Antonin Fingerland, M.D., Dr.Sc.).

Dolan, I.; Dolak, F.; [illegible]

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1. Interni oddeleni vojenske nemocnice v Jaromeri (nacelnik [illegible]) a [illegible] Lekarske fakulty v Hradci Kralove (prednosta prof. MUDr. A. Fingerland, DrSc.)

L 13309-66

ACC NR: AP6006012 SOURCE CODE: CZ/0053/65/014/004/0277/0277

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ORG: First Clinic of Internal Medicine, Faculty Hospital, Hradec Kralove (I. interni klinika fakultni nemocnice); Institute of Pathological Anatomy, Faculty Hospital, Hradec Kralove (Patologicko-anatomicky ustav fakultni nemocnice); Surgical Clinic, Faculty Hospital, Hradec Kralove (Chirurgicka klinika fakultni nemocnice)

TITLE: Effect of gastric cooling on changes in the gastric mucosa [This paper was presented during Biophysical Days, Brno, 12 Jun 64.]

SOURCE: Ceskoslovenska fysiologie, v. 14, no. 4, 1965, 277

TOPIC TAGS: dog, digestive system, animal physiology, cooling

ABSTRACT: Description of method, apparatus and recording procedure for study of the effects of gastric cooling in dogs. In the 3 dogs so far studied by gastric freezing for up to 60 minutes, comprehensively observed as to gastric mucosal condition before as well as one month after cooling, no adverse morphological changes were found by histological examination. [JPRS]

SUB CODE: 06 / SUBM DATE: none / OTH REF: 002

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HERGUT, Vladimir; VACHA, Karel

Tuberculosis in the adenomyoma of the uterus. Sborn. ved. prac. lek. fak. Karlov. Univ. 8 no.4:427-431 '65.

1. Patologicko-anatomicky ustav (prednosta: prof. MUDr. F. Fingerland, DrSc.) a Gynekologicko-porodnicka klinika (prednosta: prof. MUDr. K. Vacha, DrSc.). Karlovy University v Hradci Kralove.

HERCUT, Vladimir; VONDRACKOVA, Anna; SANDA, Zdenek; KOTRLIK, Jiri; PECHACEK, Miroslav.

Fatal herpetic encephalitis. Anatomical and virclogical findings. Sborn. ved. prac. lek. fak. Karlov. Univ. 8 no.4:433-442 '65.

1. Patologicko-anatomicky ustav (prednosta: prof. MUDr. A. Fingerland , DrSc.).; Ustav lekarske mikrobiologie (prednosta: MUDr. O. Vejbora); Interni oddeleni nemocnice v Jicine (prednosta: doc. MUDr. Z. Sanda, CSc.) a Infekcni klinika (prednosta: prof. MUDr. J. Ondracek) Karlovy University v Hradci Kralove.

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Effect of fusing autogenous and homogenous osteocartilaginous grafts and their vascularization and regenreation. Acta chir. orthop. traum. Cech. 32 no.5:409-421 O '65.

1. Ortopedicka klinika (prednosta prof. dr. J. Vavrda) a Ustav patologicke anatomie (prednosta prof. dr. A. Finkerland, DrSc.) lekarsko fakulty Karlovy University v Hradci Kralove.

CZECHOSLOVAKIA

NOVOTNY, L; HEROUT, V.

Institute of Organic Chemistry and Biochemistry of the Czechoslovak Academy of Sciences, Prague (for both)

Prague, Collection of Czechoslovak Chemical Communications,
[illegible]

"Plant Substances. XXV. Constituents of Rhizomes of Petasites japonicus (Sieb. et Zucc.) Maxim. var. giganteus Kitamura."

CZECHOSLOVAKIA

SUCHY, M; HEROUT, V; SORM, F

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague - (for all)

Prague, Collection of Czechoslovak Chemical Communications, No 7, July 19[illegible], pp 2[illegible]-2905

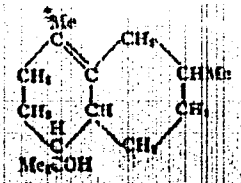
"On terpenes. Part 179: Geometry of double bonds in the ten-membered ring of costunolide."

HEROUT, V

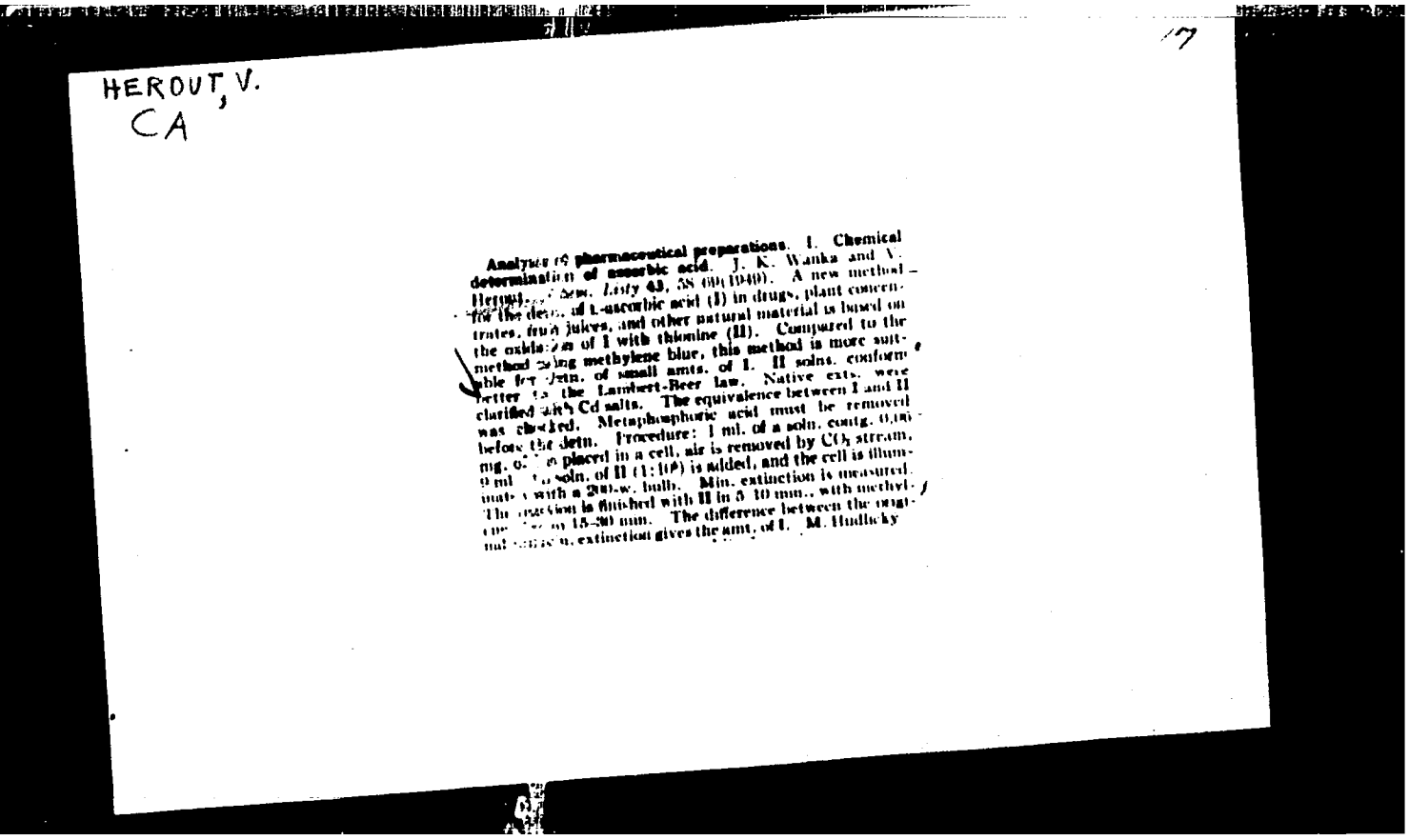
CA

10

Terpenes. V. The terpenic constituents of the essential oil of sweetflag (*Acorus calamus* L.). F. Sorm and V. Herout. *Collection Czechoslov. Chem. Communs* 13, [illegible] (1948); cf. *C.A.* 42, 7283b.—Oil of Dutch origin was subjected to fractionation after sepn. of acid and phenolic substances. The lower-boiling fraction, b. 42–70°, contained terpenes which polymerized upon standing and were not further examd. *d*-Camphor was isolated as was a terpenic alc., $C_{15}H_{26}O$ (semicarbazone m. 133°), and an alc., ($C_{15}H_{26}O$) fraction which was unsatd. (2 double bond/mol.). From these substances arose the characteristic odor of this essential oil. Calamene, $C_{15}H_{24}$, d$_4^{20}$ 0.9220, n$_D^{20}$ 1.5040, was found to be a mixture of a bicyclic hydrocarbon (2 double bonds) and a tricyclic hydrocarbon (1 double bond). A fraction ($C_{15}H_{24}$), probably possessing 2 double bonds and a carbocyclic and named acoradiene, was easily hydrogenated to $C_{15}H_{26}O$, which contained no active H and did not form a semicarbazone or react with PhMgBr. A ketone, calamone, $C_{15}H_{24}O$, b$_{10}$ 96–9°, was converted to the semicarbazone, m. 185–7°. There were also isolated 2 isomeric diketones, $C_{15}H_{24}O_2$, acorone, m. 100–1°, and isoacorone, m. 98–7°, and a substance, $C_{15}H_{24}O_2$, m. 168°, called calameone. VI. Constitution of carotol. F. Sorm and L. Ubik. *Ibid.* 12[3]–7.—A series of reactions was carried out on carotol which indicated that its structure is



M. L. Webb



HEROUT, V.
CA

17

Analysis of pharmaceutical preparations. I. Chemical determination of ascorbic acid. J. K. Wanka and V. Herout. *Österr. Chem. Ztschr.* **43**, 58-60 (1940). A new method for the detn. of L-ascorbic acid (I) in drugs, plant concentrates, fruit juices, and other natural material is based on the oxidation of I with thionine (II). Compared to the method using methylene blue, this method is more suitable for detn. of small amts. of I. II solns. conform better to the Lambert-Beer law. Native exts. were clarified with Cd salts. The equivalence between I and II was checked. Metaphosphoric acid must be removed before the detn. Procedure: 1 ml. of a soln. contg. 0.05-0.5 mg. of I is placed in a cell, air is removed by CO_2 stream, 9 ml. of soln. of II (1:10⁶) is added, and the cell is illuminated with a 200-w. bulb. Min. extinction is measured. The reaction is finished with II in 5-10 min., with methylene blue in 15-20 min. The difference between the original and min. extinction gives the amt. of I. M. Hudlicky

CA

Terpenes XVIII. Infrared investigations of terpenes II. J. Plíva and V. Herout (Tech. Univ. Prague). *Collection Czechoslov. Chem. Communs.* **15**, 760–74 (1950)(in English); cf. *C.A.* **45**, 5886i.—The infrared spectra (from 1800 to 700 cm.$^{-1}$) of myrcene, *d*- and *dl*-limonene, *dl*-, *l*-, and *dl*-α-pinene, *l*-β-pinene, Δ^3-carene, camphene, β-menthane, pinane (from α-pinene and β-pinene), cadinene, and isocamphane are reported. Certain weak bands observed in the 1550–1000 cm.$^{-1}$ and 1750–1800 cm.$^{-1}$ regions show shifts corresponding to those of the δ(CH) fundamentals and are therefore assigned to their overtones. No correlation can as yet be established between the C:C stretching frequencies of cyclic terpenes and their structures. **ZbA**

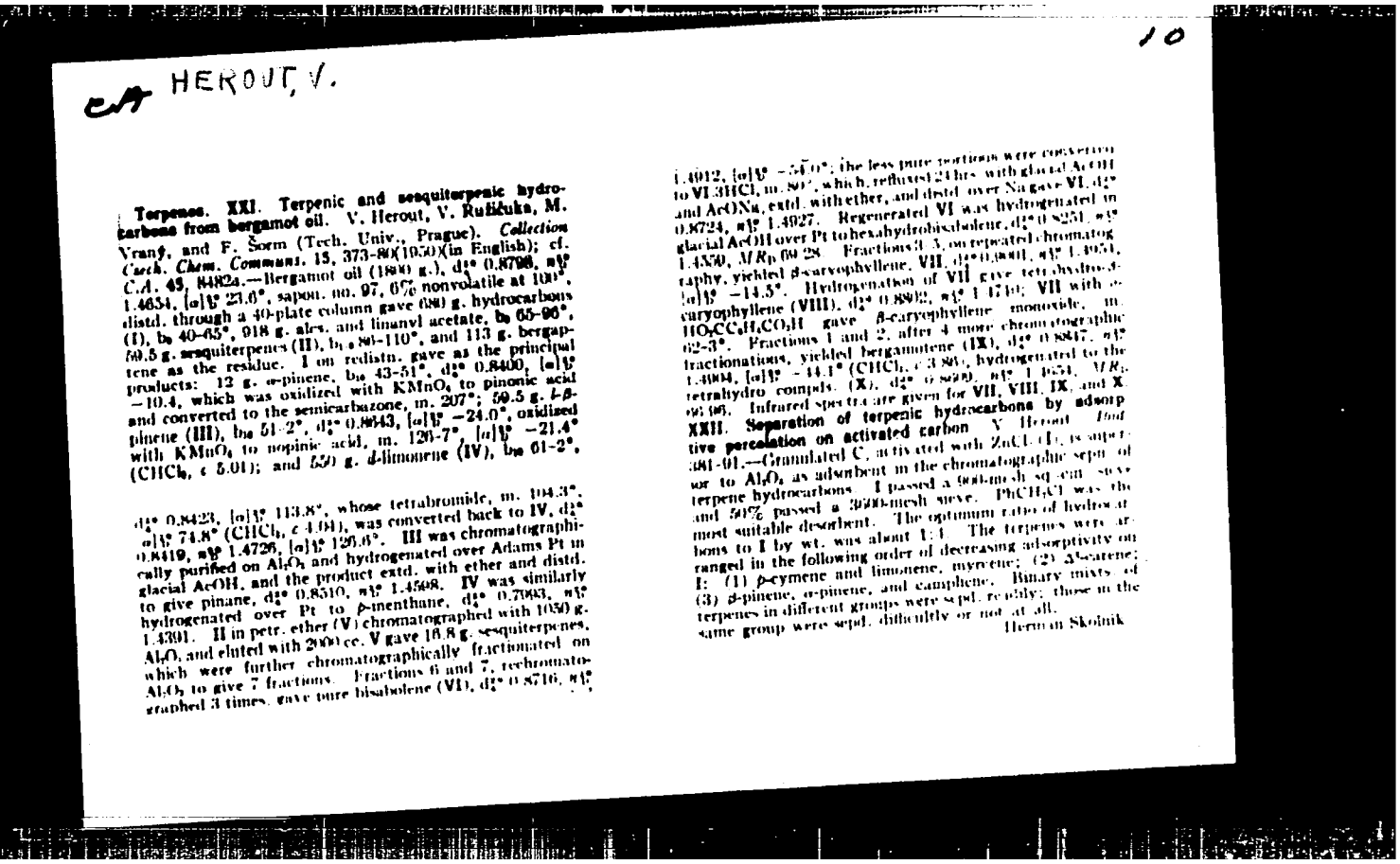
The constitution of natural farnesene; the synthesis of 2,6,10- and 2,7,10-trimethyldodecanes. F. Sorm and J. Arient, *Ibid.* 175–85; cf. *C.A.* **44**, 9385h.—The synthesis of the 2 trimethyldodecanes is described. The 2,6,10-isomer is shown by infrared spectral measurements to be identical with the octahydro deriv. of natural farnesene (a constituent of hops). $BrCH_2MeC{:}CHCO_2H$ (I) is dropped into ethereal CH_2N_2, and the crude diazo ketone dissolved in dioxane, satd. with HCl, and worked up to give 70% *5-methyl-1-chloroheptadien-2-one*, b_{11} 65°, which with $CHNa(CO_2Et)_2$ in C_6H_6 yields 65% *di-Et 6-methyl-3-oxo-1,1-hexanedicarboxylate*, b. 135.6°, hydrolyzed in HOAc-HCl to 92% of *5-methyl-6-oxoheptanoic acid*, b_{10} 161° (*semicarbazone*, m. 128–9°). The ester to acid (5 g.) suspended in 200 cc. of 40% H_2SO_4 is reduced electrolytically on activated Pb electrodes until 20 amp.-hrs. have passed through the soln., and the contents of the cathode compartment diluted with H_2O and steam-distd., yielding 72% *5-methylheptanoic acid*, b_{11} 120°. To the acid chloride (b_{10} 80–1°) (14.8 g.) is added MeMgI (from MeMgBr and 6 g. $CdCl_2$ in Et_2O), and the mixt. refluxed 2 hrs. and worked up to give 2.8 g. (97%) *6-methyl-3-heptanone* (II), b_{20} 81° (*semicarbazone*, m. 120–1°). Me isocaproate (10 g.) in ether is added to 1.5 g. $LiAlH_4$ with cooling, and the mixt. then refluxed 1 hr. and hydrolyzed with dil. H_2SO_4 to 7 g. (81%) $Me_2CH(CH_2)_3OH$, b. 151°, which with PBr_3 gives 80% *isohexyl bromide* (III), b. 145.7°. III (4 g.) converted to the Grignard reagent and treated with 2.8 g. II gives 2.5 g. *2,6,10-trimethyl-6-dodecanol*, b_{14} 124–5°, which with $KHSO_4$ is dehydrated in 87% yield to $C_{15}H_{30}$ (b_{10} 125–6°). On catalytic hydrogenation (PtO_2) the alkene gives 86% of *2,6,10-trimethyldodecane*, b_{10} 122–3°. I via the diazomethyl ketone gives 87% *β-methylvaleramide*, m. 124.5°, hydrolyzed by NaOH to the *acid*, b_{15} 95.7°. This acid is converted in the same way to *6-methylhexanoic acid*, b_{12} 110–15° (*amide*, m. 96.8°), whose acid chloride, b. 161–2°, with MeCd gives 67% *5-methyl-6-heptanone* (IV) (*semicarbazone*, m. 121°). Isocaproyl chloride, b. 141.2° (17 g.), treated with CH_2N_2 and the diazo ketone heated in a dioxane-NH_4OH soln. of 2.5 g. $AgNO_3$ gives 15 g. (85%) *5-methylhexanamide*, m. 102°, hydrolyzed to 90% of the *acid*, b_{10} 111–13°; the *Me ester*, b. 160–7°, with $LiAlH_4$ in ether gives 100% of *5-methyl-1-hexanol*, b. 167–9°. *1-Bromo-5-methylhexane* (5 g.) (45% from the alc., b. 162–3°), converted to the Grignard deriv. and treated with 3 g. IV, gives 3.4 g. (84%) of *2,7,10-trimethyl-7-dodecanol*, b_{13} 118–19°. This with $KHSO_4$ gives 97% $C_{15}H_{30}$, b_{13} 84–5°, which on catalytic hydrogena-

tion yields (40%) *2,7,10-trimethyldodecane*, b_{10} 122.3°.

