

With the given composition, the presence of one tertiary OH group and the corresponding values of the mechanical shifts of the quaternary methyl groups, position C₁₁ is the most likely for the hydroxy group. The use of Eu(DPM)₃ confirmed this assumption, since with only a small change in the signals of the tertiary methyl groups at C₁ and C₄ (0.93, 0.98 ppm), a pronounced downfield shift of the singlets of the equivalent quaternary methyl groups to 1.42 and 1.43 ppm was observed. In its turn, a strong peak with m/e 59 (60.2%) was observed in the mass spectrum of shairol, confirming the presence of a CH₃-C(OH)-CH₃ fragment in its molecule.

The absence of signals from olefinic protons unambiguously established the tetrasubstituted nature of the double bond, which could be only in the C₉-C₁₀ position, as is explained by the nature and size of the chemical shifts of the methyl groups at C₁ and C₄. However, such a position corresponds to the structure of guaiol, isolated previously from several tropical species of plants [2, 3]. On the basis of a comparison of the PMR and IR spectra, GLC, TLC, and a mixed melting point with an authentic sample (from the firm IFF), the compound shairol was shown to be identical with guaiol. Thus, the compound described previously under the name of shairol must be regarded as guaiol, and *F. ferulaeoides* as a source for its isolation (yield 0.5% on the weight of the dry raw material).

This is the first time that guaiol has been isolated from plants of the domestic flora.

In addition to guaiol we isolated β -sitosterol and hydroxyaromatic acids not previously found in plants with the compositions C₂₇H₄₆O₄ (M⁺ 154), mp 208°C, and C₈H₈O₄ (M⁺ 168), mp 188°C, which were identified on the basis of physicochemical characteristics, methylation, and independent synthesis as β -resorcylic and methoxyresorcylic acids.

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CHRYSA RTEMIN B - A SESQUITERPENE LACTONE FROM *Handelia trichophylla*

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UDC 547.314

We have previously reported the isolation from the inflorescences of *Handelia trichophylla* Heimerl., together with other sesquiterpene lactones, of a compound with mp 245°C (decomp.) from a mixture of acetone and ether [1]. The substance has the composition C₁₅H₁₈O₅ (I), mol. wt. 278 (mass spectrometry, elementary analysis), $[\alpha]_D^{20} + 20.3^\circ$ (c 0.7; chloroform). IR spectrum: $\nu_{\text{max}}^{\text{KBr}}$ 3440 (OH), 1745 (carbonyl of a γ -lactone conjugated with an exo-methylene group), 1665⁻¹ (C = C).

The hydroxy group of (I) is not acetylated by acetic anhydride under the usual conditions, which shows its tertiary nature. The two remaining oxygen atoms form epoxide groups. The signals of the protons attached to the carbon atoms of the epoxide ring in the PMR spectrum of (I) (JNM 4H-100, DMSO-d₆, 0 - HMDS) appeared in the form of doublets at 3.35 and 3.58 ppm (³J = 1 Hz). Methyls on carbon atoms with hydroxy and secondary epoxide groups are represented by two singlets at 0.89 and 1.36 ppm, and the signals of the protons of an exo-methylene group by doublets with centers at 5.54 and 5.98 ppm (⁴J = 3 Hz). A triplet with its center at 3.86 ppm (³J = 10.5 Hz) represents the signal of a proton present in the geminal position to the oxygen of a lactone ring,

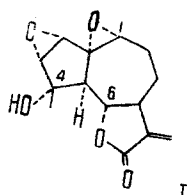
Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnkh Soedinenii, No. 5, pp. 667-668, September-October, 1976. Original article submitted May 12, 1976.

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and the vicinal protons interacting with it are represented by a doublet ($^3J = 10.5$ Hz) and by a multiplet with their respective centers at 2.77 and 3.20 ppm.

The characteristics given are similar to those of the sesquiterpene lactone chrysartemesin B from *Chrysanthemum parthenium* [2] and only the melting points show some difference. But the melting point (225°C, from ethanol) and IR spectrum of the dihydro derivative with the composition $C_{15}H_{20}O_5$ obtained by the reduction of (I) with 5% Pd/C in ethanol are similar to those for dihydrochrysartemin B, which confirms the identity of (I) with chrysartemin B.

The orientation of the substituents at C-4 in the latter remained undetermined. To answer this question we used measurements of the intramolecular nuclear Overhauser effect. Additional irradiation with a strong radio frequency field of the resonance frequency of the protons of the methyl group geminal to a hydroxy group (0.89 ppm) led to an increase in the intensity of the doublet at 3.58 ppm by 30%, which shows that it is due to the proton at C₃. Under these conditions the intensity of the doublet at 2.77 ppm remained unchanged. These facts enable the assignment of the signals of the protons of the epoxy ring at C-2 and C-3 to be refined and show that the proton at C-3 and the methyl group at C-4 both have the β orientation, as shown in structure (I):



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ISOLATION OF DIOSGENIN FROM *Solanum laciniatum*

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UDC 547.944.3

Diosgenin (I) is one of the most important starting materials for the synthesis of cortisone and its analogs [1]. It is usually found in the form of glycosides of steroid sapogenins of plants of the genus *Dioscorea* [2].

We have investigated the xylene mother solution after the extraction of solasodine from *Solanum laciniatum* Ait. By thin-layer chromatographic analysis we found in the mother liquor, apart from diosgenin, traces of solasodine and solasodiene. To isolate the diosgenin, the xylene was distilled off with steam from 5 liters of the mother solution, the residue was washed in benzene, and the solution was washed successively with 3% NaOH solution and 5% H_2SO_4 solution, and then with water to neutrality. The solvent was evaporated off and the dry residue (10.6 g) was purified by chromatography on alumina (activity grade (III)) with elution with benzene. The yield of diosgenin was 8.2 g (77.3% on the dry residue), mp 206-208°C (from ethanol), $[\alpha]_D^{20} -121.5^\circ$, ν_{max}^{KBr} 3440 cm^{-1} (OH).

The presence of a 3-hydroxy group and a double bond at C₅-C₆ in the diosgenin molecule was established by its Oppenauer oxidation [3].

Institute of Chemical Sciences, Academy of Sciences of the Kazakh SSR, Alma-Ata. Translated from *Khimiya Prirodnikh Soedinenii*, No. 5, pp. 668-669, September-October, 1976. Original article submitted April 5, 1976.

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