

IR spectra of trans-alloocimene (a) and of cis-alloocimene (b).

Two fractional distillations of dry-distillation resin turpentine (column with 50 theoretical plates) yielded fractions containing trans-C₄-trans-C₆-alloocimene (a) and trans-C₄-cis-C₆-alloocimene (b).

The alloocimene fractions were purified by the preparative GLC method on a PAKhV-OZ chromatograph at 135° C (liquid phase, diethyleneglycol adipate).

The purest fractions of the alloocimene isomers had: a) n_D^{20} , 1.5339; d_4^{20} , 0.8298; UV spectrum: λ_{\max} (in isooctane) 270, 276, 248 m μ (log ϵ : 4.39, 4.49, 4.38) (for IR spectrum, see figure); b) n_D^{20} , 1.5255; d_4^{20} , 0.8503; UV spectrum: λ_{\max} (in isooctane) 265, 273, 285 m μ (log ϵ , 4.37, 4.48, 4.35) (for IR spectrum, see figure).

With maleic anhydride, both alloocimene isomers form the adduct with mp 81–83° C appropriate to this substance [2]. By the usual method [3], a dicarboxylic acid was obtained from the adduct with the characteristic mp of 170° C [2] (mixtures of the two products with the authentic pure substances gave no depression of the melting points). Subsequently we showed that gum and resin extraction and retort dry-distillation pine turpentines contained, respectively, 0.1 and 0.6% of a mixture of alloocimenes.

It is possible that alloocimenes are formed as a result of the isomerization of α -pinene during the production of turpentines under industrial conditions.

REFERENCES

1. I. I. Bardyshev, A. I. Skrigan, L. V. Roman, S. S. Kostyanova, ZhPKh, **34**, 2, 440, 1961.
2. J. J. Hopfield, S. A. Sall, and L. A. Goldblatt, J. Amer. Chem. Soc., **66**, 115, 1941.
3. M. Goryaev and I. Pliva, Methods of Investigating Essential Oils [in Russian], Alma-Ata, 1962.

15 January 1969

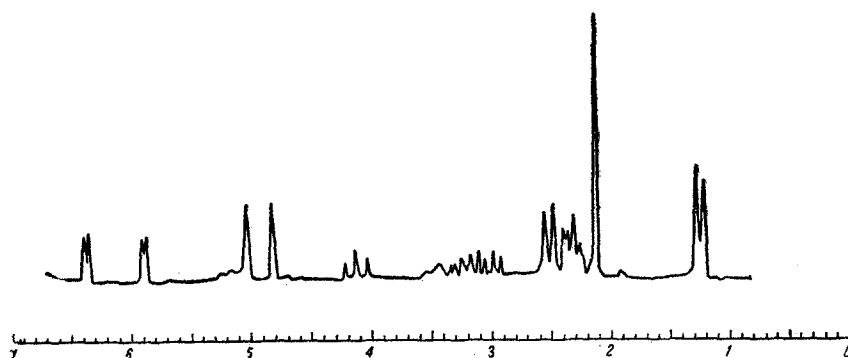
Institute of Physical Organic Chemistry, AS Belorussian SSR

UDC 547.314:633.88

ISOLATION OF GROSSHEMIN FROM CHARTOLEPIS INTERMEDIA

M. N. Mukhametzhano, V. I. Sheichenko, K. S. Rybalko, and K. I. Boryaev
 Khimiya Prirodnikh Soedinenii, Vol. 5, No. 3, pp. 184–186, 1969

From the leaves and flower heads of Chartolepis intermedia collected on August 7, 1968 in the Andreev region of the Kazakh SSR we have isolated by aqueous extraction [1] a colorless crystalline substance with the composition C₁₅H₁₈O₄, mp 200–202° C (from ethanol); $[\alpha]_D^{20} + 159.91^\circ$ (c 1.14; chloroform). IR spectrum: λ_{\max} 3480 (OH), 1740 (C=O), 1650 cm⁻¹ (C=C).