XX. The constitution of β-caryophyllene. F. Šorm, L. Dolejš, and J. Pliva. *Ibid.* 1801-05; cf. *C.A.* **41**, 3075*f*.—New degradative work on dihydro-β-caryophyllene oxide (I) suggests that β-caryophyllene (II) contains a [7.2.0]bicyclodecane ring system with a :CH$_2$ and a Me group attached to the 9-membered ring. A possible structure is (IIA).

(IIA)

The infrared spectrum of Treibs' oxido ketone, $C_{15}H_{24}O_2$, (cf. *C.A.* **41**, 3075*f*) indicates the presence of a large ring ketone, possibly a cyclononanone. The oxido glycol, $C_{15}H_{28}O_3$, m. 142°, obtained following Treibs oxidation via $KMnO_4$ of II oxide, (0.5 g.) is treated at room temp. with 0.9 g. $Pb(OAc)_4$ in C_6H_6H, to give the oxido ketone, m. 62°. The Treibs oxido glycol, m. 110°, is unaffected under these conditions. The oxidation of II oxide gives a 4th compd., $C_{15}H_{26}O_3$, m. 110° (*semicarbazone*, m. 205°). II oxide is hydrogenated in EtOH with PtO_2 to I, m. 66–7°. I (20 g.) refluxed 1 hr. with 25 g. pyridine-HBr in excess pyridine gives $C_{15}H_{26}O$ (III), felted needles, m. 80°, whose infrared spectrum indicates the presence of a :CH$_2$ group. The mother liquors give 11.3 g. of a viscous oil (IV), whose spectrum shows it is largely III. IV (10.4 g.) oxidized with 24 g. $KMnO_4$ in 100 cc. Me_2CO and 2 cc. H_2O gives 5.5 g. neutral and 4.8 g. acid material. The latter gives, from HOAc, 2.3 g. of a dibasic acid, $C_{15}H_{28}O_4$ (V), m. 133–4°. V (6.5 g.), 6.5 g. reduced Fe, and 0.75 g. powd. $Ba(OH)_2$ distd. over a free flame gives 3.5 g. (72%) $C_{14}H_{28}O$ (VI), b_{11} 111°, n_D^{25} 1.4704, d_4^{25} 0.9426; *semicarbazone*, m. 103–4°. The infrared spectrum of VI shows no C:C present and the C:O stretching frequency (1705 cm.$^{-1}$ in substance, 1683 cm.$^{-1}$ in $CHCl_3$) indicates the presence of a cycloheptanone ring. David Todd



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CA HEROUT, V.

Terpenes. XXI. Terpenic and sesquiterpenic hydrocarbons from bergamot oil. V. Herout, V. Rufikuka, M. Vrany, and F. Sorm (Tech. Univ., Prague). *Collection Czech. Chem. Communs.* 15, 373-80(1950)(in English); cf. *C.A.* 45, 8482a.—Bergamot oil (1800 g.), d_4^{20} 0.8709, n_D^{20} 1.4634, $[\alpha]_D^{20}$ 23.6°, sapon. no. 97, 6% nonvolatile at 100°, distd. through a 40-plate column gave 680 g. hydrocarbons (I), bp 40-65°, 918 g. alcs. and linanyl acetate, bp 65-90°, 59.5 g. sesquiterpenes (II), bp 80-110°, and 113 g. bergaptene as the residue. I on redistn. gave as the principal products: 12 g. α-pinene, bp 43-51°, d_4^{20} 0.8400, $[\alpha]_D^{20}$ −10.4, which was oxidized with $KMnO_4$ to pinonic acid and converted to the semicarbazone, m. 207°; 59.5 g. *l*-β-pinene (III), bp 51-2°, d_4^{20} 0.8643, $[\alpha]_D^{20}$ −24.0°, oxidized with $KMnO_4$ to nopinic acid, m. 126-7°, $[\alpha]_D^{20}$ −21.4° ($CHCl_3$, c 5.01); and 550 g. *d*-limonene (IV), bp 61-2°, d_4^{20} 0.8423, $[\alpha]_D^{20}$ 113.8°, whose tetrabromide, m. 104.3°, $[\alpha]_D^{20}$ 74.8° ($CHCl_3$, c 4.01), was converted back to IV, d_4^{20} 0.8419, n_D^{20} 1.4726, $[\alpha]_D^{20}$ 125.6°. III was chromatographically purified on Al_2O_3 and hydrogenated over Adams Pt in glacial AcOH, and the product extd. with ether and distd. to give pinane, d_4^{20} 0.8510, n_D^{20} 1.4598. IV was similarly hydrogenated over Pt to *p*-menthane, d_4^{20} 0.7993, n_D^{20} 1.4391. II in petr. ether (V) chromatographed with 1050 g. Al_2O_3 and eluted with 2000 cc. V gave 16.8 g. sesquiterpenes, which were further chromatographically fractionated on Al_2O_3 to give 7 fractions. Fractions 6 and 7, rechromatographed 3 times, gave pure bisabolene (VI), d_4^{20} 0.8716, n_D^{20} 1.4912, $[\alpha]_D^{20}$ −54.0°; the less pure portions were converted to VI.3HCl, m. 80°, which, refluxed 12 hrs. with glacial AcOH and AcONa, extd. with ether, and distd. over Na gave VI, d_4^{20} 0.8724, n_D^{20} 1.4927. Regenerated VI was hydrogenated in glacial AcOH over Pt to hexahydrobisabolene, d_4^{20} 0.8251, n_D^{20} 1.4350, MR_D 69.28. Fractions 3, 5, on repeated chromatography, yielded β-caryophyllene. VII, d_4^{20} 0.8801, n_D^{20} 1.4954, $[\alpha]_D^{20}$ −14.5°. Hydrogenation of VII gave tetrahydro-β-caryophyllene (VIII), d_4^{20} 0.8802, n_D^{20} 1.4740; VII with *o*-$HO_2CC_6H_4CO_2H$ gave β-caryophyllene monoxide, m. 62-3°. Fractions 1 and 2, after 4 more chromatographic fractionations, yielded bergamotene (IX), d_4^{20} 0.8847, n_D^{20} 1.4804, $[\alpha]_D^{20}$ −44.1° ($CHCl_3$, c 3.86), hydrogenated to the tetrahydro compds. (X), d_4^{20} 0.8699, n_D^{20} 1.4651, MR_D 69.66. Infrared spectra are given for VII, VIII, IX, and X.

XXII. Separation of terpenic hydrocarbons by adsorptive percolation on activated carbon. V. Herout *Ibid* 381-91.—Granulated C, activated with $ZnCl_2$ + H_2O, is superior to Al_2O_3 as adsorbent in the chromatographic sepn. of terpene hydrocarbons. I passed a 900-mesh sq.-cm. sieve and 50% passed a 2000-mesh sieve. $PhCH_2Cl$ was the most suitable desorbent. The optimum ratio of hydrocarbons to I by wt. was about 1:1. The terpenes were arranged in the following order of decreasing adsorptivity on I: (1) *p*-cymene and limonene, myrcene; (2) Δ³-carene; (3) β-pinene, α-pinene, and camphene. Binary mixts. of terpenes in different groups were sepd. readily; those in the same group were sepd. difficultly or not at all.

Herman Skolnik

SORM, F.; VERES, K.; HEROUT, V.

On terpenes. Part 36. The constitution of calamenene [in English with summary in Russian]. Sbor.Chekh.khim.rab. 18 no.1:106-115 F '53. (MLRA 7:6)

1. Central Chemical Research Institute, Prague.
(Sesquiterpenes)

SORM, F.; ZAORAL, M.; HEROUT, V.

On terpenes. Part 38. On the constitution of natural bisabolol and bisabolol monoxide from matricaria oil [with summary in English]. Sbor.Chekh.khim.rab. 18 no.1:116-121 F '53. (MLRA 7:6)

1. Central Chemical Research Institute, Prague.
(Bisabolol) (Matricaria oil)

HEROUT, V.; ZAORAL, M.; SORM, F.

On terpenes. Part 39. Synthesis of two tetrahydrobisabolols [with summary in English]. Sbor.Chekh.khim.rab. 18 no.1:122-126 F '53. (MLRA 7:6)

1. Central Chemical Research Institute, Prague.
(Bisabolol) (Matricaria oil)

SORM, F.; CEKAN, Z.; HEROUT, V.; RASKOVA, H.

Isolation spasmolytically active substance from Matricaria chamomilla L. [with summary in English]. Sbor.Chekh.khim.rab. 18 no.1:127-130 F '53. (MLRA 7:6)

1. Central Chemical Research Institute, Prague. 2. Institute of Pharmacology of the Medical Faculty, Charles University, Prague.
(Matricaria oil) (Flavones)

HEROUT, V.; BENESOVA, V.; PLIVA, J.

On terpenes. Part 41. The sesquiterpenes of ginger oil [with summary in English]. Sbor.Chekh.khim.rab. 18 no.2:248-256 Ap '53. (MLRA 7:6)

1. Central Chemical Research Institute, Prague.
(Sesquiterpenes) (Gingerol)

HEROUT, V.

1706* On Terpenes. XLIII. Infrared Investigations of Terpenes. IV. (English.) J. Pliva, V. Herout, B. Schneider and F. Sorm. *Collection of Czechoslovak Chemical Communications*, v. 18, no. 4, Aug. 1953, p. 500-511.

Infra-red spectra of cadinanes, tetrahydroisozingiberene, and calacorane show that these hydrocarbons differ from each other merely in their spatial configuration. Tables, graphs. 22 ref.

HEROUT, V.; SORM, F.

Components of wormwood (Artemissia absinthium L.) and the isolation of a crystalline pro-chamazulogenogen [in English with summary in Russian]. Sbor.Chekh.khim.rab. 18 no.6:854-869 D '53. (MLRA 7:6)

1. Department of Natural Substances, Institute of Organic Chemistry, Czechoslovak Academy of Science, Prague. (Wormwood) (Chamazulogen)

HEROUT, V.; KOLOS, T.; PLIVA, J.

Terpenes. Part 49. Sesquiterpenes of the cadinene type in Javanese citronella oil [abstract; in English]. Sbor.Chekh.khim.rab. 18 no.6: 886 D '53. (MLRA 7:6)

1. Department of Natural Substances, Institute of Organic Chemistry, Czechoslovak Academy of Science, Prague. (Cadinene)

Tetrenes, L. Contribution to the constitution of elemol. Vladimír Sýkora, Vlastimil Herout, Josef Pliva, and František Sorm (Czech. Akad. Věd, Prague, Czech.). *Chem. Listy* 47, 880–98(1953); *Collection Czechoslov. Chem. Communs.* 19, 124–34(1954)(in English); cf. *C.A.* 47, 8704*h*.—Comparison of the infrared spectra of *elemene* and of synthetic 1,1-dimethyl-2-*sec*-butyl-4-isopropylcyclohexane (I) contradicts the Ruzicka- van Veen formula (*C.A.* 24, 607) of elemol (II). Dehydrogenation of *tetrahydroelemene* (III) to 1-methyl-2,4-diisopropylbenzene (IV) proves that I has the skeleton of 1-methyl-1-ethyl-2,4-diisopropylcyclohexane (V). II isolated from the distn. residues of citronella oil by vacuum distn. was chromatographed and purified through its phenylurethan, m. 111–12°, to give pure II, m. 52.5–3.5°. Dehydration of 40 g. *tetrahydro*-II (obtained by hydrogenation of II over PtO_2) by heating with 220 g. 85% HCO_2H 1 hr. on the steam bath gave, after chromatography and distn., 31 g. III, b_{23} 128–30°. Heating 2.1 g. III and 0.05 g. S 7 hrs. at 180°–240° gave 0.95 g. IV, b_{12} 100–5°, d_{20} 0.8563, n^{20}_D 1.4945. Quant. ozonization of II indicated 1.80 double bonds. I was synthesized as follows: refluxing 21 g. 3,2-dimethylcyclohexanone in 210 ml. CCl_4 with 37.2 g. *N*-bromosuccinimide under ultraviolet illumination 40 min. gave 37 g. 2,2-dimethyl-6-bromocyclohexanone, m. 55.5–7° (from petr. ether); the dehydrobromination of which (35 g.) with 250 ml. collidine gave 11.9 g. 2,2-dimethyl-5-cyclohexenone (VI), b. 175–82° (decompn.). Refluxing 1 hr. 11.9 g. VI with a soln. obtained from 10.7 g. Mg and 31.4 g. iso-PrCl in Et_2O gave, by way of the *semicarbazone*, m. 157–8°, 2.22 g. *2,2-dimethyl-5-isopropylcyclohexanone*, (VII), $b_{14.5}$ 103–5.5°, d_{20} 0.8982, n^{20}_D 1.4540. VII (1.03 g.) in petr. ether refluxed 1 hr. with a soln. of *sec*-BuLi made from 1.5 g. Li and 12 ml. *sec*-BuCl, gave, after chromatography, 0.6 g. *1-sec-butyl-2,2-dimethyl-5-isopropylcyclohexanol*, $b_{1.5}$ 98–9°, the dehydration of which with HCO_2H yielded *1,1-dimethyl-2-sec-butyl-4-isopropylcyclohexene* (VIII), b_{18} 105–8°. Hydrogenation of VIII in AcOH over PtO_2 gave I, d_{20} 0.8412, n^{20}_D 1.4601. Dehydrogenation of VIII with S (7 hrs. at 180–240°) gave a compd. distg. at 27 (+5°, n^{20}_D 1.4990)(2.3 g.) and *sec*-BuLi from 2.1 g. Li and 11 g. *sec*-BuCl refluxed 1 hr. in petr. ether gave 1.5 g. crude *1-sec-butyl-2-methyl-5-isopropenyl-2-cyclohexenol*, b_{12} 96–103°, which was aromatized by boiling with HCO_2H (0.35 g.) *1-methyl-2-sec-butyl-4-isopropylbenzene* (X), b_{16-18} 98–105°, d_{20} 0.8614, n^{20}_D 1.4904. The same compd. was obtained as follows: carvomenthone (3 g.) refluxed 75 min. with *sec*-BuLi (from 1.5 g. Li and 12 ml. *sec*-BuCl) in petr. ether yielded, after chromatography, *1-sec-butyl-2-methyl-5-isopropylcyclohexanol*, b_6 87–91°. This heated with 90% HCO_2H gave *1-sec-butyl-2-methyl-5-isopropylcyclohexene* (IX), b_{17} 108–15°, which was dehydrogenated with S at 240–50° to 0.03 g. X, b_{12} 103–6°, d_{20} 0.8927, n^{20}_D 1.4920. *2-Methyl-2,4-diisopropylbenzene* (XI) was synthesized as follows: carvomenthone (d_{20} 0.9124, n^{20}_D 1.4564)(3.1 g.), refluxed 90 min. with iso-PrLi, prepd. from 2.8 g. Li and 19 ml. iso-PrCl, gave 3.5 g. *2-methyl-1,5-diisopropylcyclohexanol*, $b_{4.5}$ 70–81°. This (3 g.) was dehydrated with HCO_2H to 1.34 g. of the compd., $b_{10.5}$ 86–90.5° which yielded, by heating 6 hrs. with S at 180–240°, 0.7 g. XI, b_{10} 104–8°, d_{20} 0.8773, n^{20}_D 1.4946. LI. The composition of the chamazulene. Preliminary communication. F. Sorm, J. Novák, and V. Herout. *Chem. Listy* 47, 1097–8(1953); *Collection Czechoslov. Chem. Communs.* 18, 537–9(1953)(in English).—On the basis of all known data on the elementary analyses of chamazulene and its derivs., on the basis of oxidation products, and of infrared spectra detns., the correct formula for chamazulene, *1,4-dimethyl-7-ethylazulene*, $C_{14}H_{16}$, is suggested. LII. The structure of laserpitine. František Sorm, Miroslav Holub, and Vlastimil Herout. *Chem. Listy* 47, 1499–1503(1953); *Collection Czechoslov. Chem. Communs.* 19, 135–40(1954)(in German).—*Laserpitine* (I), the bitter principle of the root of *Laserpitium latifolium*, which seems to be which is a diester of angelic acid and *laserol* (II), a bicyclic tetrahydroxy ketone. Out of the 5 O atoms, 3 are bound to three neighboring C atoms, and 2 to two adjacent C atoms in some other part of the mol. I, isolated by petr. ether extn., m. 117°, $[\alpha]^{20}_D$ 110°, mol. wt. (Rast) 448, hydrogenated over PtO_2 in AcOH gave *tetrahydrolaserpitine*, m. 83–5° (from petr. ether). Saponn. of 2.8 g. I with 5.2 ml. 1.2 *N* $Ba(OMe)_2$ in 10 ml. MeOH at room temp. gave,

