The base of the acetone fraction (49.3%) consisted of polymeric forms of the catechins and leucoanthocyanidins. A flavan, K-5, was also detected in this fraction.

From the ethereal fraction of the polyphenols of beech bark, by chromatography on type KSK silica gel, we isolated three flavans (K-1, K-2, and K-3) and four phenolic acids.

Flavan K-1 was a white crystalline substance with mp 173-174°C, $\lambda_{max}^{C_2H_5OH}$ 280 nm, $[\alpha]_D^{20}$ +17.0° [acetone–water (1:1)]. It contained 11.6% of ortho-hydroxy groups. From its physicochemical constants and the products of its transformations, the substance was characterized as (+)-catechin.

Flavan K-2 was identical with an authentic sample of (±)-gallocatechin in its melting point and spectral characteristics.

On the basis of a study of the products of acid hydrolysis and alkaline cleavage, and other properties, flavan K-3 was assigned to the dimeric flavans.

The phenolic acids isolated were identified from the results of a study of their physicochemical properties as protocatechuic, vanillic, syringic, and p-hydroxybenzoic acids.

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PYRETHRIN — A NEW GUAIANOLIDE FROM *Pyrethrum parthenifolium*. II.

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UDC 547.314+582.998

Continuing a study [1, 2] of the sesquiterpene lactones of *Pyrethrum parthenifolium* Willd., we have isolated a substance with mp 161-162°C (flavonoid), and a lactone with the composition $C_{15}H_{20}O_4$, mp 198-200°C. By direct comparison, this lactone has been identified as isoridentin [3].

To confirm the structure of pyrethin [1], we performed its de-epoxidation [4]. On eliminating the epoxy group from pyrethin we obtained a substance with mp 118-119°C identical in its physicochemical constants with 8-deoxycumambrin B [5]. Consequently, pyrethin is 10α-hydroxy-3,4-epoxyguai-11(13)-en-6,12-olide.

We investigated this plant from a different growth site (environs of Saivan, Turkmen SSR). By column chromatography, together with the known lactones (chrysartemin B, artecalin, and isoridentin), we isolated a new lactone with the composition $C_{18}H_{22}O_5$, mp 168°C, $[\alpha]_D^{20}$ +107° (c 0.06; CH_3OH), which we have called pyrethrin (I). The IR spectrum of (I) has absorption bands at (cm^{-1}) 1775 (γ-lactone carbonyl), 1740 (carbonyl group of a saturated ester), and 1670 and 1645 (double bond). In the mass spectrum are the peaks of ion with m/z 318 (M^+), 262 $(M - CH_2CH_2CO-)^+$, 244 $(M - CH_3CH_2COOH)^+$. In the PMR spectrum of (I) (deuteropyridine; 0 — HMDS) in the strong-field region the following signals are observed: triplet (^3J about 10 Hz) at 1.02 ppm (3 H) from the methyl group of propionic acid and a singlet at 1.53 ppm (3 H) from a methyl group at an epoxide ring. In the 3.18 ppm region there is a broadened singlet (1 H) from an epoxide proton. The signal of a lactone proton appears at 4.10 ppm in the form of a quartet (^3J = 10, 9 Hz), which unambiguously shows the position of the lactone ring at C_6—C_7 and the trans linkage of it with the guaiane skeleton.

The presence of a guaiane nucleus in this compound was confirmed by the formation of chamazulene, identified by TLC with a marker. Two one-proton broadened singlets are located at 4.71 and 4.90 ppm and have been assigned to the protons of an exomethylene group in a sev-

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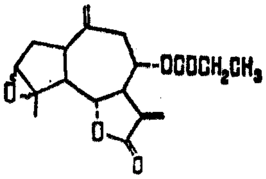
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 532-533, July-August, 1983. Original article submitted February 25, 1983.

en-membered ring. In the weak fields there are doublets of one proton each at 5.49 and 6.07 ppm with $^4J = 3$ Hz each, the protons of an exomethylene group at a lactone ring. A multiplet signal (5.07 ppm, $\Sigma J = 24$ Hz) of a hemiacyl proton presupposes interaction with several vicinal protons, which permits the C-8 position to be assigned to the proprionic acid residue.

It follows from the facts given that pyrethrin is a guaianolide and has the following structure:



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FEROLIDE — A NEW LACTONE FROM *Ferula penninervis*

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UDC 547.314

On separating a chloroformic extract of *Ferula penninervis* Rgl. et Schmalh., together with the grilactone and the coumarin aurapten isolated previously [1], by chromatography on silica gel [hexane—ethyl acetate (3:1)] we isolated a new lactone, which we have called ferolide (I).

Ferolide has the composition $C_{22}H_{26}O_7$, M^+ 402; mp 178-179°C (decomp), $[\alpha]_D^{20}$ −10.3° (c 0.55; chloroform). UV spectrum: λ_{max} 255 nm (log ε 4.33). IR spectrum, ν_{max}^{KBr} cm^{-1}: 1800 (C=O of a γ-lactone with an ester grouping in the α position to the lactone carbonyl); 1745 ($OCOCH_3$); 1710 (OCO—HC=C), 1690 (—C=C—CO—C=C—) 1640 and 1620 (C=C).

The following resonance signals have been observed in the PMR spectrum of ferolide ($CDCl_3$): H-3 (br.s, 6.05 ppm); H-6 (q, 4.55 ppm, $J_{6,7} = 10$ Hz, $J_{6,5} = 11.0$ Hz); and H-8 (sx, 5.52 ppm $J_{8,9} = 2.0$ Hz, $J_{8,9'} = J_{8,7} = 11$ Hz).

A broadened singlet (6 H) at 2.16 ppm and a singlet (1 H) at 6.05 ppm in association with the results of UV and IR spectroscopy show the presence of a guaiadiene grouping in the molecule.

The fact that ferolide is a guaianolide was confirmed by the production of chamazulene on dehydrogenation with selenium. On the sextet at 5.52 ppm is superposed the singlet of a H-17 olefinic proton. The singlet nature of the olefinic proton together with the singlets of vinylmethyl groups at 2.16 ppm (3 H) and 2.04 ppm (3 H) indicates that one of the acid residues in the ferolide molecule is that of senecioic acid, as was shown by the saponification of ferolide at room temperature with 5% ethanolic caustic soda and the isolation of the acid.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, p. 533, July-August, 1983. Original article submitted February 25, 1983.