ESSENTIAL OIL OF Artemisia lagocephala

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UDC 547:913.2

Samples of essential oil for analysis were obtained by steam distillation from the epigeal part of Artemisia lagocephalus (Bess.) DC. gathered in the flowering phase in the Far East on the Primorskie rocks in the environs of the village of Ayan (lowland sample) and on carbonate alluvia in a broad-leaved forest on a mountain massif in the Ayano-Maiskii region at a height of 900 m above sea level (highland sample). The time of collection was August.

The oil consisted of a light clear greenish-yellow liquid with a strong odor of camphor. The oil obtained from the highland sample of A. lagocephala partially crystallized on storage.

By the generally adopted procedure [1] acids and phenols and a terpene fraction were isolated from the essential oil. The acid and phenol fractions were analyzed by paper, thin-layer and column chromatographies [2, 3]. The following substances were identified: formic, acetic, butyric, isovaleric, caproic, and enanthic acids and the phenols p-cresol and creosol.

The analytical gas-liquid chromatography of the terpene fraction was conducted on a Chrom-5 instrument in glass capillar columns (25 m) with the phase XE-60. The temperature of analysis was 60-240°C, 5°C/min, and the carrier gas was helium. The components were identified by the method of additives and from their relative retention times. The amounts of the components were determined by the internal normalization procedure [4, 5]. The results are given in Table 1.

It must be mentioned that the highland sample of A. lagocephala was quite clearly characterized by the accumulation of the more oxidized components of the essential oil. This feature has also been observed for other Artemisia species [6].

Earlier, Belova [7] had detected ℓ-borneol, ℓ-camphane, and sesquiterpenes of the azulene series in the essential oil of A. lagocephala. In the essential oil of this species we have identified 35 components, 34 of them for the first time in this species of Artemisia.

TABLE 1. Percentage Contents of the Components in the Essential Oils of Highland and Lowland Samples of Artemisia lagocephala

Component	Sample		Component	Sample	
	highland	lowland		highland	lowland
Acids	0,71	1,07	Bornyl acetate,	1,76	7,22
Phenols	1,07	2,67	Artemisyl alcohol acetate	32,84	—
α-Pinene	—	5,68	α-Terpenyl acetate	—	0,69
Sabinene	—	0,32	Caryophyllene	—	1,95
β-Pinene	0,30	0,51	Germacrene-D	—	7,11
p-Cymen	2,82	2,40	β-Farnesene	3,87	—
Limonene	1,64	8,16	α-Humulene	1,60	—
trans-β-Ocimen	—	0,58	γ-Muurolene	—	0,73
Terpinolene	—	1,96	α-Cadinene	—	2,55
Artemisyl alcohol	0,39	—	Palustrol	64,03	15,25
Linalool	—	1,08	Ledol	2,05	—
Camphane	33,82	20,32	Caryophyllene oxide	—	1,59
Menthol	—	7,45	α-Cadinol	—	1,14
Terpineol-4	—	0,73	Ajanol	—	0,10
α-Terpineol	—	0,06			

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0009-3130/91/2703-0373$12.50

We are the first to have isolated plaustrol and ledol from the essential oil of A. lagocephala, which we achieved with the aid of gradient elution on silica gel (the eluents being mixtures of petroleum ether and diethyl ether); they were identified by PMR spectroscopy (the PMR spectra were obtained on a Varian HA 56/60 A instrument for CCl_4 solution, with HMDS as internal standard, its chemical shift being taken as 0.05 ppm).

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OXIDATION OF BETULIN, DIHYDROBETULIN, AND 3β-28-DIHYDROXY-18-LUPENE BY RUTHENIUM TETRAOXIDE

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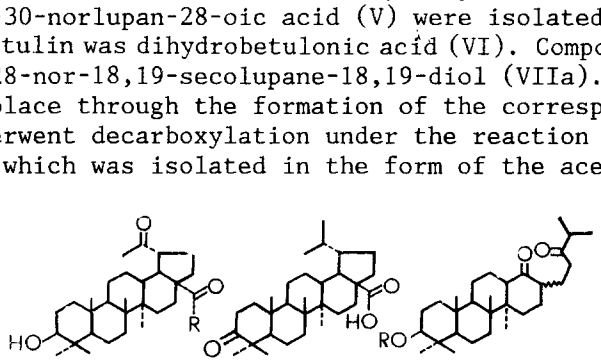
UDC 547.597:542.943:546.968-31-41+542.96

We have previously reported the successful conversion of 3β,28-dialkoxy-18-lupenes into the corresponding 18,19-secolupane-18,19-dione derivatives on their oxidation in a two-phase system of solvents, ethyl acetate–H_2O, with a catalytic amount of RuO_4, which was regenerated in situ from $RuO_2 \cdot xH_2O$ under the action of $NaIO_4$ [1].

Here we give the results of the analogous oxidation of diols: 3β,28-dihydroxy-20(29)-lupene (betulin) (I), 3β,28-dihydroxylupane (dihydrobetulin) (II), and 3β,28-dihydroxy-18-lupene (III).

After the oxidation of betulin (I), 5% of 3β-hydroxy-30-norlupane-20,28-diol (IV) and 60% of 3β-hydroxy-20-oxo-30-norlupan-28-oic acid (V) were isolated. The main product of the oxidation of dihydrobetulin was dihydrobetulonic acid (VI). Compound (III) [1, 2] gave as the main product 3β-hydroxy-28-nor-18,19-secolupane-18,19-diol (VIIa). In this case, as well, oxidation probably took place through the formation of the corresponding 28-oic acid, which, being a β-keto acid, underwent decarboxylation under the reaction conditions with the formation of compound (VIIa), which was isolated in the form of the acetate (VIIb).



IV. R=H; V. R=OH VI VIIa. R=H; VIIб. R=Ac

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Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 430-431, May-June, 1991. Original article submitted June 20, 1990.

0009-3130/91/2703-0374$12.50