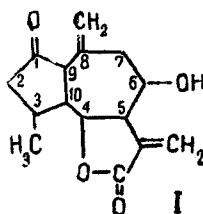
NMR spectrum of acetylgrosshemin in pyridine at a frequency of 100 MHz

The dehydrogenation of the substance over selenium at 280–350° C for 20 min yielded chamazulene [2], which was identified by thin-layer chromatography with a reference sample.

Our substance proved to be identical with grosshemin. However, the UV spectrum of the substance isolated had a maximum characteristic for the conjugation of the double bonds, which is absent from the published UV spectrum of grosshemin [3]. The UV spectrum of grosshemin, recorded again, also showed the presence in the latter of a maximum at 210 mμ, ε 11 000, which is typical for an exocyclic methylene group conjugated with a carbonyl group.

The structure that we proposed previously for grosshemin [3] had to be reconsidered, since in establishing the position of the two exocyclic methylene groups we used, as it has appeared, erroneous information on the absence of conjugated double bonds. Now, on the basis of the new information from the UV and NMR spectra, we propose for grosshemin the structure I.

The NMR spectrum of grosshemin has a doublet at 1.6 ppm ($J = 7$ Hz); the forms and positions of this signal in acetylgrosshemin (II) and tetrahydrogrosshemin (III) are almost the same—1.28 ppm ($J = 7$ Hz) and 1.20 ppm ($J = 7$ Hz), respectively. We ascribed this signal to a secondary methyl group present in the β -position with respect to the carbonyl group of cyclopentanone. The solitary peaks at 4.78 and 5.06 ppm in I and at 4.82 and 5.05 ppm in II are due to the exocyclic methylene at C_8 . In III, as was to be expected, instead of these signals there is a doublet at 0.89 ppm ($J = 7$ Hz) due to the CH_3 group at C_8 . Two quartets of one proton unit each at 6.39 and 6.48 ppm correspond to an exocyclic methylene in conjugation with a lactone carbonyl; in II these signals are found in the form of doublets at 5.80 and 6.38 ppm ($J = 3$ Hz). This chemical shift shows the immediate propinquity of the chemical changes that have taken place; in III the signals of the exocyclic methylene are absent and a new doublet has appeared at 1.68 ppm ($J = 7$ Hz). The lactone proton (at C_4) and the hemihydroxylic proton (at C_6) in I are superposed upon one another in the 3.8–4.8 ppm region; in the acetyl derivative the C_6 proton is shifted into the 5.19 ppm region (multiplet), and the lactone proton is represented by a triplet with its center at 4.0 ppm ($\Sigma JH_4 = 18$ Hz); in III, this proton is likewise represented by a triplet at 4.14 ppm. A keto group is present at C_1 , as is shown by the presence in the spectrum of grosshemin and also of acetylgrosshemin (II) of a doublet of one proton unit at 2.5 ppm ($J = 7.5$ Hz) in I and at 2.54 ppm ($J = 8$ Hz) in II. In a consideration of the signals, it was noted that signals in the form of a doublet can be expected only for a H_β proton in the α -positions of which there are a carbonyl and an exocyclic methylene group.



The assignment of all the signals mentioned agrees completely with literature data [4–6].

REFERENCES

1. K. S. Rybalko, A. N. Ban'kovskaya, and R. I. Evstratova, *Med. prom. SSSR*, no. 3, 13, 1962.
2. K. S. Rybalko, *Med. prom. SSSR*, no. 1, 26, 1958.
3. K. S. Rybalko and V. I. Sheichenko, *KhOKh*, 3, 580, 1965.

4. Werner Herz and P. S. Santhanam, J. Org. Chem., 30, no. 12, 1965.
5. F. Sanchez-Viesca and J. Romo, Tetrah., 19, no. 8, 1285, 1963.
6. A. Romo de Vivar, A. Cabrera, A. Ortega, and J. Romo, Tetrah., 23 (10), 3903-3907, 1967.