di-Me norcaryophyllenate, b_{8} 100-2°, 70 g. *di-Me caryophyllenate*, b_{8} 120-1.5°, and 40 g. *di-Me homocaryophyllenate*, b_{8} 130-2°, n_D^{20} 1.4403, $[\alpha]_D^{20}$ 32.00. Refluxing 37.4 g. II 4 hrs. with 10 ml. MeOH and a few drops of H_2SO_4 gave 12.8 g. (30.0%) *Me H homocaryophyllenate*, b_{8} 180° (III). III (3.2 g.) was treated with $SOCl_2$ in 30 ml. C_6H_6, the solvent evapd. *in vacuo*, the ester acid chloride dild. with C_6H_6 and added to a benzene soln. of 1.25 equiv. Me_2Cd to give, after heating 10 min., decompn. with 10% H_2SO_4, and ether extn., 2.60 g. (83%) *Me 3-(2,2-dimethyl-4-acetylcyclobutyl)-propionate* (IV), b_{15} 132-8°; *semicarbazone* of the *free keto acid*, m. 165-6°. To 14 g. $HgCl_2$-activated Zn in 70 ml. C_6H_6 were added 6.5 g. IV and 14 g. $BrCH_2CO_2Me$ in 30 ml. C_6H_6, the mixt. boiled 10 min, decompd. with 10% H_2SO_4 and extd. with Et_2O, the residue dehydrated by boiling 2 hrs. with 40 ml. Ac_2O to give, after chromatography, 2.43 g. *Me β-[2-(2-carbomethoxyethyl)-3,3-dimethylcyclobutyl]crotonate*, $b_{0.15}$ 110-17°, which hydrogenated over PtO_2 in AcOH gave Me β-[2-(2-carbomethoxyethyl)-3,3-dimethylcyclobutyl]butyrate, 1.18 g., b_{15} 156-64°; *β-[2-(2-carbomethoxyethyl)-3,3-dimethylcyclobutyl]butyric acid*, $b_{0.4}$ 190° (bath temp.) (obtained by alk. sapon. of the ester) (0.65 g.) distd. with 0.65 g. Fe dust and 0.15 g. $Ba(OH)_2$ gave 260 mg. (54%) *2,8,8-trimethylbicyclo[0.2.5]nonan-4-one* (V), b_{12} 130° (bath temp.); *semicarbazone*, m. 176-7°. Another prepn. started with IV (3.53 g.) which was refluxed 5 hrs. with 1.88 g. $NCCH_2CO_2Et$, 1.2 g. AcOH, 1.2 g. AcONa and 5 ml. C_6H_6 to give 2.31 g. (45%) *Et α-cyano-β-[2-(2-carbomethoxyethyl)-3,3-dimethylcyclobutyl]crotonate*, $b_{0.4}$ 164-6°, which hydrogenated over Pd o CaCO$_3$ yielded 2.15 g. *Et α-cyano-β-[2-(2-carbomethoxyethyl)-3,3-dimethylcyclobutyl]butyrate*, $b_{0.4}$ 160-3° (VI). Heating 1.98 g. VI 15 hrs. with 10 ml. HCl and 5 ml. AcOH yielded 1.53 g. (98%) *β-[2-(2-carboxyethyl-3,3-dimethylcyclobutyl]butyric acid*, $b_{0.4}$ 180°, which yielded by cyclization 48% V, b_{12} 112-14°. The *semicarbazone* of V (369 g.), 450 ml. Na and 9 ml. EtOH were heated 20 hrs. at 200°, the mixt. dild. with H_2O and extd. with Et_2O, and the residue after evapn. of the Et_2O, was chromatographed to yield 105 mg. (41%) I, b_{18} 95-105°. I was also obtained by the Kishner reduction of the *semicarbazone*

2/2

VLADIMIR SYKORA, VLASTIMIL HEROUT, & others

of IIa by 50% yield. I [illegible] the 2 methods of prepn. had d_{20} 0.8811, 0.88[illegible] and [illegible] 1.4926, 1.4629. The infrared spectrum of I is given. LV. The structure of lactarazulene and lactaroviolin. František Šorm, Věra Benešová, and Vlastimil Herout. *Ibid.* 1910-61.—A new structure for *lactarazulene* (from *Lactarius deliciosus*) (I), $C_{15}H_{16}$, was confirmed as 7-isopropenyl-1,4-dimethylazulene by partial hydrogenation, which transformed I to guaiazulene (II). *Lactaroviolin* (III) also belongs to the guaiane (IV) type. Ozonization of I showed the presence of methylene double bond. Hydrogenation of I in EtOH over Pd on C, deactivated with quinoline vapors, gave II, *trinitrobenzene compd.*, m. 151°. III, m. 57.5-8° (from petr. ether-C_6H_6), which showed the presence of 1 CH_2 group, gave, by hydrogenation over PtO_2 in AcOH, IV, $C_{15}H_{28}$, d_{20} 0.8810, n_D^{20} 1.4811, and an alc., $C_{15}H_{28}O$, $b_{0.4}$ 180-5° (bath temp.). Partial hydrogenation over deactivated Pd gave dihydrolactaroviolin, $b_{0.02}$ 130-5° (bath temp.). Infrared spectra of I and IV are given. LVI. Paper chromatography of azulenes. Otto Knessl and Alice Vlastiborová. *Ibid.* 48, 272-10 (1954).—The analysis of trialkylazulenes is based on different R_F values obtained by paper chromatography with petr. ether as stationary and 35-70% H_3PO_4 as mobile phases. The R_F values with 35, 45, 50, 55, 60, 65, and 70% H_3PO_4, resp., are listed for *S-guaiazulene* (0.0, 0.08, 0.30, 0.43, 0.68, 0.87, 1.0), *vetivazulene* (0.0, 0.02, 0.13, 0.23, 0.47, 0.65, 1.0), *chamazulene* (0.03, 0.23, 0.47, 0.65, 0.79, 0.93, 1.0), and values for 50 and 55% H_3PO_4, resp., are given for *Se-guaiazulene* (0.36, 0.50), *isoguaiazulene* (0.50, 0.72), and *lactarazulene* (0.01, 0.08). The chromatograms were developed with H_2O or dry NH_3. LVII. Identity of lindazulene with chamazulene. F. Šorm, V. Herout, and K. Takeda. *Ibid.* 281-3; *Collection Czechoslov. Chem. Communs.* 19, 186-8 (1954) (in English).—Identity of lindazulene (*C.A.* 34, 91[7]; 48, 7716f) with chamazulene (1,4-dimethyl-7-ethylazulene) was proved by mixed m.ps. of the trinitrobenzene compds. and by comparison of visible and ultraviolet spectra. The partial synthesis of lindazulene (*Pharm. Bull. Japan* 1, 243 (1953)) is, at the same time, proof of the correct structure of chamazulene as proposed by Šorm, *et al.* (see 5th preceding abstr.). M. Hudlický

Substances of Artemisia absinthium and isolation of crystalline prochamazulenogen. Vlastimil Herout and František Sorm (Czech. Akad. Věd, Prague, Czech.). *Chem. Listy* 47, 1041–52(1953); *Collection Czechoslov. Chem. Communs.* 18, 854–69(1953)(in English).—From the petr. ether ext. of *A. absinthium*, a hydroxylactone $C_{15}H_{18}O_3$ has been isolated which is believed to be a compd. from which originate the chamazulenogenic substances (*pro-chamazulenogen*) (I). Extn. of the dry drug (720 g.) with petr. ether gave 7.1% of an ext. contg. 1.48% *chamazulene* (II). The ext. dissolved in 3 l. petr. ether extd. with 8 250 ml. portions of 50% EtOH, washed three times with 300 ml. 3% NaOH, dried and evapd. gave 42 g. of a waxy substance (fraction *A*). Acidification of the alk. washings with dil. H_2SO_4 and extn. with Et_2O gave 1.8 g. dark-green acids. Evapn. of the EtOH from the aq.-alc. exts. and extn. with Et_2O yielded 10.5 g. (fraction *B*), contg. 5.44% II. Chromatography of fraction *A* (20 g.) gave 10 g. $C_{15}H_{26}$, m. 63–5° (after subl. 150°/0.1 mm.), waxy carotenoid compds., (0.8 g.) ester with sapon. no. 97.5 ($C_{31}H_{50}O_2$ acid), a *compd.* m. 103° (from AcOEt and petr. ether), a mixt. of (3.55 g.) alcohols $C_{15}H_{26}O$ and $C_{15}H_{24}O$ (III), m. 74–5° (from AcOEt and Me_2CO), a mixt. of 30 mg. of *phytosterols*, m. 139–41° ($C_{29}H_{48}O$) (*acetyl-deriv.*, m. 117°, from EtOH), and *palmitic acid*, m. 61° (approx. 1 g.). Fraction *B* deposited 1.1 g. $C_{15}H_{26}O_3$, m. 165.5° (from C_6H_6–EtOH). Chromatography of the rest (0.4 g.) yielded 0.5 g. III, 150 mg. of a *compd.*, m. 114°, 0.45 g. *absinthin*, m. 234–7°, and 850 mg. I, m. 129–32° (decompn.) (from C_6H_6), sol. in EtOAc, Me_2CO, Et_2O, and EtOH, slightly in sol. petr. ether, CS_2, CCl_4, H_2O. Hydrogenation of I in AcOH over PtO_2 gave, after chromatography, $C_{15}H_{28}O_3$, $b_{0.5}$ 160–5° (bath temp.), $C_{15}H_{24}O_3$, $b_{0.05}$ 130° (bath temp.), and a *compd.* m. 108°. Sapon. of I with 5% alc. KOH under standard conditions yielded upon decarboxylation 18.3% II.

M. Hudlický

Herout, V.

1

Herout, V., Keil, B., Protiva, M., Hudlicky, M., Ernest, I., and Gut, J.: Laboratorní technika organické chemie. Prague: Nakl. CSAV. 1954. 756 pp. Kčs 86. Reviewed in *Chem. Listy* 49, 1415(1955).

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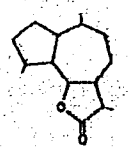
Herout, V., Keil, B., Protiva, M., Hudlicky, M., Ernest, I., and Gut, J.: Organic Chemistry Laboratory Techniques. Publishing House CSAV. 1954. 756pp. Kcs. 86. Reviewed in Chem. Listy49, 1415(1955).

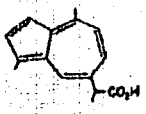
Herout, V.

CZECH

/Chamazulene precursor from chamomile (Matricaria chamomilla L.). Z. Čekan, V. Herout, and F. Šorm (Czech. Acad. Sci., Prague). *Chemistry & Industry* 1954, 684–5; cf. *C.A.* 49, 997*c*.—Cryst. I, $C_{15}H_{18}O_4$, m. 158–60° (decompn.), having 3 double bonds, an acetyl and hydroxyl group of unassigned position has been isolated in cryst. form from *Matricaria chamomilla* L. as a precursor of chamazulene (II). The ultraviolet absorption spectrum showed a max. at 243 μ, log E 4.32. On hydrogenation



(I)



(III)

2.9 equivs. of H were absorbed and 2, probably stereoisomeric, lactones, $C_{15}H_{18}O_4$, m. 115.5° and 123–3°, were isolated. Steam distn. of I gave 70–75% II by the elimination of 3 HO groups and subsequent decarboxylation. III is proposed as an intermediate in this reaction (Jung and Wendler, *C.A.* 47, 10809*g*) and the name guaiazulenic acid is suggested. The name guaianolides is proposed for compds. contg. a lactone group on a guaiane skeleton. The antiphlogistic activity of I has been found to be at least equal to that of II.

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HEROUTY

CZECH

Presence of 1,7-dimethyl-4-isopropyldecahydronaphthalene in the carbon skeleton of lineolene. [illegible] Holub, and V. Herout (Czech. Acad. Sci., Prague). *Chemistry & Industry* 1951, 665.—The C skeleton of hinesolene is established by treating dehydrolineol with HI and subsequent dehydrogenation with S, which yielded a naphthalenic hydrocarbon. The consts. of the free hydrocarbon, the picrate, and styphnate correspond to those of 1,7-dimethyl-4-isopropylnaphthalene and its appropriate derivs.

George H. Pleiss

HEROUT, Vlastimil

New possibilities of preparation of chemazulene. Cesk. farm. 3 no.10:333-336 Dec 54.

1. Z oddeleni prirozenych latek, Ustav organicke chemie Cs. akademie ved, Praha
(DRUGS
chamazulene prep.)

HEROUT, V.; SANTAVY, F.

Terpenes. Part 48. Constitution of ϵ- and δ-cadinene [in English with summary in Russian]. Sbor.Chekh.khim.rab. 19 no.1:118-123 F '54. (MLRA 7:6)

1. Department of Natural Substances, Institute of Organic Chemistry, Czechoslovak Academy of Science. (Cadinene)

SYKORA, V.; HEROUT, V.; PLIVA, J.; SORM, F.

Terpenes. Part 50. Contribution to the constitution of elemol [in English with summary in Russian]. Sbor.Chekh.khim.rab. 19 no.1:124-134 F '54. (MLRA 7:6)

1. Department of Natural Products, Institute of Organic Chemistry, Czechoslovak Academy of Science, Prague. (Elemol)

SORM, F.; HOLUB, M.; HEROUT, V.

Terpenes. Part 52. Constitution of laserpitine [in German with summary in Russian]. Sbor.Chekh.khim.rab. 19 no.1:135-140 F '54. (MLRA 7:6)

1. Otdeleniye prirodnykh veshchestv, Institut organicheskoy khimii Chekhoslovatskoy Akademii nauk, Praga. (Laserpitine)

HEROUT, V.

SORM, F.; HEROUT, V.; TAKEDA, K.

Terpenes, Part 54. Identity of lindazulene and chamazulene [in English with summary in Russian]. Sbor.Chekh.khim.rab. 19 no.1:186-188 F '54. (MLRA 7:6)

1. Department of Natural Substances, Institute of Organic Chemistry, Czechoslovak Academy of Science, Prague and Research Laboratory, Shionogi & Co., Imafuku, Amagasaki, Hyogo-ken, Japan.
(Lindazulene) (Chamazulene)

HEROUT, VLASTIMIL

CZECH

Terpenes. LV. Synthesis of elemane (1-methyl-1-ethyl-2,4-diisopropylcyclohexane. Vladimír Sýkora, Jiří Černý, Vlastimil Herout, and František Šorm (Czech. Acad. Sci., Prague). Collection Czechoslov. Chem. Communs. 19, 503–9(1954)(in English).—See C.A. 49, 1655i.
B. J. C.

[illegible]

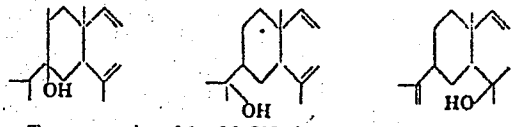
[illegible], V.; SORM, F.; CEKAN, Z.

