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With the aid of column chromatography, the following compounds have been isolated from the roots of *Ferula tschatcalensis* M. Pimen. and identified: juniferin, ferocinin, xeroferol, and fexerin, and also the new sesquiterpene ester chatferin,  $C_{20}H_{32}O_4$ ,  $[\alpha]_D^{20} +6.2^\circ$  (1.53; ethanol),  $n_D^{20}$  1.5136. On the basis of spectral characteristics and a transition to known substances, it has been established that chatferin has the structure of 2-tigloyl-7,8-epoxyjuniferol.

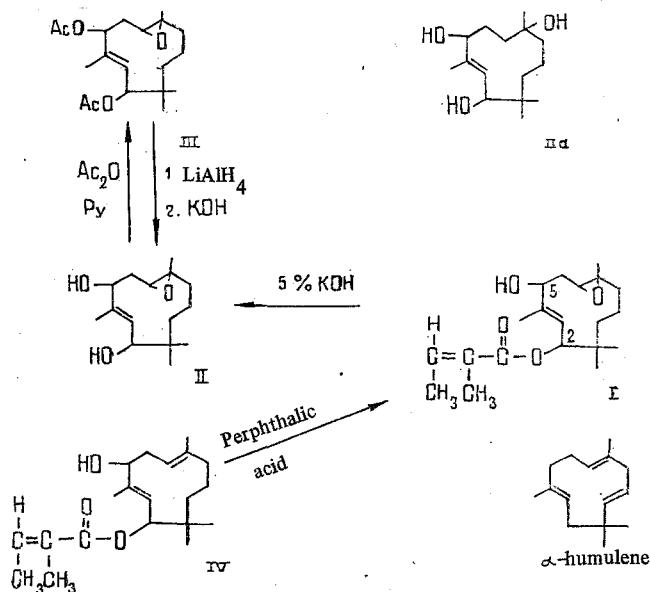
We have studied an ethanolic extract of the roots of the new species of giant fennel *Ferula tschatcalensis* M. Pimen.\* (Chatkalian giant fennel), which has not previously been subjected to chemical study. The plant was collected in the environs of Tashkumyr in the Kirghiz SSR in August, 1979, in the fruit-bearing period.

An ethanolic extract was separated into phenolic and neutral fractions and was chromatographed on a column of silica gel.

The phenolic fraction yielded juniferin [1] and ferocinin [2], which were identified by their physicochemical constants and the products of their hydrolysis. From the neutral fraction were isolated and identified xeroferol, obtained previously by the hydrolysis of the xeroferin [3], fexerin, which has been isolated from *F. xeromorpha* [4], and a new substance which we have called chatferin  $C_{20}H_{32}O_4$  (I).

Chatferin is a monoester of a sesquiterpene diol with an aliphatic acid, as is confirmed by IR and PMR spectra and hydrolysis products.

In its IR spectrum the strongest characteristic absorption bands are found at  $1720\text{ cm}^{-1}$  ( $C=O$  of an ester of an aliphatic acid),  $3400\text{--}3600\text{ cm}^{-1}$  (hydroxy group),  $1360$  and  $1380\text{ cm}^{-1}$  (gem-dimethyl group), and  $910$  and  $1255\text{ cm}^{-1}$  (1,2-oxide ring [5, 6])



\*The species affiliation of the plant was determined by M. G. Pimenov (Botanical Garden of Moscow State University).

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The PMR spectrum of chatferin consists of the signals of tertiary methyl groups — narrow signals at 0.88 and 0.95 ppm (3 H each) — of a methyl on a carbon atom bearing oxygen at 1.35 ppm (s, 3 H), and of two methyls at a double bond — 1.74 and 1.75 ppm (s, 3 H each). On the signal of the methyl group at 1.74 ppm is superposed the signal of the  $\beta$ -methyl group of an angeloyl or tigloyl residue split through coupling with the geminal proton ( $J = 7.5$  Hz) and through homoallyl interaction with the second methyl group ( $J = 1.5$  Hz). The value of the chemical shift of the signal of the vinyl proton (6.72 ppm) permits the choice to be made in favor of tiglic acid [7, 8]. At 2.5 ppm is observed the signal of an epoxide proton in the form of a quartet with  $J_1 = 10$  Hz,  $J_2 = 5$  Hz; at 4.83 ppm (q,  $J_1 = 10$ ,  $J_2 = 5$  Hz) is the signal of a hemihydroxylic proton. Two doublets — at 5.15 and 5.3 ppm with the same SSCC ( $J = 10$  Hz) — are due to olefinic and gem-acyl protons, respectively. The alkaline hydrolysis of chatferin yielded sesquiterpene alcohol identical with fexerol (II) [9] according to its IR and PMR spectra and a mixed melting point with an authentic sample.

In order to effect the transition from juniferol [1] to fexerol, we made an attempt to open the epoxide ring in the 7,8-epoxyjuniferol diacetate (III) with lithium tetrahydroaluminate, with the formation of a tertiary hydroxy group at C-8 [10]. But the spectral characteristics of the product obtained showed that no opening of the epoxide ring had taken place, but in the course of the reaction the acetyl groups [11] had been split off, and juniferol epoxide (II), identical with fexerol had been obtained (scheme). This confirms literature information that the 7,8-epoxy ring of the humulenes is the most stable, and in the epoxidation of  $\alpha$ -humulene this epoxide is formed as the main product [5, 12].

