ESTERS OF THREE SPECIES OF *Ferula*

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UDC 547.992:547.37

Continuing systematic investigations of plants of the genus *Ferula* L., which is widely represented in the flora of Central Asia [1], we give information on a study of the terpenoid composition of *F. lapidosa* Korov. and *F. tenuisecta* Korov. from two growth sites and of a new species – *F. helenae* U. Rahmankulov and S. Melibaev (Helen's giant fennel) which we have discovered on the rocky slpes of Balyklytau (Nura-Tau range, Uzbek SSR) [2, 3].

The sum of the terpenoid components obtained by ethanolic extraction of the roots of *F. helenae* were separated on a column of silica gel, giving two humulane esters – ferocin, $C_{22}H_{28}O_3$, mp 127-128°C, $[\alpha]_D$ −193° (c 1.0; ethanol) and ferocinin, $C_{23}H_{30}O_4$, mp 107-108°C, $[\alpha]_D$ −195° (c 1.0; ethanol) [4], which were identified by comparison with authentic samples on the basis of their physicochemical constants and spectral characteristics.

Esters of the camphane, germcrane, and carotane types have been found previously in the roots of *F. lapidosa*, collected in the Buam gorge, Susamyr valley, and in the Chigirik pass (Kirghiz SSR) [5-7]. The object of our investigations was the roots of the above-mentioned species gathered in the valleys of the rivers Koko-Meren and Ul'ken-Sai (Kirghiz SSR). In the first case, chromatography of an ethanolic extract gave four compounds, ferolin, $C_{22}H_{30}O_4$, mp 190-191°C, $[\alpha]_D$ −40.2 (c 1.0; ethanol), chimganidin, $C_{23}H_{32}O_5$, mp 140-141°C, $[\alpha]_D$ −97.1° (c 1.0; ethanol) (esters of the germacrane alcohol angrendiol) [8, 9], ferocin, and ferocinin, and in the second case only the last two compounds.

As reported, *F. tenuisecta* growing in the upper reaches of the R. Angren (Tashkent province) produce acyl derivatives of sesquiterpenes of the carotane and germacrane series [10].

From the phenolic fraction of an extract of the roots of this species gathered close to the village of Gushsai (Tashkent province) we isolated ferolin and chimganidin, and their epoxy derivatives – rubaferidin, $C_{22}H_{30}O_5$, mp 162-164°C, $[\alpha]_D$ −40° (c 1.0; chloroform) and rubaferinin, $C_{23}H_{32}O_6$, mp 105-106°C, $[\alpha]_D$ −36° (c 1.0; chloroform) [11].

By chromatography of the phenolic fraction of the extract of the roots of *F. tenuisecta* gathered in the village of Leont'evka (Chimkent province) we obtained 1-chimgin (camphane), $C_{17}H_{22}O_3$, mp 158-160°C, $[\alpha]_D$ −40.7° (c 1.0; chloroform), ferocin, and ferocinin.

This is the first time that derivatives of the humulane series – ferocin and ferocinin – have been detected in *F. lapidosa* and *F. tenuisecta*.

It must be mentioned that the accumulation of information on the chemical composition of giant fennels in dependence on the growth site and the vegetation period will not only show the chemotaxonomic characteristics of the species but will also enable the biogenetic links between the individual types of terpenoids to be elucidated.

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CONVERSION OF CARYOPHYLLENE α-OXIDE INTO 1R,10R-SELINA-4,6-DIEN-1-OL

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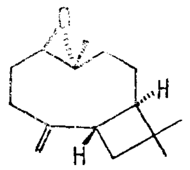
UDC 547.91

It is generally accepted that the immediate precursors in the biosynthesis of selinane compounds are sesquiterpenoids with the carbon skeleton of germacrene [1]. There is information on rearrangements of humulene [2] and of spirovetivane [3] into selinane compounds. At the same time, caryophyllene and the elinanes are not biogenetically connected with one another and all known rearrangements of caryophyllene lead to carbon skeletons differing from the bicyclic system of selinane [4]. In an investigation of the behavior of caryophyllene α-oxide (I) in superacids, we unexpectedly obtained a compound that was a derivative of δ-selinene — 1R,10R-selina-4,6-dien-1-ol (II).

When 1 g of the oxide (I) with $[\alpha]D^{20}$ −62.3° (c 2.67; $CHCl_3$) was dissolved in the acid system HSO_3F (2 ml)–SO_2FCl (16 ml) at −130°C and the solution was rapidly neutralized (CH_3OH–$(C_2H_5)_2O$, −125°C, then treatment with sodium carbonate followed by chromatography on SiO_2, the secondary alcohol (II) was isolated in a yield of 35% with mp 83-86°C (hexane) and $[\alpha]D^{20}$ +254! (c 3.41; $CHCl_3$). The alcohol (II) was unstable, and readily polymerized during crystallization. The p-nitrobenzoate of the alcohol (II) had mp 112-114°C (hexane). ^1H NMR spectrum of the alcohol (II) (200 MHz); $CDCl_3 + CCl_4$ (1:1); δ, ppm; internal standard $CHCl_3$, δ 7.24 ppm): 0.88 (3 H, singlet, $CH_3C<$); 1.05 (6 H, doublet, J = 7 Hz, $(C\underline{H}_3)_2CH-$); 1.66 (3 H, broadened singlet, $CH_3-\underset{|}{C}=C-$; 1.70-2.20 (8 H, superposed multiplets, $-C\underline{H}_2-$); 2.28 (1 H, septet, J = 7 Hz, $(CH_3)_2C\underline{H}-$); 3.43 (1 H, doublet of doublets, J = 11 Hz and 5.5 Hz, $>C\underline{H}OC$); 6.03 (1 H, broadened singlet, $-\underset{|}{C}=CH-\underset{|}{C}-\underset{|}{C}=C-$). ^{13}C NMR spectrum ($CDCl_3 + CCl_4$, 1:1; ppm from TMS; internal standard $CDCl_3$, δ 76.9 ppm): 142.8 s (C^7); 132.0 s (C^5); 124.7 s (C^4); 117.0 d (C^6); 76.0 s (C^1); 37.1 s (C^{10}); 35.4 d (C^{11}); 33.2 t (C^9); 31.8 t and 26.7 t (C^2 and C^3); 22.7 t (C^8); 21.7 q and 21.2 q (C^{12} and C^{13}); 18.1 q (C^{14}); 16.3 q (C^{15}).

The selinane carbon skeleton was confirmed by the dehydrogenation of the alcohol (II) in the presence of selenium to endesmane. The absolute configuration of C^{10} was deduced on the basis of a comparison of the specific rotations of the alcohol (II), of δ-selinene [3], and a number of selinane derivatives [3]. The equatorial nature of the hydroxy group followed from an analysis of the vicinal spin–spin coupling constants of the carbinol hydrogen atom (see [3]). The absolute configuration at C^1 was determined by the configuration of this center in the initial compound (I) [5].



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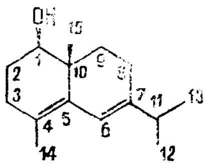

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Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 413-414,, May-June, 1985. Original article submitted January 17, 1985.

0009-3130/85/2103-0389$09.50