On terpenes. [illegible] Isola[illegible] [illegible] [illegible] L., a [illegible] [illegible] I[illegible] (Collection of Czechoslovak Ch-mical Communication. Praha. Vol. 19 no. 4, Aug. 1954)

SO: [illegible] List of East European Accessions ([illegible]), [illegible], Vol. [illegible], [illegible], June 19[illegible], Uncl.

HEROUT, VLASTIMIL

Terpenes. LV. Synthesis of elemane (1-methyl-1-ethyl-2,4-diisopropyl cyclohexane). Vladimír Sýkora, Jiří Černý, Vlastimil Herout, and František Sorm (Csl. akad. věd, Prague, Czech.). *Chem. Listy* 48, 76–9(1954); cf. preceding abstr.—Synthetic *1-methyl-1-ethyl-2,4-diisopropyl-cyclohexane* (I) is identical with *elemane*, a reduction product of elemol. However, *1,5-diisopropyl-3-methyl-2-ethyl-cyclohexanol* (II) is not identical with tetrahydroelemol. One of the three formulas is suggested for elemol.



To a suspension of dry MeONa (prepd. from 23 g. Na) in 200 ml. C_6H_6 was added 75 g. HCO_2Et in 200 ml. C_6H_6, and to the ice-cooled mixt. was added a soln. of 51.5 g. carvomenthone (b_{11} 94–4.5°, n_D^{25} 1.4543) in 300 ml. C_6H_6. After 48 hrs. at room temp. under N atm., the mixt. was decompd. with H_2O, the C_6H_6 layer repeatedly extd. with 7% NaOH, the alk. ext. was extd. with Et_2O, then acidified with HCl (1:1) to pH 6, and extd. again with Et_2O to give 47 g. (83%) *2-methyl-5-isopropyl-6-formylcyclohexanone (formylcarvomenthone)* (III), b_{11} 122–2.5°. Etherification of III (47 g.) with 38 g. iso-BuOH yielded 49 g. (80%) *2-methyl-5-isopropyl-6-(isobutoxymethylene)cyclohexanone* (IV), $b_{0.6}$ 112–16°. To ethylate IV, KNH_2, prepd. from 10 g. K in 160 ml. liq. NH_3 with 0.1 g. $Fe(NO_3)_3$, was added to 300 ml. boiling Et_2O, the NH_3 was driven off under N atm., 44.7 g. IV in 200 ml. Et_2O was added during 2 hrs. after 1.5 hrs. boiling, in the course of 2 hrs., 90 g. EtI in 150 ml. Et_2O was added, and the mixt. refluxed 12 hrs., treated with H_2O, the aq. layer extd. with Et_2O, the ext. washed with 5% KOH, H_2O, dried, the Et_2O evapd., and the residue mixed with 250 ml. *M* methanolic $FeCl_3$. Treating the Fe complex with 400 ml. HCl (1:1), extg. the mixt. with Et_2O, washing the ext. with dil. HCl and H_2O, extg. the ether soln. repeatedly with 5% KOH, and steam distg. the alk. soln. yielded 17.5 g. (51.2%) *3-methyl-2-ethyl-5-isopropylcyclohexanone* (V), pure, $b_{12.6}$ 113–3.5° (15.5 g.); *semicarbazone*, m. 111.5–12.5° (from aq. MeOH). Adding 1.82 g. V to a soln. of iso-PrLi (prepd. from 0.7 g. Li and 10 ml. iso-PrCl), and heating the mixt. 1.5 hrs. gave 2.1 g. 1,5-diisopropyl-2-methyl-2-ethylcyclohexanol (VI), b_{11} 141–5°. Dehydration of 1.5 g. VI by heating 40 min. on the steam bath with fivefold excess of 80% HCO_2H, chromatography, and hydrogenation of the petr. ether fraction (0.9 g., b_{11} 112–13°) over PtO_2 gave *1-methyl-1-ethyl-3,4-diisopropylcyclohexane* (VII), d_{20} 0.8480, n_D^{20} 1.4638. Infrared spectra of VII and of elemane obtained by total reduction of elemol are identical.

M. Hudlický

HEROUT, V.; TAKEDA, K.: SORM, F.

"Terpenes. LVII. Identity of Linderazulene with Chamazulene", P. 281, (CHEMICKE LISTY, Vol. 48, No. 2, Feb. 1954, Praha, Czechoslovakia)

SO: Monthly List of East European Accessions, (EEAL), LC, Vol. 3, No. 12, Dec. 1954, Uncl.

[illegible] V.; [illegible]

"Terpenes. IX. Composition of Juniper Oil", p. 569, ([illegible]
Vol. 48, No. 4, April 1954, Praha, Czech.)

SO: Monthly List of East European Accessions (EEAL), LC, Vol. 4, No. 3,
March 1955, Uncl.

HEROUT, Vlastimil

CZECH

Terpenes. LXI. Constitution of prochamazulenogen, natural precursor of chamazulene in Artemisia absinthium

Vlastimil Herout and František Šorm (Czech. akad. věd, Prague). *Chem. Listy* 48, 703–11; *Collection Czechoslov. Chem. Communs.* 19, 792–7(1954)(in English); cf. *C.A.* 49, 4585*d*.—Prochamazulenogen (I)(2 double bonds) (*C.A.* 49, 997*c*), m. 133–5° (from EtOH), $[\alpha]_D^{20}$ −40°, reduced with $LiAlH_4$ in Et_2O, gave a glassy product, a twice unsatd. triol (II), the dehydration of which by 90% HCO_2H, by $KHSO_4$, or by *p*-$MeC_6H_4SO_3H$ gave only slight amt. of an azulene. Dehydrogenation of 200 mg. II by heating with 20 mg. S 30 min. at 180–195° yielded by petr. ether elution 2 g. guaiazulene (III), and by C_6H_6 elution, 45 mg. of a new blue azulene, *artemazulen*- $C_{15}H_{16}O$ (IV) (infrared, visible, and ultraviolet spectra given); $C_6H_3(NO_2)_3$ compd., m. 192° (from EtOH). Reduction of the mother liquors of prochamazulenogen (*loc. cit.*) with $LiAlH_4$, and dehydrogenation with S yielded, besides small amts. of chamazulene and III, IV and a violet azulene $C_{14}H_{16}O$; $C_6H_3(NO_2)_3$ compd., m. 153–4° (from EtOH) (visible and ultraviolet spectra are given). A lactone (V) obtained from I by catalytic hydrogenation, was reduced with $LiAlH_4$ to give a diol $C_{15}H_{28}O_2$ (VI), $b_{0.4}$ 165–7°, the dehydration of which by refluxing 5 min. with *p*-$MeC_6H_4SO_3H$ in xylene yielded an ether (VII) $C_{15}H_{26}O$, b_{12} 147°, d_{20} 0.9081, n_D^{20} 1.4951. A

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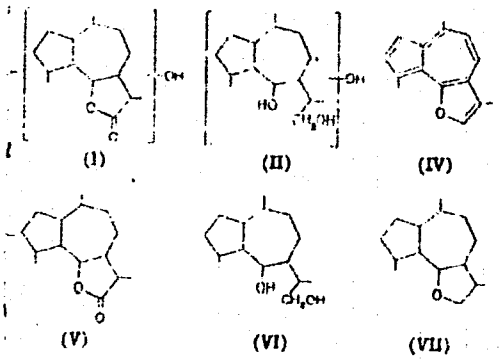

(I) (II) (IV)

(V) (VI) (VII)

hydroxy lactone prepd. from I by hydrogenation gave by $LiAlH_4$ reduction a compd., m. 180-4°. LXII. Isolation and properties of prochamazulenes from Matricaria chamo-

Vlastimil Herout

milla, a further compound of the guaianolide group. Zdeněk Čekan, Vlastimil Herout, and František Šorm. *Chem. Listy* 48, 1071-7; *Collection Czechoslov. Chem. Communs.* 19, 798-804(1954)(in English).—A bicyclic hydroxy acetoxy lactone $C_{17}H_{20}O_5$ (I) contg. 2 double bonds, isolated from *M. chamomilla*, is a source of chamazulene. Extg. 4.3 kg. dried flowers of *M. chamomilla* with cold petr. ether gave 198 g. of an ext. which was dissolved in 3 l. petr. ether, extd. with ten 1000-ml. portions of 2% aq. $KHCO_3$, the aq. layers were extd. 4 times with 500 ml. Et_2O, and the ether ext. evapd. to give 8.4 g. slurpy residue which yielded 2.5 g. I (prochamazulene), m. 158–60° (from Me_2CO-iso-Pr_2O). Hydrogenation of 647 mg. I over PtO_2 in AcOH gave satd. compds. $C_{17}H_{26}O_4$, one eluted with petr. ether, m. 123° (from petr. ether), the other eluted with C_6H_6, m. 115.5° (from petr. ether). Heating 100 mg. I in 10 ml. EtOH with 50 ml. 2% AcOH 30 min. at 50°, extg. the emulsion with Et_2O, treating the ext. with 2% Na_2CO_3, extg. the soln. with Et_2O, acidifying the aq. layer with AcOH, and extg. it with Et_2O gave 32 mg. dark blue liquid, *guaiazulenic acid* (II); Me ester, prepd. by CH_2N_2, dark blue oil (III). Infrared spectra of I and of the two satd. lactones, and ultraviolet spectra of II, III, and chamazulene are given.

M. Hudlický

HEROUT, VLASTIMIL

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/ Plant substances. III. Substances from Lactarius deliciosus L. Věra Benešová, Vlastimil Herout, and František Šorm (Czech. akad. věd, Prague). *Chem. Listy* 48, 882–5(1954); cf. *C.A.* 47, 7735g; 49, 907c.—EtOH extn. of 23.5 kg. *Lacturius deliciosus L.* gave 1.6 g. *mannitol*, m. 166°. From the C_6H_6 ext. (6 g.) were isolated: *ergosterol stearate*, m. 110.5°, $[\alpha]^{18}_D$ −53.4° (*ergosterol*, m. 161°, $[\alpha]^{18}_D$ −121°; *acetate*, m. 174°, $[\alpha]^{18}_D$ −93°); 0.49 g. *octyl stearate*, m. 35.5°, b$_{0.4}$ 150–67° (infrared spectra given); 0.19 g. *lactarazulene*; 0.11 g. *verdazulene*, m. 94.5°; and *lactarofolin*, m. 54°.

M. Hudlický

HEROUT, VLASTIMIL

Azulenes from Artemisia plants. Vlastimil Herout and František Šorm. Czech. 85,240, Dec. 1, 1956. A mixt. of 3 kg. dry finely cut *Artemisia* and 1 kg. NaOH was dissolved in 20 l. water, heated for 18 hrs. on a steam bath, and slowly acidified with a soln. of 1.35 kg. 94% H_2SO_4 in 2 l. water. The mixt. was steam-distd. and the azulene layer sepd. to give 17.3 g. of a crude mixt. contg. 31% azulines (I). Sepn. was facilitated by addn. of 1 l. of ligroine which was then distd. off *in vacuo*. The residue was dissolved in 100 ml. of ligroine and extd. with 30 ml. of concd. HCl. The acid soln. was dild. with 900 ml. of icewater and shaken with 250 ml. of Et_2O. After evapg. the Et_2O, the residue (5.8 g.) was taken up in ligroine and chromatographed over 60 g. Al_2O_3, yielding 5.3 g. of a pure mixt. of I, b_{10} 150–80°.
L. J. Urbánek

HEROUT, V.

CA further chamazulene precursor; the bitter principle of *Artemisia absinthium*. F. Sorm, L. Novotný, and V. Herout (Czechoslovak Acad. Sci., Prague). *Chemistry & Industry* 1955, 569; cf. *C.A.* 49, 8241c.—Extn. of *Artemisia absinthium* with petr. ether or EtOH yields a compd. (I), m. 183–5° (decompn.) (from alc.). Alk. hydrolysis of I in the presence of air, followed by acid distn., yields 13% chamazulene. The infrared spectra of I and anabsinthine (II) ($C_{15}H_{18}O_3$), m. 260°, are almost identical, but their relation is not clear. II is formed from I during extn. The infrared spectrum of II exhibits the characteristic infrared absorption of a γ-lactone.

J. A. Gilles

HEROUT, V.

HOLUB, M.; HEROUT, V.; SORM, F.

Synthesis of ∝-bisabolol - a spasmolytically active sequiterpenic alcohol. Cesk.farm. 4 no.3:129-131 Apr 55.

1. Oddeleni prirozenych latek, Ustav organicke chemie, Ceskoslovenska akademie ved, Praha.

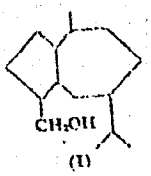
(ALCOHOLS,
∝-bisabolol, synthesis, spasmolytic eff.)
(MUSCLE RELAXANTS,
spasmolytic eff. of ∝-bisabolol alcohol)

HEROUT, V.

CZECH

C.A.

The nature of azulenogenic compounds from Lactarius deliciosus. Preliminary communication. V. Benešová, V. Herout, and F. Sorm (Czech. Akad. věd, Prague). *Chem. Listy* 49, 779–80(1955).—*Lactarius deliciosus L.* contains originally only orange prozulenes, one of which (I) has primary OH group and guaiane skeleton, and probably 4–5 double bonds. The other two orange compds. isolated by chromatography are an *aldehyde* having fewer double bonds than lactaroviolin, and a *hydrocarbon* contg. fewer double bonds than lactarazulene. Infrared spectra of I and of the product obtained by catalytic hydrogenation of lactaroviolin are given. Also in *Collection Czechoslov. Chem. Communs.* 20, No 2, 510–11(1955)(in English).

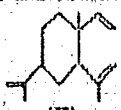


(I)

M. Hrdlicka

HEROUT, V.

Sesquiterpenes. LXVI. The structure of β-elemene. V. Sýkora, V. Herout, and F. Šorm (Czech. Acad. Vida, Prague). Chem. Listy 49, 942-3 (1955); cf. C.A. 49, 11698. — A hydrocarbon $C_{15}H_{24}$ isolated from sweet-flag and juniper oils and also obtained by pyrolysis of elemol benzoate (I), was named β-elemene and structure II proposed for it.



(II)

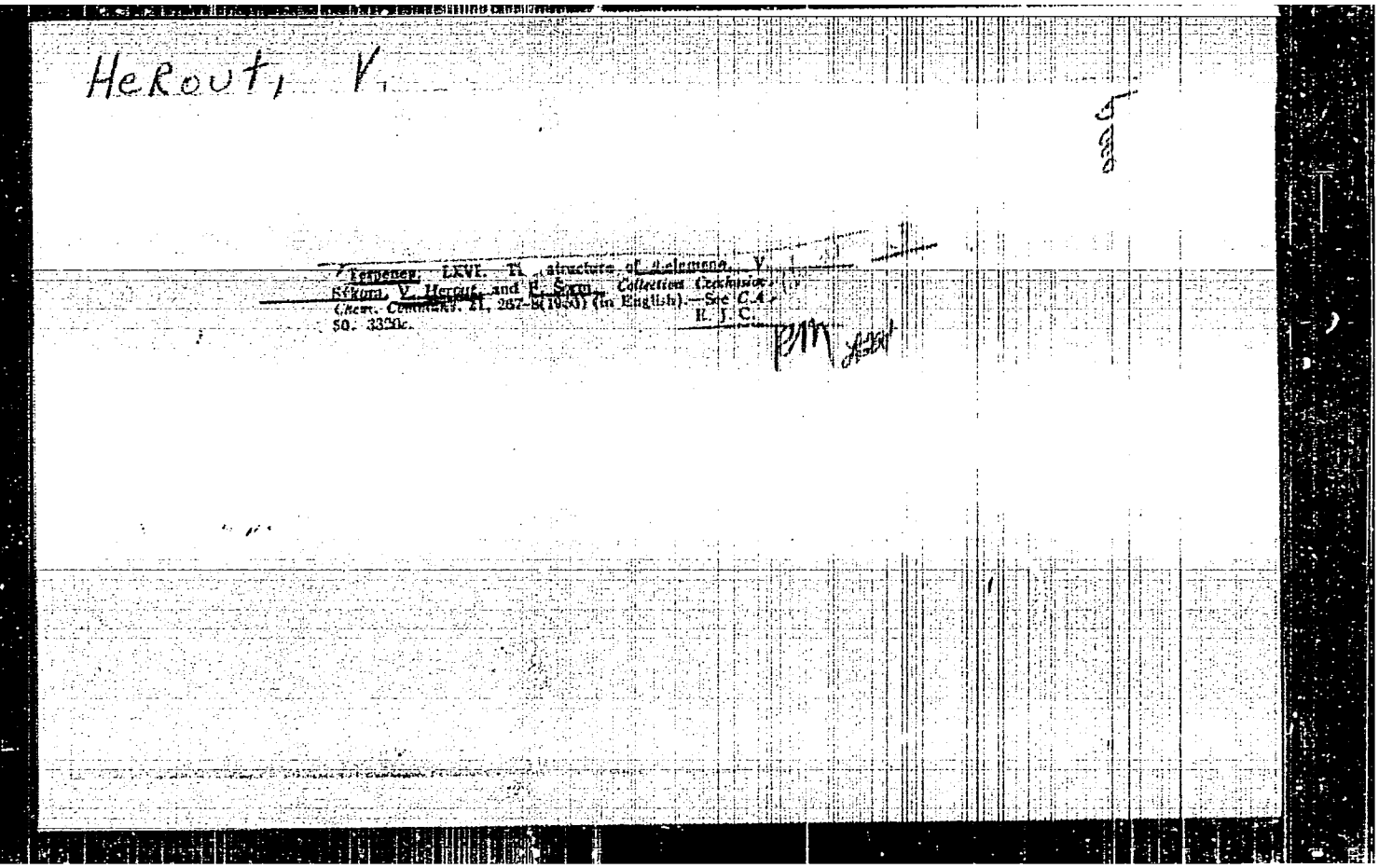
II isolated from the natural oils, b_9 113–14°, d_{25} 0.8802, n_D^{25} 1.4943, $[\alpha]_D^{25}$ −16.9°. Its ozonization gave 3.2 moles CH_2O. I, purified by heating the crude product 1 hr. at 90–100° with MeOH, $b_{0.4}$ 160°, was decompd. by heating (15.6 g.) at 100 mm. and 210–40° to give 7.4 g. crude and 3 g. pure II, b_{20} 128–9°, d_{24} 0.8803, n_D^{25} 1.4949, $[\alpha]_D$ −11.1°.