25 October 1968

All-Union Scientific-Research Institute for Medicinal Plants

UDC 547-314:633.88

SESQUITERPENE γ -LACTONES FROM ARTEMISIA JACUTICA

V. Benesheva, M. V. Nazarenko, and L. V. Sleptsova

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, p. 186, 1969

From a petroleum ether extract obtained from the epigeal part of *Artemisia jacutica* Drob. (*A. sieversiana* var. *septentionalis* Pamp.) (collected on August 15, 1967 in the village of Ytyk-Kol, Alekseev region of the Yakut ASSR), we have isolated two sesquiterpene γ -lactones. From a comparison of their spectra (IR, UV, NMR) with those of known compounds of this class and from the absence of the depression of the melting point of mixtures with authentic samples, we have identified one of them ($C_{15}H_{20}O_3$, mp 141-142° C) as the guaenolide arborescin (sieversinin) [1] and the other $C_{15}H_{20}O_3$, mp 169° C) as oxopelenolide "b", a sesquiterpene γ -lactone of the germacrane type [2].

REFERENCES

1. M. V. Nazarenko and L. I. Leont'eva, KhPS [Chemistry of Natural Compounds], 2, 399, 1966.
2. M. Suchy, Z. Samek, V. Herout, R. B. Bates, G. Snatzke, and F. Sorm, Coll. Czech. Chem. Comm., 32, no. 11, 3917, 1967.

14 January 1969

Komarov Botanical Institute, AS USSR

UDC 547-314:633.88

ISOLATION OF REPIN FROM CENTAUREA HYRCANICA

R. I. Evstratova, M. N. Mukhametzhano, V. I. Sheichenko, A. I. Shreter, and D. A. Pakaln

Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, p. 186, 1969

From the leaves and flower heads of *Centaurea hyrcanica* Bornm., family Compositae [1], collected on June 19, 1968, we have isolated by aqueous extraction [2] a colorless crystalline substance with the composition $C_{19}H_{22}O_7$, mp 155-156° C (from ethanol), $[\alpha]_D^{18} + 85.32^\circ$ (c 1.17; chloroform). Yield 0.1%. IR spectrum: 3480 (OH), 1770 (γ -lactone), 1745 (C=O), 1660 and 1640 cm^{-1} (C=C). The NMR spectrum has a pair of doublets with an intensity of one proton unit in the 5.58 and 6.23 ppm regions ($J = 3$ Hz), a pair of singlets also of one proton unit in the 5.00 and 5.21 ppm regions, a multiplet at 5.12 ppm (1H), a quartet at 4.65 ppm (1H), a broadened signal at 4.00 ppm (1H), and a singlet (3H) at 1.62 ppm.

By comparing the information obtained with literature data, we came to the conclusion that the substance obtained is identical with repin—a sesquiterpene lactone from *Acroptilon repens* (L.) D.C. [3]. On chromatography in a thin layer of neutral alumina (activity grade IV) in the benzene-methanol (9:1) and petroleum ether-benzene-chloroform-ethanol (5:4:2:1) systems with a 0.5% solution of $KMnO_4$ in 0.5% H_2SO_4 as revealing agent, the R_f values of repin and the substance isolated coincided. A mixture of the two substances gave no depression of the melting point.

REFERENCES

1. Flora of the USSR [in Russian], Moscow-Leningrad, vol. 28, p. 460, 1963.
2. K. S. Rybalko, A. N. Ban'kovskaya, and R. I. Evstratova, Med. prom., no. 3, 13, 1962.
3. R. I. Evstratova, R. Ya. Rzazade, and K. S. Rybalko, KhPS [Chemistry of Natural Compounds], 2, 290, 1966.

15 January 1969

All-Union Scientific-Research Institute for Medicinal Plants