In the mass spectrum of juniferol epoxide (fexerol) there is the molecular peak  $M^+$  254, and also fragments with  $m/z$  236 ( $M - H_2O$ )<sup>+</sup>, 221 ( $M - H_2O - CH_3$ )<sup>+</sup>, and 218 ( $m - 2H_2O$ )<sup>+</sup>.

The acetylation of fexerol with acetic anhydride in pyridine gave the diacetate  $C_{19}H_{30}O_5$  (III),  $M^+$  338, identical, according to its composition, its IR and PMR spectra, and a mixed melting point, with the diacetate of juniferol epoxide [1], its IR spectrum lacking the absorption band of a hydroxy group. All these facts indicate that fexerol corresponds to the composition  $C_{15}H_{26}O_3$  and to the structure of juniferol 7,8-epoxide (II) in contrast to the formula (IIa) previously assumed [9]. The position of the acyl residue in chatferin was determined by a comparison of the PMR spectra of fexerol and chatferin, and also by the passage from fexerol (IV) to chatferin by its epoxidation with perphthalic acid (see scheme).

In the PMR spectrum of fexerol there are the signals of two gem-hydroxylic protons: at 4.23 ppm (d,  $J = 10$  Hz), and 4.50 ppm (q,  $J_1 = 12$ ,  $J_2 = 5$  Hz), and the signal of one olefinic proton at 5.34 ppm (d,  $J = 10$  Hz). In the PMR spectrum of chatferin there is a paramagnetic shift of the doublet signal relating to the proton at C-2, which interacts only with the neighboring olefinic proton at C-1, by 1.07 ppm.

Thus, chatferin is 2-tigloyl-7,8-epoxyjuniferol (I).

#### EXPERIMENTAL

Spectral analyses were carried out under the conditions described in [1], PMR spectra being recorded in  $CDCl_3$ .

The isolation and separation of the phenolic components were carried out by methods described previously [1, 2], giving juniferin  $C_{23}H_{32}O_5$ , mp 85–86°C,  $[\alpha]_D^{20} -1.6^\circ$  (c 5.8; ethanol); and ferocinin,  $C_{23}H_{30}O_4$ , mp 107–108°C,  $[\alpha]_D^{20} -196.7^\circ$  (c 1.0; ethanol).

Separation of the Neutral Substances. The sum of the neutral components (19.25 g) was chromatographed on a column of silica gel (Czechoslovakia, L 100/160) with the eluents hexane and hexane-ethyl acetate (with an increase in the concentration of the latter to 20%). This gave 2.5 g of fexerol,  $C_{20}H_{32}O_3$ ,  $[\alpha]_D^{20} -46.3^\circ$  (2.44; ethanol),  $n_D^{20} 1.5145$ ; 0.290 g of chatferin  $C_{20}H_{32}O_4$ ,  $[\alpha]_D^{20} +6.2^\circ$  (1.53; ethanol),  $n_D^{20} 1.5136$  and 0.2 g of xeroferol,  $C_{15}H_{26}O_2$ , mp 144–145°C,  $[\alpha]_D^{20} +13.0^\circ$  (0.54; ethanol).

The hydrolysis of chatferin was carried out with 5% aqueous ethanolic caustic soda by the usual method. The neutral fraction of the hydrolysate yielded  $C_{15}H_{26}O_3$  (II) with mp 141–142°C,  $[\alpha]_D^{20} +26.9^\circ$  (c 1.1; ethanol), and from the acid hydrolysate tiglic acid,  $C_5H_8O_2$ , mp 65–66°C,  $M^+$  100, was isolated.

The acetylation of fexerol was carried out in pyridine with acetic anhydride. This gave  $C_{19}H_{30}O_5$  (III),  $M^+$  338, mp 87–88°C.

Reaction with Lithium Tetrahydroaluminate. A solution of 1.6 g of (III) in absolute ether prepared at room temperature was added slowly to an ethereal solution of  $\text{LiAlH}_4$  (0.003 M) with stirring by a magnetic stirrer. The course of the reaction was monitored by TLC. After the end of the reaction and the decomposition of the excess of the reagent with ethyl acetate, the voluminous precipitate of aluminum and lithium hydroxides was separated on Buchner funnel and was washed with ether. The ethereal solution was dried with sodium sulfate, and the ether was distilled off. The residue (1.52 g) was chromatographed on a column of silica gel (L 100/160, Czechoslovakia) with elution by hexane-acetone (2:1). This gave 0.62 g of (III), 0.5 g of (II), and 0.4 g of intermediate fractions. The hydrolysis of (III) was carried out with 5% KOH by the usual method, giving fexerol (II).

The epoxidation of fexerin was carried out as described in [1] for 4 h. This gave chatferin,  $\text{C}_{20}\text{H}_{32}\text{O}_4$  (I),  $M^+$  336.

#### SUMMARY

The components of a new species of *Ferula* — Chatkalian giant fennel — has been studied for the first time. From the roots have been isolated and identified juniferin, ferocinin, xeroferol, fexerin, and the new sesquiterpene ester chatferin. It has been established that chatferin is 2-tigloyl-7,8-epoxyjuniferol.

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