M. Hudlický

HEROUT, VLASTIMIL

Plant substances. IV. Isolation of 5-hydroxy-3,3',4',6,-7-pentamethoxyflavone from Artemisia absinthium L. Zdeněk Čekan and Vlastimil Herout (Czech. Akad. Věd, Prague). *Chem. Listy* 49, 1063-6(1955); cf. *C.A.* 49, 9604h.—A compd. $C_{20}H_{20}O_8$, m. 161.5° (*C.A.* 49, 997c, erroneously reported as m. 165.5°), isolated from *A. absinthium* was identified as *5-hydroxy-3,3',4',6,7-pentamethoxyflavone* (I) for which a name *artemetin* is suggested. Methylation of 0.5 g. I with 6.5 g. Me_2SO_4 in 20 ml. 10% NaOH and 10 ml. Me_2CO gave 0.4 g. *3,3',4',5,6,7-hexamethoxyflavone* (hexamethylquercetagetin) (II), m. 142-3° [from Me_2CO-(iso-$Pr)_2O$]. Refluxing 0.5 g. I 3.5 hrs. with 20 ml. 48% HBr, and acetylating the crude product by refluxing 3 hrs. with 20 ml. Ac_2O gave 0.3 g. *3,3',4',5,6,7-hexaacetylquercetagetin* (III), m. 216–17° (from Me_2CO). Refluxing 0.25 g. III 2 hrs. with 25 ml. MeOH, 0.25 g. $KHCO_3$, and 5 ml. H_2O, and crystg. the product after acidification of the mixt. from EtOH gave quercetagetin (IV), decomp. 300–5°. Alk. hydrolysis of 0.5 g. I by refluxing 10 hrs. with 35 ml. 50% KOH gave 3,4-$(MeO)_2C_6H_3CO_2H$. To prove the position of the free OH group in I, I (1 g.) was dissolved in 20 ml. C_5H_5N, 0.75 g. KOH and 25 ml. H_2O added, and the mixt. treated with 1.5 g. $K_2S_2O_8$ in 50 ml. H_2O and 0.75 g. KOH in 35 ml. H_2O. The mixt. was acidified after 24 hrs., the ppt. filtered off, the filtrate extd. with Et_2O and heated 45 min. at 100° with 20 ml. concd. HCl and 3 g. Na_2SO_3. The product, *5,8-dihydroxy-3,3',4',6,7-pentamethoxyflavone*, m. 249–51° (from Me_2CO), gave with *p*-benzoquinone a red ppt. of a quinone of the flavone 5-ols. Ultraviolet spectra of I, II and IV are given.

M. Hudlický



Vlastimil Herout

Terpenes. LXVII. Hydrogenation products of santonin and allo-santonin. Otto Kovács, Vlastimil Herout, Milan Horák, and František Sorm (Čsl. akad. věd, Prague). *Chem. Listy* 49, 1858–69 (1955); cf. *C.A.* 50, 3320c.—Hydrogenation of santonin (I) under various conditions gave *3-oxo-5,12-santanolides* (II) belonging to 3 stereoisomeric groups (IIa, b, and c). More intensive hydrogenation yielded *3-hydroxy-5,12-santanolide* (III). The II were transformed to *5,12-santanolides* (IV), either by the Clemmensen reduction (which caused a rearrangement from the series *c* to *a*), or via ethylene thioketals (V) by desulfuration with Raney Ni. Reduction of IV with $LiAlH_4$ gave *5,12-santandiol* (VI); reduction of *5,12-alantanolide* (*alantolactone*) (VII) gave *5,12-alantandiol* (VIII). The diols VI and VIII were purified by way of their *cyclic sulfites* (IX, X). Dehydration of VI yielded *5,12-santanoxide* (XI), that of VIII yielded an unsatd. alc., *alanten-12-ol* (XII). Hydrogenation of 24.6 g. I, m. 171–2°, in 200 ml. MeOH over 600 mg. Pd on $BaCO_3$ yielded 18.5 g. IIa, m. 158°, $[\alpha]_D^{20}$ 30°. Hydrolysis of the mother liquors yielded 2.85 g. (10.8%) *3-oxo-5-hydroxysantanoic acid* (*b*-series), m. 190–2° (from 50% MeOH), $[\alpha]_D^{20}$ 20.7°. The acid with *p*-$MeC_6H_4SO_3H$ in AcOH gave 1.05 g. IIb, m. 163–5° (from 70% MeOH), $[\alpha]_D^{20}$ 11.3°. Hydrogenation of IIb over PtO_2 in AcOH gave IIIb, m. 213–15° (from MeOH), $[\alpha]_D^{20}$ −8.5°. Hydrogenation of 4 g. I in 40 ml. MeOH over Raney Ni W-1 (5 ml. alc. suspension) at room temp. and 120 atm. gave 4.1 g. glassy product, yielding on oxidation with CrO_3 and lactonization 2.8 g. IIa, m. 154–7°, $[\alpha]_D^{20}$ 28.1°. I (4 g.) hydrogenated in 40 ml. MeOH over 0.2 g. PtO_2 at room temp. and 120 atm. gave 1.8 g. IIIc, m. 135° (from 50% MeOH), $[\alpha]_D^{20}$ 42.7°. Adding 252 mg. IIIc in 6 ml. AcOH to 70 ml. CrO_3 in 0.1 ml. H_2O, allowing the mixt. to stand 20 hrs. at room temp., dilg. with 6 ml. H_2O, evapg. *in vacuo*, dissolving the residue in H_2O, extg. with Et_2O, and evapg. the ext. gave IIc, m. 145–6° (from C_6H_6-petr. ether and from

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H_2O), $[\alpha]^{25}_D$ 77.5°; an addnl. 650 mg. IIc was obtained by oxidation of the mother liquors after the pressure hydrogenation over PtO_2. Chromatography of the mother liquors after the crystn. of IIc gave 620 mg. IIa, $[\alpha]^{25}_D$ 32.2°. Reducing 2.5 g. IIa with 8 g. Zn-Hg and 15 ml. HCl (1:2), refluxing the mixt. 12 hrs. with the addn. of six 3-ml. portions of concd. HCl, and extg. the mixt. with Et_2O gave 2.25 g. IVa, m. 164° (from 90% EtOH), $[\alpha]^{25}_D$ 20.8°. Similar treatment of IIb and IIc yielded 70% IVb, m. 86–7°, $[\alpha]^{25}_D$ −27.0°, and 46.5% IVa, $[\alpha]^{25}_D$ 28.2° (rearrangement owing to the acidic medium during the reduction). Treating 2.5 g. IIa in 40 ml. AcOH with 0.96 ml. $(CH_2SH)_2$ and 0.96 g. p-$MeC_6H_4SO_3H$ in 10 ml. AcOH 3 hrs. at room temp., and pouring the mixt. onto ice gave 3.25 g. (99%) Va, m. 185–7° (from AcOEt), $[\alpha]^{25}_D$ 44.7°. Refluxing 1.63 g. Va in 120 ml. dioxane and 15 ml. Raney

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Terpenes - Odon Novaes

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Ni in dioxane, 8 hrs., filtering off the catalyst, and evapg. the solvent gave 1.16 g. IVa. Similar treatment of IIb and IIc gave 81% and 93.5% Vb and Vc, m. 122–3° (from MeOH), $[\alpha]^{25}_D$ −11.08°, and 106–7° (from AcOEt), $[\alpha]^{25}_D$ 37.9°, resp., the desulfuration of which yielded 95% IVb, m. 86–7°, $[\alpha]^{25}_D$ −27.2°, and 89% IVc, m. 137–9° (from EtOH, $(iso\text{-}Pr)_2O$, and sublimation at 110°/13 mm.), $[\alpha]^{25}_D$ +92.2°, resp. Adding 11.8 g. IVa in 300 ml. Et_2O to 8.9 g. $LiAlH_4$ in 300 ml. Et_2O, stirring the mixt. 2 hrs. at room temp., decompg. with 6 ml. H_2O and 200 ml. 25% H_2SO_4, and extg. the diol with Et_2O gave 11.9 g. VIa, m. 154–5° (from C_6H_6), $[\alpha]^{25}_D$ −25.3°. Treating 481 mg. VIa with 5 ml. $SOCl_2$, distg. off the excess $SOCl_2$, dissolving the residue in 10 ml. C_6H_6-MeOH 1:1, evapg. the soln. to dryness, and chromatographing over Al_2O_3 gave 410 mg. IX, m. 75–6° (from EtOH), $[\alpha]^{25}_D$ −253°. Treating 57 mg. IX in 1 ml. EtOH 24 hrs. with 0.2 ml. 5*N* NaOH at room temp., evapg. the mixt. at 40°, dilg. with H_2O, and extg. with Et_2O gave 44 mg. VIa, $[\alpha]^{25}_D$ −24.8°. Heating 0.6 g. VIa in 12 ml. C_6H_6 with 0.1 g. *p*-$MeC_6H_4SO_3H$ 30 min. on the steam bath, distg. off the solvent, dilg. the residue with 15 ml. H_2O, and extg. with Et_2O gave 460 mg. XI, b_8 132–3°, d_{25} 0.9788, n^{25}_D 1.4972, $[\alpha]^{25}_D$ −39.54°. Crude VII (23.2 g.), made by hydrogenation of 48.3 g. crude oil of *Inula helenium* (3 kg. roots), recrystd. 3 times from EtOH gave 10.3 g. VII, m. 147–7.5°, $[\alpha]^{25}_D$ 14.6°. Reduction of VII with $LiAlH_4$ gave 93% VIII, m. 112–13° (from petr. ether-C_6H_6 3:1), $[\alpha]^{25}_D$ −6.2° to −6.85°. VIII and $SOCl_2$ gave 47% X, m. 114–16° (from EtOH), $[\alpha]^{25}_D$ −53.4°. Dehydration of VIII with *p*-$MeC_6H_4SO_3H$ gave 88% XII (double-bond position uncertain), b_8 133–5°, d_{25} 0.9879, n^{25}_D 1.5073, $[\alpha]^{25}_D$ −32.7°. Infrared spectra of IIa,b,c,

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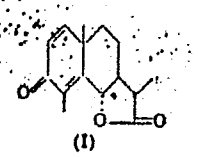
Terpenes -- Odon Kovacs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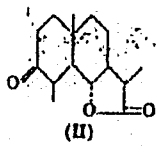
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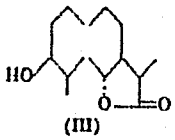
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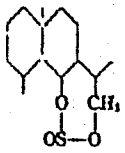
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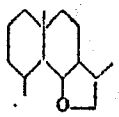
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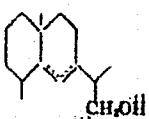
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Terpenes -- Azulenes

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IIIc, IVa,b,c, VI, VII, VIII, XI, and XII are given. LXVIII. Formation of two tetraalkylazulenes in the working up of wormwood. Miloš Suchý, Vlastimil Herout, and František Sorm. *Ibid.* 1870–8.—Two new azulenes, *methylchamazulene*, $C_{15}H_{18}$ (I), and *ethylchamazulene*, $C_{16}H_{20}$ (II), were isolated during the working up of the wormwood by heating with 10% NaOH and steam distn. of the acidified soln. The crude mixt. of I and II was sepd. by countercurrent extn. with equal parts of 52.5% H_3PO_4 and petr. ether (bu 60–75°). Dilg. the H_3PO_4 fractions with H_2O and extg. with petr. ether gave 0.16 g. I, bu 150°, R_f 0.741 (Nujol–48% H_3PO_4); $C_6H_2(NO_2)_3$ *compd.*, m. 150° (from EtOH). I with $KMnO_4$ at room temp. gave AcOH and $EtCO_2H$; hydrogenation in AcOH over PtO_2 gave $C_{15}H_{28}$ (5 double bonds). From the petr. ether fractions was obtained 0.25 g. II, bu 173°; $C_6H_2(NO_2)_3$ *compd.*, m. 133° (from EtOH). Oxidation with $KMnO_4$ yielded AcOH and $EtCO_2H$, hydrogenation over PtO_2 in AcOH gave $C_{16}H_{32}$ (5 double bonds). For I (R = Me, R′ = H) and A (R = H, R′ = Et) are suggested for I and II, resp. Both azulenes are supposed to be formed by the alkylation of hydroxyguaidieneolide (III, with 2 double bonds) with CH_2O and AcH, resp., during the alk. hydrolysis of crude wormwood (IV). In fact, AcH was found in IV, and absinthin worked up in the

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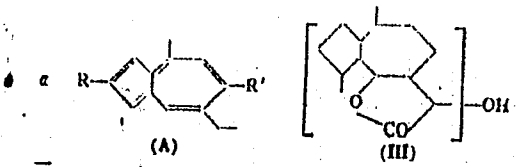

(A) (III)

presence of IV gave I and II. I and II were obtained, resp., by heating III or absinthin, with CH_2O and AcH, resp., in alk. solns. For comparison, *1,4-dimethyl-7-sec-butylazulene* (V) and *1,4-dimethyl-3,7-diethylazulene* (VI) were prepd. Adding 2.2 g. 2,8-dimethylbicyclo[5.3.0]decan-5-one in 30 ml. Et_2O to an ether soln. of MeEtCHLi prepd. from 27 g. *sec*-BuCl and 2.2 g. Li in 50 ml. petr. ether, refluxing the mixt. 6 hrs., decompg. with H_2O and H_2SO_4, extg. with Et_2O, and distg. the ext. gave 1 g. (39%) *2,8-dimethyl-5-sec-butylbicyclo[5.3.0]decan-5-ol* (VII), $b_{0.5}$ 157°. Heating 1 g. VII 20 min. with 1.5 g. $KHSO_4$ at 180°, gave 0.7 g. (78%) *2,8-dimethyl-5-sec-butylbicyclo[5.3.0]decene*, d_4^{20} 0.8813, whose dehydrogenation by heating 16 min. at 180° with S yielded 11% V [$C_6H_2(NO_2)_3$ compd., m. 136° (from EtOH)]. Treating 0.4 g. chamazulene in 50 ml. CH_2Cl_2 48 hrs. at room temp. with 8.2 ml. Ac_2O and 1.5 ml. BF_3-

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Aldon Korach

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Terpenes

Et_2O, dilg. the soln. with 250 ml. H_2O acidified with 1.5 ml. HCl, and chromatographing the residue after the evapn. of CH_2Cl_2 gave 0.25 g. *3-acetylchamazulene* (VIII), m. 86°; $C_6H_2(NO_2)_3$ *compd.*, m. 123° (from EtOH). Adding 0.15 g. $LiAlH_4$ to 0.22 g. VIII in 30 ml. Et_2O, decompg. the mixt. after 24 hrs. with 100 ml. H_2O, and chromatographing the residue after the evapn. of the Et_2O gave VI [$C_6H_2(NO_2)_3$ *compd.*, m. 148° (from EtOH)]. Infrared spectra of I, II, their decahydro derivs., of V, and ultraviolet spectra of II, V, VI, and chamazulene are given. LXIX. The structure of dehydrocostuslactone. Miroslav Romaňuk, Vlastimil Herout, and František Šorm. *Ibid.* 1879–86.—Extg. 248 g. Costus oil (from *Saussurea lappa*) in 250 ml. Et_2O with three 100-ml. portions of satd. $NaHCO_3$, acidifying the soln. with H_2SO_4, extg. with Et_2O, refluxing the evapd. ext. (3 g.) with 25 g. NaOH in 100 ml. H_2O and 250 ml. EtOH, distg. off the EtOH, dilg. with 1 l. H_2O, extg. the neutral portions with 500 ml. Et_2O, acidifying the soln. with H_2SO_4, extg. with 500 ml. Et_2O, removing the phenols by extn. with 5% NaOH, and evapg. the ether ext. to dryness *in vacuo* gave 11.4 g. cryst. *dehydrocostuslactone* (I), b$_{0.4}$ 140–3°, m. 61°, $[\alpha]_D^{19}$ −12.9°; an addnl. 2.8 g. of I was obtained from the alk. washing. Heating 50 mg. I with 45 mg. Se 6 min. at 300° and chromatography gave chamazu-

