Plants of the genus Ligularia (family Compositae) are widely distributed in Central Asia [1, 2]. We have investigated the roots of L. macrophylla D. C. Prodr. and L. thomsonii (Clark) Pojark [1, 2], collected in the Aksu-Dzhabaglinskii reserve, in the upper reaches of the Rivers Ugam and Ak-su, in the mountains of Karatau, and in the Kzylchi-sai gorge.

Substances were found which gave the lactone test, and the IR spectra of chloroform extracts showed an absorption band at 1780 cm⁻¹ which is characteristic for sesquiterpene lactones (these substances were absent from the epigeal part of the plant). TLC revealed seven substances, with Rf 0.98 (violet coloration), 0.95 (crimson), 0.85 (violet-blue), 0.76 (red), 0.65 (red), 0.48 (lilac), and 0.3 (blue). The qualitative compositions of these substances in different species were similar and differences were shown only in the ratio of the individual components.

When a concentrated ethanolic extract of the roots of L. macrophylla was treated with petroleum ether, a lactone was obtained with the compositions C₁₅H₁₅O₅, mp 136-137°C, [α]D²⁰ -50° (c 0.5; dioxane). IR spectrum, νmax, cm⁻¹: 1770 (carbonyl of a γ-lactone), 1640, 1570 (double bond).

NMR spectrum (in CDCl₃): singlets at 7.01 and 5.03 ppm, 1 H each (proton of a furan ring and lactone proton, respectively), 1.96 and 1.21 ppm (3 H each, methyl on a double bond and angular methyl, respectively), and a doublet at 2.56 ppm, J = 7.5 Hz, 2 H (methylene protons at C-9). Reduction of the lactone with NaBH₄ gave a known ether of a diol C₁₅H₂₀O₂ with mp 114-115°C [3]. On the basis of its physicochemical constants and IR and NMR spectra, this lactone was identified as furoeremophilan-14β,6α-olide isolated previously from L. hodgsonii Hook. [3], L. gaureri and L. angusta [4]. By chromatography, we isolated the same lactone from the roots of L. thomsonii collected in the Kzylchi-sai gorge. This is the first time that furoeremophilan-14β,6α-olide has been isolated from plants of the genus Ligularia growing in the Soviet Union.

By chromatography of an ethanolic extract of L. macrophylla we isolated two hydrocarbons with the compositions C₁₁H₁₈, M⁺ 150, and C₁₇H₂₆ M⁺ 240, and a crystalline substance with mp 136°C identified by a mixed melting point as β-sitosterol.

Elution with acidified methanol gave a second sesquiterpene lactone with the composition C₁₅H₂₁O₅, mp 191-192°C, which proved to be new and which we have called ligolide.

In its UV spectrum, maxima at 225 nm (log ε 4.38) and 265 nm (inflection) show the presence of three multiple bonds in the molecule. The IR spectrum (Fig. 1) shows adsorption bands at 3200-3500 (hydroxy group), 2860, 2930, and 2960 (C-methyl groups), a broadened band at 1730-1750 (carbonyl of an unsaturated five-membered lactone), and bands at 1700 and 1660 (double bond in a lactone ring). The substance was not saponified by alkali and did not react with 2,4-dinitrophenylhydrzone.

The mass spectra contained the peaks of the molecular ion, M⁺ 278, and fragments with m/e 260 [M⁺ - H₂O]⁺ and 246 [M⁺ - OCH₂]⁺, showing the presence of one hydroxy and one methoxy group, and also at 218 [M⁺ - OCH₂ - CO]⁺, 203 [M⁺ - OCH₂ - CO - CH₃]⁺, and 188 [M⁺ - OCH₂ - CO - 2CH₃]⁺, which are characteristic for eremophilanolides [8].
Fig. 1. IR spectrum of ligolide (in KBr).

The NMR spectrum (in deuteropyridine) of the lactone showed three-proton signals in the form of a singlet at 1.85 ppm (methyl on a double bond), a singlet at 0.8 ppm (angular methyl), and a doublet at 0.86 ppm (secondary methyl). The presence of these signals is characteristic for ligularenolide [5]. However, as compared with the latter, the absorption maximum in the UV spectrum of ligolide is further towards the shortwave region, which shows the presence of not four but three multiple bonds, i.e., the absence of a double bond at C_1-C_10. This is confirmed by the NMR spectrum, in which there is the signal of only one olefinic proton — a sharp singlet at 5.70 ppm. The fact that it is not split shows that there is no proton on the neighboring carbon atom (C_10), which is possible only if a hydroxy group is present in this position.

The h_{FR} spectrum also contains a three-proton singlet at 3.02 ppm and a broadened one-proton singlet at 4.15 ppm caused by a methoxy group and a methine proton in a CH_3OCH fragment, respectively. Since the latter signal is not split, it may be concluded that the adjacent carbon atoms are quaternary and, consequently, the methoxy group is located in position 6. This conclusion is in harmony with biogenetic considerations [6, 7]. The nature of the signal of the hemimethoxy proton and literature information [3] permit the assumption that the methoxyl at C_6 and the hydroxyl at C_10 each have the β orientation. Thus, ligolide most probably has the structure of 10β-hydroxy-6α-methoxyeremophilan-7-olide or 6-methoxy-10-hydroxyligularenolide, as shown in Fig. 1.

By a chromatographic method, the roots of _L. thomsonii_ yielded a lactone with mp 190°C which we have designated L2. Its IR spectrum contains bands at 1730-1760 cm^{-1} (carbonyl of an unsaturated lactone), 1440-1460 cm^{-1} (double bonds), 3400-3500 cm^{-1} (hydroxyl), and 2860, 2920, 2950, and 2980 cm^{-1} (C-methyl groups). A comparison of its IR spectrum with that of ligolide and a mixed melting point showed that they were different. In addition to the lactones mentioned we have established the presence of noncrystallizing lactones in both species the study of which is a matter of undoubted interest.

**EXPERIMENTAL**

The NMR spectra were taken on a "Jeol" instrument at 60 MHz, the IR spectra on a Hitachi spectrophotometer, and the mass spectra on an MKh-1303 instrument. TLC was performed on "Silufol" plates in the benzene-methanol-ethyl acetate (12:3:1) system. The spots were revealed by spraying the chromatograms with a 1% solution of vanillin in concentrated H_2SO_4.

_L. macrophylla._ Furoerenophilan-14β,6α-olide. The comminuted roots collected in the Karatau mountains in the flowering period (6.5 kg) were comminuted and extracted with ethanol (3 × 6 liters). The extracts were combined, the ethanol was distilled off, and the concentrated extract was diluted with water (1:3). The curd-like precipitate that deposited (197 g) was filtered off with suction, and 57 g of it was extracted with petroleum ether in a Soxhlet apparatus. Concentration of the extract yielded 30 g (1.62%) of a crystalline substance with mp 136-137°C (from petroleum ether) with the composition C_{15}H_{18}O_{3}, M^+ 246, R_f 0.76-0.8 (red coloration).

**Diol Ether.** To 0.5 g of the substance in 25 ml of ethanol was added 2.5 g of sodium tetrahydroborate, and the mixture was left for 12 days. Then the solvent was distilled off.