(over)

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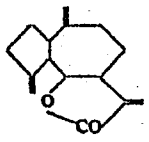
Adon Korach 9

Terpenes

lene (II). Hydrogenation of I in AcOH over PtO_2 gave hexahydrodehydrocostuslactone (III), $b_{0.4}$ 135–7°, d_{20} 1.0545, n_D^{19} 1.5076, $[\alpha]_D^{19}$ 46.5°. Heating 11.4 g. III with 11.6 g. Se 17 hrs. at 320–5° removing periodically the distillate after 2, 3, and 6 hrs., chromatographing the crude product, and extg. the azulenic fraction with 79% H_3PO_4 gave 230 mg. of a mixt. whose paper chromatography in 20% paraffin oil in petr. ether with 48% H_3PO_4 in ascending arrangement gave *guaiazulene*, *Se-guaiazulene*, 20 mg. II [$C_{15}H_{18}(NO_2)_3$ *compd.*, m. 130°], and 67 mg. of a new azulene, *Se-chamazulene* (IV) [$C_9H_6(NO_2)_3$ compd., m. 112° (from EtOH)], to which the structure of *2,4-dimethyl-7-ethylazulene* is ascribed. Ozonization of I showed the presence of 2.5–3.1 double bonds, and the following structure is therefore suggested for I:



M. Hudlický

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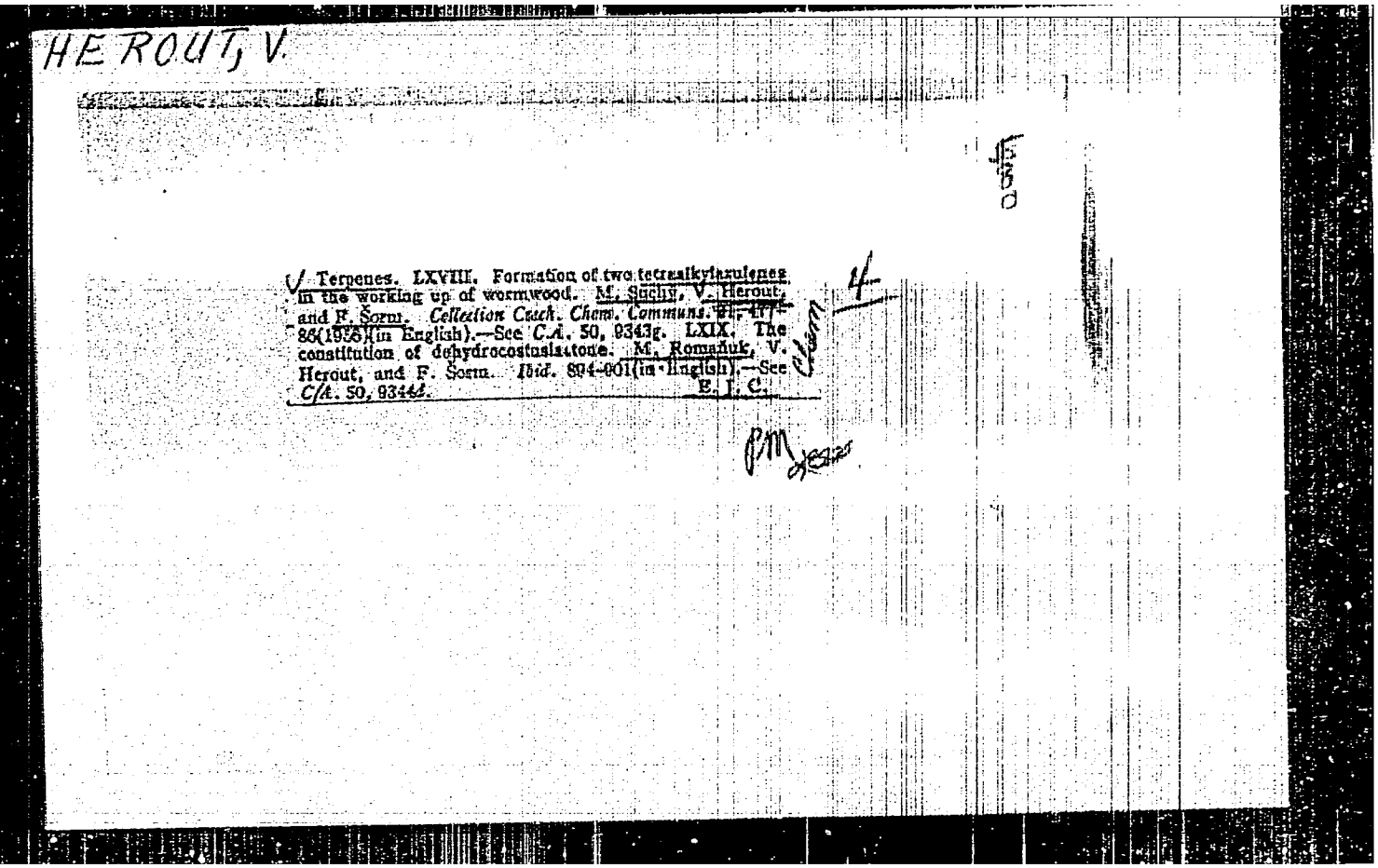
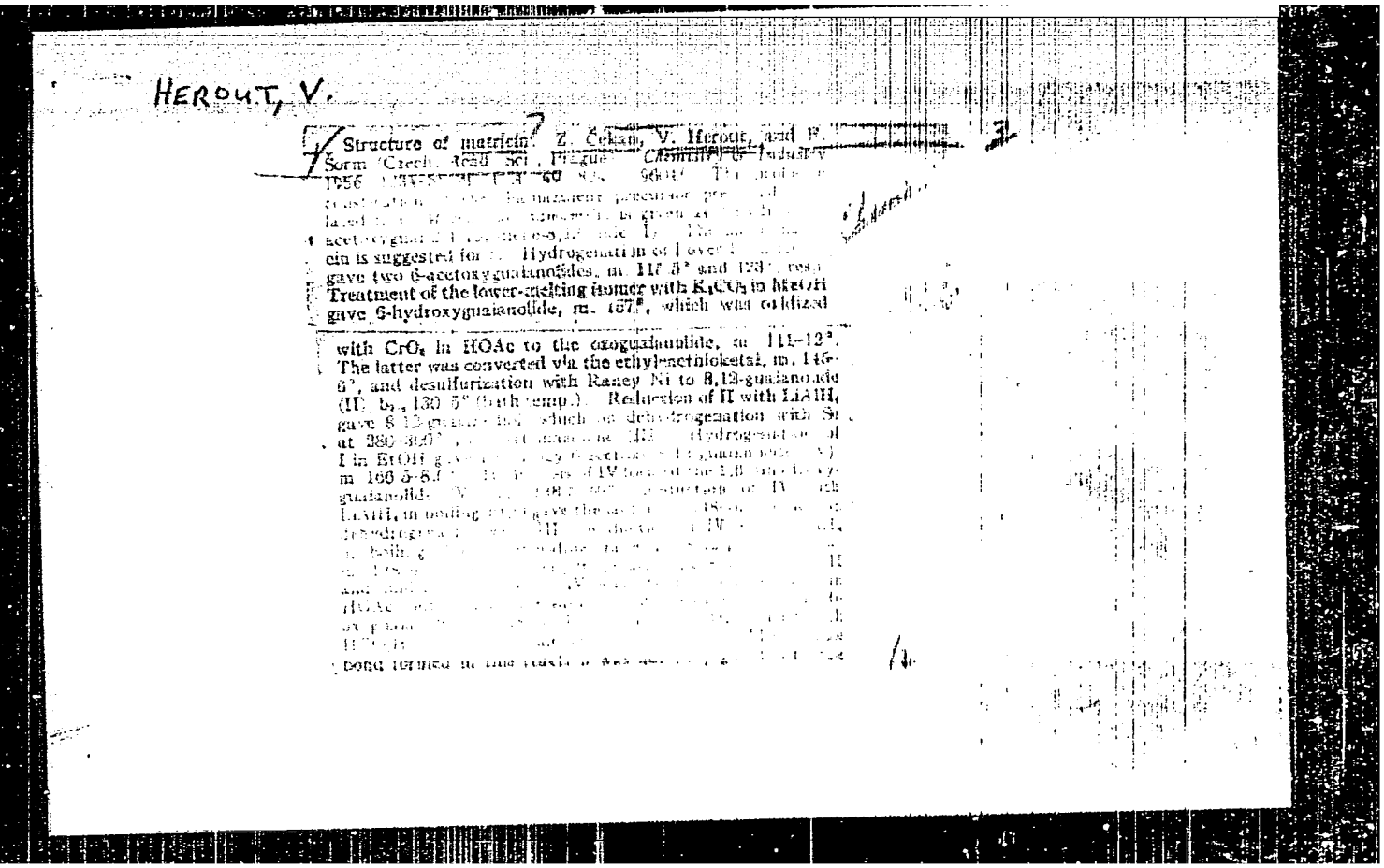


HEROUT, V.

Terpenes. LXVIII. Formation of two tetramethylnaphthalenes in the working up of wormwood. M. Suchý, V. Herout, and F. Šorm. *Collection Czech. Chem. Communs.* 11, 417–86(1939)(in English).—See *C.A.* 50, 9343g. LXIX. The constitution of dehydrocostuslactone. M. Romaňuk, V. Herout, and F. Šorm. *Ibid.* 894-901(in English).—See *C.A.* 50, 9344d.

E. J. C.



HEROUT, V.

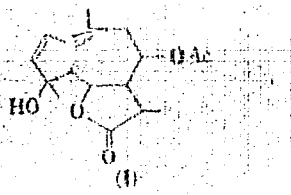
Structure of matricin. Z. Čekan, V. Herout, and F. [illegible]
Sorm (Czech. Acad. Sci., Prague) *Chemistry & Industry* 1956 [illegible]

[illegible] acetoxyguaianolide [illegible] cin is suggested for [illegible] Hydrogenation of [illegible] gave two 6-acetoxyguaianolides, m. 117.5° and 123° [illegible] Treatment of the lower-melting isomer with K_2CO_3 in MeOH gave 6-hydroxyguaianolide, m. 167°, which was oxidized with CrO_3 in HOAc to the oxoguaianolide, m. 111–12°. The latter was converted via the ethylenethioketal, m. 146–6°, and desulfurization with Raney Ni to 8,12-guaianolide (II, $b_{0.1}$ 130.5° [bath temp.]). Reduction of II with $LiAlH_4$ gave 8,12-guaianediol [illegible] which on dehydrogenation with Se at 380–420° [illegible] hydrogenation of I in EtOH [illegible] m. 166.5–6.5° [illegible] guaianolide [illegible] $LiAlH_4$, in boiling [illegible] gave the [illegible] dehydrogenation [illegible]

[illegible] bond formed in this reaction [illegible]

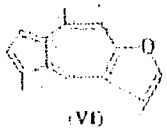
Čekan, Z., Herout, V., Šorm, F.

lactone or ketone carbonyl as shown by ultraviolet and infrared spectra.



(I)

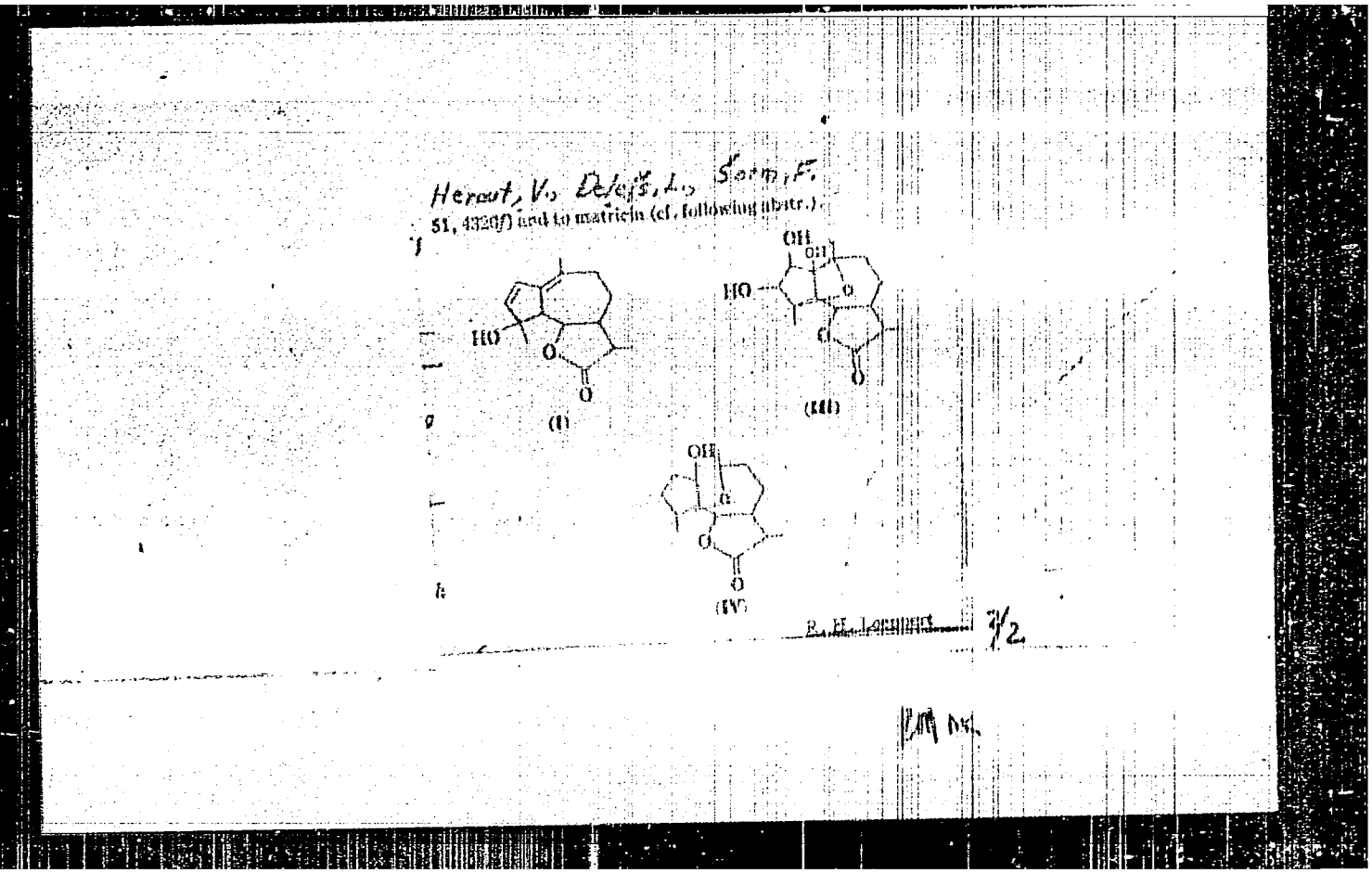
(III)



(VI)

Herout, V.

The structure of artabsin, the psoduunmanitenogen from Artemisia absinthium, V. Herout, L. Dolejš, and F. Sorm (Czech. Acad. Sci., Prague). *Chemistry & Industry* 1955, 1538; cf. C. A. 49, 9671e.—Artabsin the chamazulene precursor previously isolated from *Artemisia absinthium*, is shown to have the constitution 1-hydroxyguai-3,4(10)-dien-8,12-olide (I). Hydrogenation of I on Pt in EtOH gave a dihydro deriv. (II) with the 4(10) double bond retained. Hydrogenation with Pt in HOAc gave a mixt. which was resolved by chromatography into 8,12-guaianolide, m. 111°, and 3 stereoisomeric 1-hydroxyguaianolides, m. 109-10°, 159-60°, and 136°, and $[\alpha]_D$ 0°, −8.0°, and 20.4°, resp. The latter compds. were inert to CrO_3 and hence contained tertiary OH groups. Dehydrogenation of the product, m. 108-9°, with $SOCl_2$ in pyridine gave an impure product which was shown by ozonolysis to contain 30% of an isomer with a terminal methylene group. I was oxidized by $KMnO_4$ to III, m. 188°. Periodate oxidation of III pointed to the presence of the vicinal triol. Hydrogenolysis of the ozonide of II provided IV, m. 160°, which on oxidation with CrO_3 in HOAc gave the corresponding ketone, m. 145°. The latter showed absorption at 1733 cm^{-1}, indicative of a carbonyl group in a 5-membered ring. I is closely related structurally to arborescin (cf. Mazur and Menon, C.A.



Herout, V., Dolejš, L., Sorm, F.
51, 4329(f) and to matricin (cf. following abstr.)

(I)

(III)

(IV)

R. H. Lorimer 3/2

HERCUT, V.

HEROUT, V. Report on the 14th International Congress of Pure and Applied Chemistry held July 21-27, 1955, in Zurich, p. 489. Vol. 50, no. 3, Mar. 1956. CHEMICKE LISTY. Praha, Czechoslovakia.

SOURCE: East European Accessions List (EEAL) Vol. 6, No. 4--April 1957

HEROUT, V.

HEROUT, V. Terpenes. LXX. Monocyclic lactones from wormwood (Artemisis absinthium L.). p. 586. Vol. 50, no. 4, April, 1956. CHEMICKE LISTY. Praha, Czechoslovakia.

SOURCE: East European Accessions List (EEAL) Vol. 6, No. 4--April 1957

Vlastimil Herout

Herout, Vlastimil

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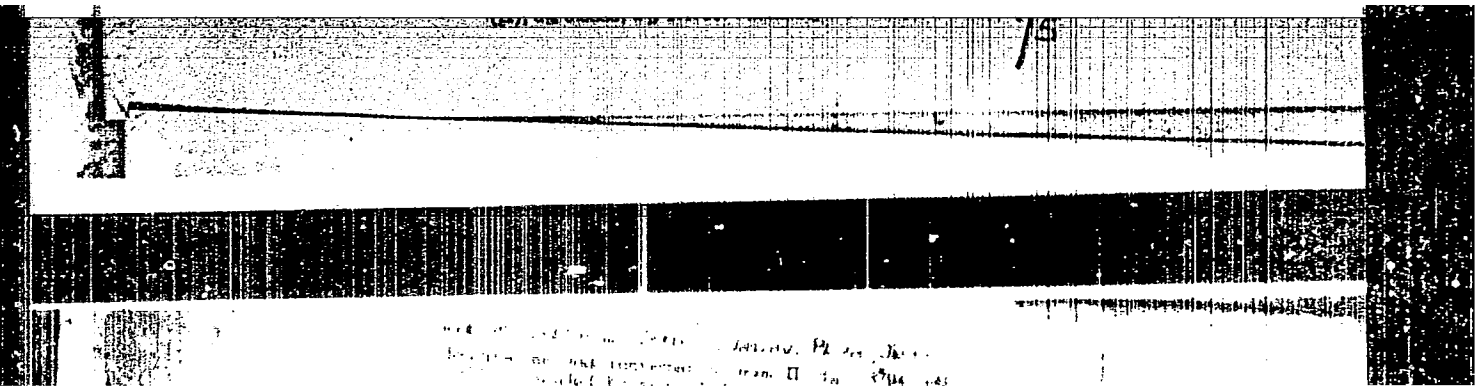
Plant substances. V. Isolation of further crystalline compounds from wormwood. Vlastimil Herout, Ladislav Novotný, and František Šorm (Czech. Acad. Sci., Prague). *Chem. Listy* 50, 591–7(1956); cf. *C.A.* 49, 13228*i*.—Chromatography of ligroine-ext. of *Artemisia absinthium* (*loc. cit.*) on neutral Al_2O_3 yielded cryst. compds. in the following sequence: a yellow lactone, $C_{20}H_{30}O_3$, m. 207° (from $CHCl_3$–$(Me_2CH)_2O$); hydroxyguaidienolide, m. 133–5°; a compd., m. 156° (from EtOH), $[\alpha]_D^{19}$ 285°; a hydroxy lactone, $C_{15}H_{18}O_3$, m. 98° (dimorphic form m. 108°, $[\alpha]_D^{19}$ −14.0°); absinthin dehydrogenated to chamazulene; a keto lactone, $C_{15}H_{22}O_3$, m. 114°, $[\alpha]_D^{19}$ −377°, (semicarbazone m. 222°); a compd., m. 124°; a keto lactone, $C_{15}H_{22}O_3$, m. 173°. The extd. drug was then treated with 96% EtOH, cryst. quebrachitol was sepd., and the filtrate was chromatographed, yielding absinthin, anabsinthin, a compd. m. 63°, and a compd. m. 252° which gave an acetyl deriv., m. 232°.

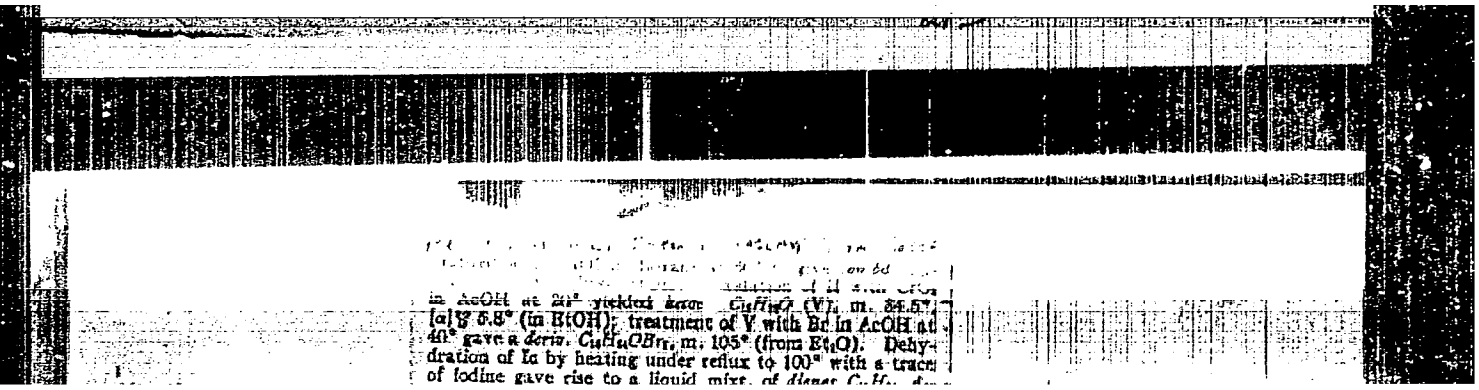
L. J. Urbánek

Herout, Vlastimil

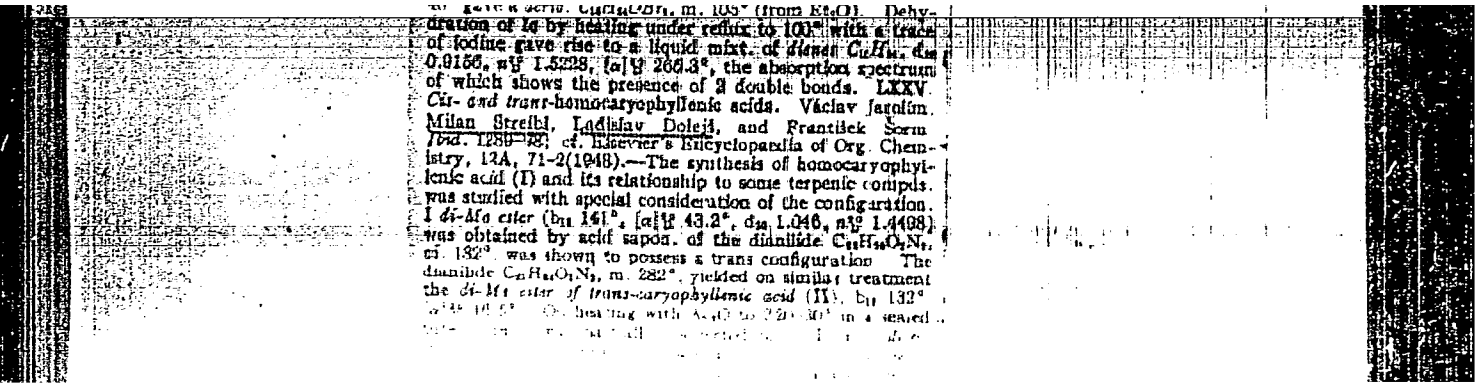
Terpenes. LXXVI. The nature of arctiopicrin, an α,β-unsaturated lactone from *Arctium minus*. Milan Hudlický, Vlastimil Herout, and František Šorm (Czechoslov. Acad. Sci., Prague). *Chem. Listy* 46, 182–93(1952); cf. *C.A.* 46, 297g.—A lactone, arctiopicrin (I), isolated from *A. minus*, has the formula $C_{15}H_{18}O_5$, contrary to the previous formulation as $C_{15}H_{20}O_5$. Hydrogenation of I yielded two stereoisomers (II and III), $C_{15}H_{22}O_5$, and two stereoisomers (IV and V), $C_{15}H_{24}O_5$. The main product of hydrogenation, IV, yielded on hydrolysis $MeCH(CH_2OH)CO_2H$ (VI) and a monocyclic diol-lactone (VII) called *arctiodiole* ($C_9H_{16}O_4$). I, m. 115°, $[\alpha]_D^{20}$ 130°, was obtained in a yield of 0.05% from dried leaves of *A. minus*. I in alk. hydrolysis consumed 2.19 equivs. base. Hydrogenation of 5.1 g. I in 30 ml. MeOH over PtO_2 (equiv. of 2.35 double bonds), chromatography over 5 kg. Al_2O_3, and crystn. from 10:1 iso-PrOH-EtOH gave 200 mg. II, m. 98°, $[\alpha]_D^{20}$ −6.2°, 1.15 g. III, m. 108°, $[\alpha]_D^{20}$ −21.7° (*phenylurethan*, m. 134°), 1.63 g. IV, m. 134°, $[\alpha]_D^{20}$ 52.48° (*bis(phenylurethan)*, m. 149°, *diacetate*, m. 53°), and 550 mg. V, m. 116°, $[\alpha]_D^{20}$ 79.7°. Refluxing IV (1.2 g.) with 20 ml. 10% KOH in MeOH, neutralizing the cold mixt. with a calcd. amt. of HCl in MeOH, treating it with CH_2N_2 in Et_2O, filtering off the KCl, and distg. the filtrate gave 210 mg. VI *Me ester*, b$_{18}$ 74°, $[\alpha]_D^{20}$ 6.4°, reduction of which with $LiAlH_4$ in Et_2O gave *HOCH*$_2$*CH(Me)CH*$_2$*OH*, b$_{18}$ 140°. *Bis(phenylurethan)*, m. 137°. VI and its transformation products were identical with those prepd. synthetically. The residue after the removal of VI Me ester yielded *tetrahydroarctiidide*, m. 146° [from EtOH-(iso-Pr)$_2$O], b$_{18}$ 176°, $[\alpha]_D^{20}$ 35°. Infrared spectra of I–V are given.

M. Hudlický

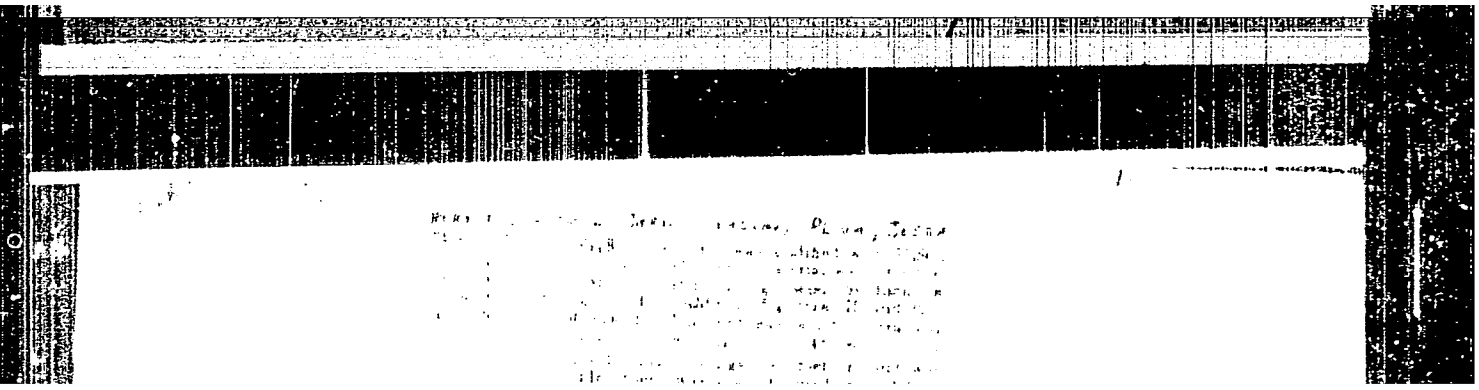




in AcOH at 20° yielded some $C_{15}H_{16}O$ (V), m. 84.5°, [α]$_D^{20}$ 6.8° (in EtOH); treatment of V with Br in AcOH at 40° gave a deriv. $C_{15}H_{14}OBr_2$, m. 105° (from Et_2O). Dehydration of Ia by heating under reflux to 100° with a trace of iodine gave rise to a liquid mixt. of dienes $C_{15}H_{14}$, d$_4^{20}$



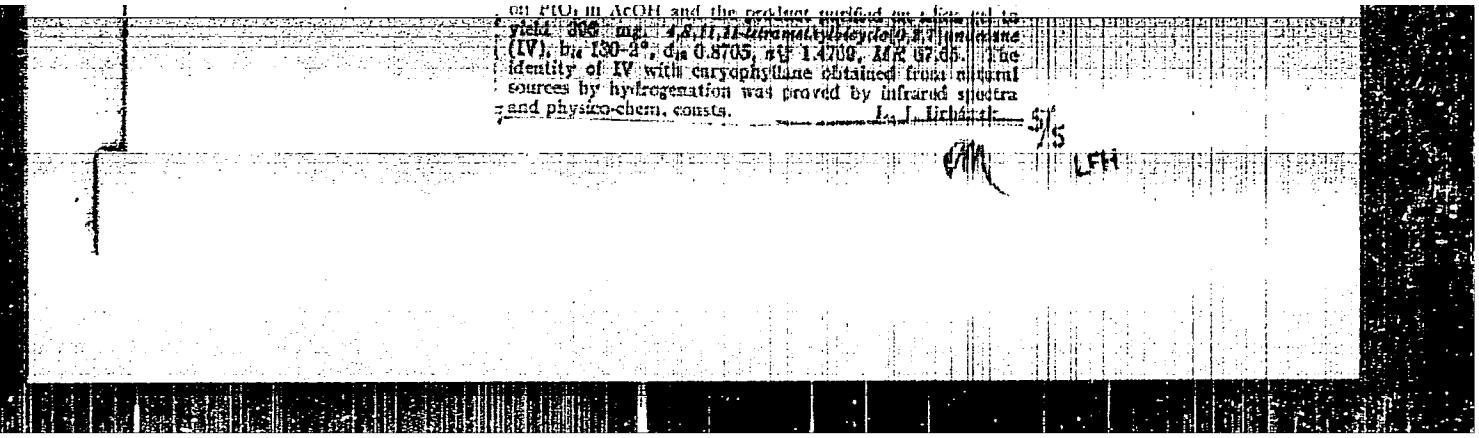
dration of *Ia* by heating under reflux to 100° with a trace of iodine gave rise to a liquid mixt. of *dianet* $C_{15}H_{24}$, d_{20} 0.9156, n_D^{20} 1.5228, $[\alpha]_D^{20}$ 266.3°, the absorption spectrum of which shows the presence of 2 double bonds. LXXV. *Cis- and trans*-homocaryophyllenic acids. Václav Jarolím, Milan Streibl, Ladislav Dolejš, and František Šorm. *Ibid.* 1289–98; cf. Elsevier's Encyclopaedia of Org. Chemistry, 12A, 71–2(1948).—The synthesis of homocaryophyllenic acid (I) and its relationship to some terpenic compds. was studied with special consideration of the configuration. *I di-Me ester* (b_{11} 141°, $[\alpha]_D^{20}$ 43.2°, d_{20} 1.046, n_D^{20} 1.4498) was obtained by acid sapon. of the dianilide $C_{31}H_{38}O_2N_2$, cf. 132°, was shown to possess a trans configuration. The dianilide $C_{31}H_{38}O_2N_2$, m. 282°, yielded on similar treatment the *di-Me ester of trans-caryophyllenic acid* (II), b_{11} 132°, [illegible] on heating with [illegible] in a sealed [illegible]



KEFOUT, VLASTIMIL; JAROLIM, VACLAV; PLIVA JOSEF

[illegible]

II and III (5.0 g.) was subjected to acyloin cyclization with 2 g. powdered Na in 600 ml. boiling xylene to give, after decompn. with dil. H_2SO_4, 2.7 g. fraction $b_{0.5}$ 95-100°, consisting of *4,8,11,11-tetramethylbicyclo[0.3.7]undecan-5-ol-6-one* and *4,8,11,11-tetramethylbicyclo[0.3.7]undecan-6-ol-7-one*. The acyloin fraction (1.0 g.) was reduced by boiling with 10.5 g. Zn-Hg in 40 ml. AcOH and 15 ml. concd. HCl which was added gradually during 80 hrs. The reaction mixt. was dild. with H_2O, extd. with ligroine and chromatographed on 80 g. alk. Al_2O_3 to give 150 mg. ketonic fraction, apparently of *4,8,11,11-tetramethylbicyclo[0.3.7]undecan-(?)-one* (*semicarbazone*, m. 190° from EtOH) and 400 mg. hydrocarbon fraction which was hydrogenated (400 mg.) on PtO_2 in AcOH and the product purified on silica gel to yield 335 mg. *4,8,11,11-tetramethylbicyclo[0.2.7]undecane* (IV), b_{12} 130-2°, d_{20} 0.8705, [illegible]



on PtO_2 in AcOH and the product purified in the usual way to yield 308 mg. 4,8,11,11-tetramethylbicyclo[6.3.1]undecane (IV), b_{12} 130-2°, d_4 0.8705, n_D^{25} 1.4700, MR_D 67.05. The identity of IV with caryophyllene obtained from natural sources by hydrogenation was proved by infrared spectra and physico-chem. consts.

L. J. Richard 5/5

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APPROVED FOR RELEASE: 08/10/2001 CIA-RDP86-00513R000618020001-3"

Czechoslovakia / Organic Chemistry - Naturally occuring substances and their synthetic analogs E-3

Author : Sykora V., Herout V., Sorm F.
Title : On Terpenes. LXVI. Structure of β-Element.

Orig Pub : O terpenich. LXVI. Konstituce β-elemenu. Chem. listy, 1955, 49, No 6, 942-943 (Czech); Sb. chekhoslov. khim. rabot., 1956, 21, No 1, 267-268 (English; Russian summary)

Abstract : To determine the disposition of the double bonds of β-element (I) (RZhKhim, 1955, 9563) its ozonization was carried out, which yielded 3.2 mole formaldehyde, that indicates a location of all three double bonds of I outside the ring. On pyrolysis of 15.6 g elemol benzoate by distillation, in a current of CO_2, at 210-240°/100 mm, and chromatography on Al_2O_3, of the fraction of neutral substances boiling at 125-129°/21 mm, were obtained 3 g I, BP 128-129°/20 mm, $n^{20}D$ 1.4949, d^{24} 0.8803, α D -11.1°.

Communication LXV see RZhKhim, 1955, 43104.

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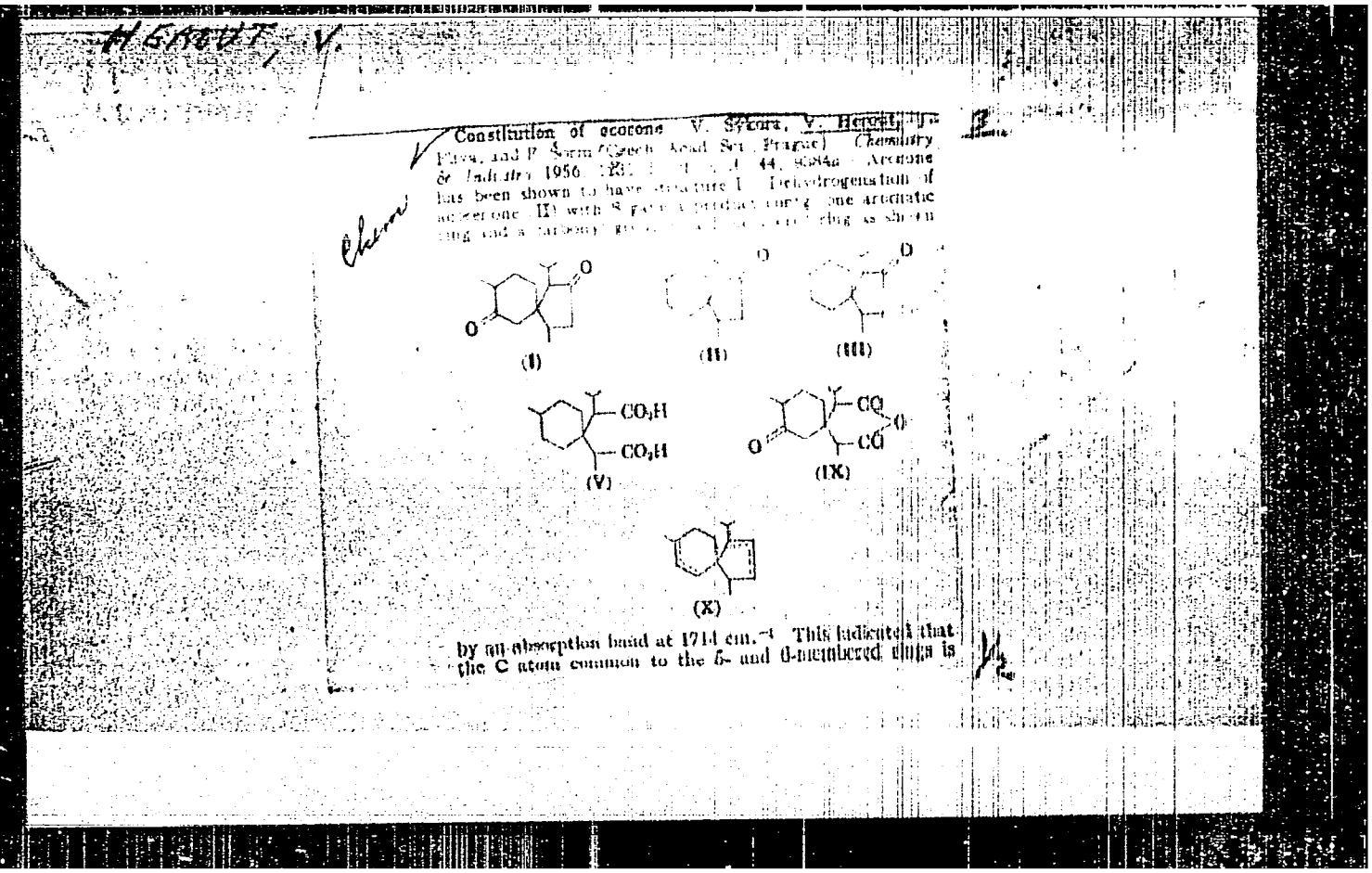

Constitution of ecotone. V. Sýkora, V. Herout, [illegible] (Chemistry Fac., and P. Sorm (Czech. Acad. Sci., Prague). *Chemistry & Industry* 1956 [illegible] 44, 9584a. Ecotone has been shown to have structure I. Dehydrogenation of ecotone (II) with S [illegible] one aromatic ring and a carbonyl [illegible] ring as shown

(I) (II) (III)

(V) (IX)

(X)

by an absorption band at 1714 cm.$^{-1}$. This indicated that the C atom common to the 5- and 6-membered rings is

SYKORA, V., HEROUT, J.P., SORM, F.

quaternary since aromatization did not take place without rearrangement. Acoruuone (III) was converted to a hydroxymethylene deriv. (IV) which on oxidation yielded V. Catalytic dehydrogenation of V gave a mixt. of p-MeC_6H_4Et (VI) and p-$MeC_6H_4CH_2CHMe_2$ (VII) together with $EtCO_2H$ and $Me_2CHCH_2CO_2H$. I and BzH gave a benzylidene deriv. (VIII) which on ozonolysis gave IX, m. 127.5°. Pyrolysis of the Ba salt of IX gave a mixt. of 2 α,β-unsatd. ketones which were converted in 4 steps to VI and VII. Dehydrogenation of isoacordiene (X) produced 1,7-dimethyl-4-isopropylnaphthalene. Acorone is the first naturally-occurring compd. shown to have a spirane skeleton.

K. H. Lopmeier

1/2

HEROUT, V.; ROMANUK, M.; SORM, F.

Terpenes. LXXI. Helenalin, a further lactone of the guaianolide group. p. 985. (chemicke Listy, Praha. Vol. 50, no. 6, June 1956.)

SO: Monthly List of East European Accession (EEAL) LC, Vol. 6, no. 7, July 1957. Uncl.

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

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26960.

Author : Šantavý, F., Herout, V.
Inst :
Title : Substances of Meadow Saffron and Their Derivatives. XLIV. Separation of Substances from Petroleum Ether Extract of Meadow Saffron (Colchicum Autumnale L.) Flowers.

Orig Pub: Chem. listy, 1956, 50, No. 4, 672 - 674; Sb. chekhosl. khim. rabot, 1956, 21, No. 6, 1659 - 1660.

Abstract: 60 to 70% of non-saponifying substances were obtained by treating the petroleum ether extract from meadow saffron flowers with alcohol solution of NaOH. The following was separated

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

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26960.

from them: 60% of paraffin (I) $C_{26}H_{56}$ or $C_{28}H_{58}$, 35% of a higher, optically inactive inactive alcohol (II) $C_{22}H_{46}O$ and a mixture of phytosterols containing sitosterol. 5 kg of meadow saffron flowers were extracted with 30 lit of petroleum ether. 84 g of oil was received after concentration by evaporation. 50 g of oil were saponified with 50 ml of 12%-ual alcohol solution of NaOH (20°, 7 days). The yield was 33 g of non-saponifying substances and 4.5 g of substances of acid nature. I, melting point 48 to 60°, boiling point 140°/0.004 mm, was washed out with petroleum ether by chromatographing non-saponifying substances on Al_2O_3 (activity of I). According to the infrared

Card 2/3

HEROUT, V.; JAROLIM, V.; PIVA, J.

"Terpenes. LXXII. Preparation of pure compounds of the α and β santalene series. In English."

p. 773 (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

HEROUT, V.

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

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

Author : Vlastimil Herout, Ladislav Dolejs, Frantisek 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, 34560), 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 Inst. Appl. Physics

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

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

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

CZECHOSLOVAKIA / Organic Chemistry. Natural Substances and Their Synthetic Analogues.

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

Author : Zdenek Cekan, Valstimil Herout, Frantisek Sorm
Inst : Not given
Title : Terpenes. LXXX. Structure of Matricine, Gaianolide from German Camomile.

Orig Pub : Chem. listy, 1957, 51, No 4, 756-763; Sb. chekhosl. khim. rabot, 1957, 22, No 6, 1921-1929.

Abstract : The authors proved that matricine (I) - a prochamazulenic substance from German camomile (Matricaria chamomilla L.) - seems to be 1-oxy-6-acetoxyguaiano-2,4(10)--diene-2,4(10)-olide-8,12. It was proved already in the foregoing reports that I contained an oxygroup, a -lactone, an acetoxyl group and two conjugate binary bonds (see RZhKhim, 1955, 16437, 35386). Two stereoisomeric hydrogenolysis pro-

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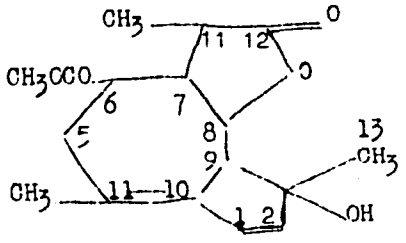
CZECHOSLOVAKIA / Organic Chemistry. Natural Substances and Their Synthetic analogues. G-3

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

ducts, 6-acetoxyguaienolides-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).



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

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

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

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

Author : Sykora Vladimir, Herout Vlastimil, Pliva Josef, Sorm Frantisek.

Inst :

Title : On Terpenes. LXXXII. Structure of Acorone

Orig Pub: Chem. listy, 51, No 9, 1704-1712.

Abstract: It has been shown (Sorm F., Herout V., Collection, 1948, 13, 177) that acorone (I) can be represented as 1-isopropyl-4,7-dimethylspiro -[4,5]-decandione-2,6. (I) is converted by means of monothioethylene-ketal into acoranone (II), containing according to UV-spectral evidence a keto-group in the 5-member ring

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APPROVED FOR RELEASE: 08/10/2001 CIA-RDP86-00513R000618020001-3

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 formyl-acoranone (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).

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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 monothioethyleneketal 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).

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

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)/

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

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

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

(9.2 g) in ether (boiling for 15 minutes) yields a product with m.p. 90-110° (yield 19.5 g), dehydration of which (30 g phthallic anhydride, 230-235°, 1 hour) leads to isoacordiene, b.p. 116-118°/12 mm (7.2 g). Dehydrogenation of this last product (6.7 g) with S (3.1 g) for 4 hours at 190-250° gives (XIX), yield 0.15 g, m.p. 59.5°; picrate, m.p. 86-87°. For Report LXXXXI, see RZhKhim, 1958, 57552.

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

Author : Holub Miroclav, Herout Vlastimil, Sorm Frantisek
Inst :
Title : On Terpenes, LXXXIII. The Structure of Laserpitine

Orig Pub: Chem. listy, 1957, 51, No 9, 1713-1724.

Abstract: For laserpitine (I), isolated from the roots of the Laserpitium latifolium L. plant, the structures 2,7-alpha-dimethyl-crotonate 3,5-dimethyl-8-isopropyldecalintetraol-2,3,7,8-ona-1 are suggested. From 6 g dihydroxylaserole (II) (see RJKhim, 1954, 44683) at 130-150°, distilled with 56% HI (60 ml), distilled in a vacuum at 115-130°/20 mm, chromatographed on Al_2O_3 in petroleum ether and percolated on silica gel (thence displaced by

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

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 $C_{17}H_{24}O_5$, 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 $C_{25}H_{36}O_6$ (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 $C_{25}H_{34}O_5$, 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

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CZECHOSLOVAKIA

MOTL, O; HOMANUK, M; HEROUT, V

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague (for all)

Prague, Collection of Czechoslovak Chemical Communications, No 5, May 1966, pp 2025-2033

"On terpenes. Part 178: Composition of the oil from Amorpha fruticosa L. fruits structure of (-)-γ-eserphene."

Dietz 4E2c(1) 2

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 (1652 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), $C_{30}H_{44}O_6$, 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*, $C_{30}H_{46}O_8$, 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 *1,2,4-trimethyl-7-ethylazulene* and with AcH gave *1,4-dimethyl-2,7-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. Ried

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COUNTRY : Hungary F
CATEGORY :

ABS. JOUR. : RZKhim., No. 21 1959, No. 74771

AUTHOR : Herout, V. and Kovacs, O.; Kovacs, O.
INST. : Not given
TITLE : Preparation Work with Small Quantities of Organic Reagents. I, II.

ORIG. PUB. : Magyar Kem Lapja, 13, No 3, 61-67 (1958)

ABSTRACT : The authors review and discuss in detail techniques and practices developed and perfected at the Chemical Institute of the Czech Academy of Sciences. The bibliography lists 62 titles.

I. Krishtofori

CARD: 1/1

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Country : CZECHOSLOVAKIA G
Category : Organic Chemistry. Natural Substances and Their Synthetic Analogs

Abs. Jour : Ref Zhur - Khim., No 5, 1959, No. 15497

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.

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Country : Czechoslovakia G-3

HERCUT, V.; [illegible], F.; EMANUL, M.

"Terpenes. XCIII. Composition of costus 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. 8, No. 7, July 1959, Unclas.

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

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-

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

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

Abstract: carbons (III). On hydrogenation of III there was obtained selinan (IV), identified by the infrared spectrum. Ozonization of I gives 1,10-dimethyl-decalol-1-one-7 (V) and acetone (identified as phonylsemicarbazone). The infrared spectrum revealed a CH_2-group in III; and in fact, on ozonization of III there was isolated 10-methyl-7-isopropyldecalone-1 (VI). Study of optical activity of I and of II-VI derivatives, as well as study of rotational dispersion curves of the derivatives V and VI, has shown that these substances are optically inactive racemates. 684.6 mg I are hydrogenated in glacial CH_3COOH over Pt (from PtO_2), to get II, yield 622 mg, MP 77.5°. Analogous hydrogenation of III gives IV, $n^{20}D$

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

CH_2COOH). 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_4^{20} 1.1090, [R/D [sic] 87.2 (calculated 86.9); saponification of the latter product gives

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

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

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.

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

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

Author : Ognyanov, I., Ivanov, D., Herout, V., Horak, M., Plíva, 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 (Geranium macrorhizum L.), previously designated germacrol, does not have the oxide structure (I) [see insert below], as

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

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, $n^{17}D$ 1.4840, d_4^{17} 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.

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

Abs Jour: Ref Zhur-Khim., No 11, 1959, 38776.

Author : Herout, V. and Suchy, M.
Inst :
Title : Chemistry of the Terpenes. LXXXIX. Direct Proof of the Carbon Skeleton of Germacrone.

Orig Pub: Chem Listy, 52, No 6, 1174-1179 (1958) (in Czech; Collection Czechoslov Chem Commun, 23, No 12, 2169-2174 (1958) (in English with a Russian summary)

Abstract: The ozonolysis of tetrahydrogermacrone (I) by the Kuhn and Rot method yields 1 mol of acetone and alpha-diketone (II), which on oxidation by CH_3CO_3H gives β, γ'-dimethylsebacic acid (III). The

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