was treated with a solution of 0.3 g of chromium trioxide in 8 ml of pyridine, and the mixture was left at room temperature for a week. Then it was poured into 200 ml of cooled 15% sulfuric acid and was treated with hexane—ether (2:1; 3 × 70 ml). The residue obtained after washing and the distillation of the solvent was chromatographed on a column of silica gel (2 × 20 cm). The column was washed with the benzene—hexane (1:1) system. Fractions 4-6 were combined and evaporated in vacuum to give 0.05 g of the ketone (VI), R_f 0.73 (revealed with 2,4-dinitrophenylhydrazine).

Oxidation of Fecerol. Compound (III) (0.5 g) was oxidized with chromium trioxide (0.5 g) in 15 ml of pyridine with stirring for 6 h. The reaction mixture was treated in the manner described above. The residue after the distillation of the solvent was chromatographed on a column of silica gel treated with 5% $AgNO_3$ solution (2 × 15 cm). Elution was performed with benzene. Fractions 3-10 were combined and evaporated in vacuum, and the residue was crystallized from hexane giving 0.15 g of the ketone (VI) with mp 76-77°C, R_f 0.7.

SUMMARY

Ferocin and ferocinin — esters of the new sesquiterpene alcohol fecerol with p-hydroxybenzoic and vanillic acids, respectively — have been isolated from the roots of *Ferula ceratophylla*.

On the basis of spectral characteristics and chemical transformations, the structure of 1,1,8-trimethylcycloundeca-2,4(14),7-trien-10-ol is proposed for fecerol.

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A NEW LACTONE, ISORIDENTIN, FROM *Achillea biebersteinii*

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Sesquiterpene lactones (I), (II), and (III), isolated from *Achillea biebersteinii*, have been identified by spectral characteristics and chemical transformations as rupicolins A and B and artecalin, respectively [1, 2].

A fourth lactone with the composition $C_{15}H_{20}O_4$, mp 197-199°C, $[\alpha]_D^{22}$ + 181° (c 0.46; methanol) has proved to be new and has been called isoridentin (IV). It is soluble in ethyl acetate and ethanol.

The PMR spectrum of isoridentin taken in deuteropyridine showed the following characteristic signals: singlet at 1.83 ppm (H_3C-C=C-); triplet at 4.42 ppm (^3J 9.8 Hz each — lactone proton); singlets at 4.80 and 5.21 ppm (H_2C=C-); doublets at 5.29 and 6.12 ppm (exomethylene group conjugated with a lactone carbonyl); multiplets with broadened lines at 4.19 and 4.4 ppm (protons located geminally with respect to hydroxy groups); and doublets at 6.19 and 6.60 ppm (protons of hydroxy groups). Consequently, there are three double bonds in (IV). The elementary composition given and the results of a study of the PMR spectrum of the lactone show that it belongs to the sesquiterpene lactones of the germacrane series.

The presence in the isoridentin molecule of two secondary hydroxy groups was also shown by the preparation of a diacetyl derivative (V), the IR spectrum of which had the characteristic bands of the vibrations of an ester group at 1740 and 1240 cm^{-1}.

The hydrogenation of (IV) with $NaBH_4$ gave dihydroisoridentin (VI), $C_{15}H_{22}O_4$, mp 187-

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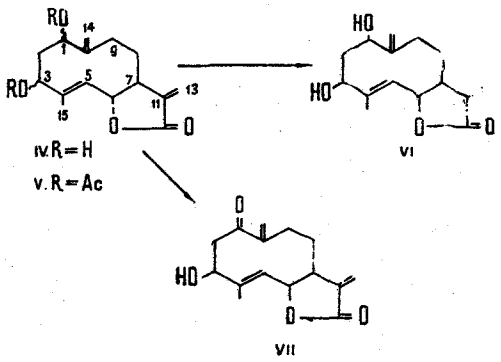
189°C, mol. wt. 266 (mass spectrometry). From the products of the hydrogenation of the lactone in the presence of PtO_2 we isolated a tetrahydro derivative, $C_{15}H_{24}O_4$, mp 228-230°C, mol. wt. 268 (mass spectrometry). Selective oxidation of isoridentin led to a keto compound (VII) the IR spectrum of which showed an absorption band at 1650 cm^{-1} (C=O conjugated with a double bond).

On comparing the PMR spectra of diacetylisoridentin and of the lactone itself it was found that the signal of the protons of the methyl group in the latter appears in the weaker field by 0.29 ppm. This fact shows that the methyl group and one of the hydroxy groups are present on adjacent carbon atoms.

Analysis of the PMR spectra of (V) taken with the addition of the paramagnetic shift reagent $Eu(FOD)_3$ showed that both the groups of protons geminal to hydroxy groups interact vicinally with the protons of the same methylene group. Consequently, the OH groups are present on the C-1 and C-3 atoms and the lactone ring is trans-linked to the germacrane skeleton at C-6 and C-7.

Thus, isoridentin is a stereoisomer of ridentin [3] and has the structure (IV).



EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument (KBr tablets), the mass spectra on an MKh-1303 instrument, and the PMR spectra on a JNM-4H-100 spectrometer in $CDCl_3$ and deuteropyridine solutions, 0 — HMDS.

Diacetylisoridentin (V). A solution of 70 mg of the lactone in 1 ml of pyridine was treated with 1.5 ml of acetic anhydride. After 2 h, the spot of the initial lactone had disappeared. The solvent was evaporated off and then chromatography on silica gel (KSK, 200 mμ) yielded 40 mg of crystals with mp 136-138°C (hexane—benzene) and the composition $C_{19}H_{24}O_6$ (II).

Oxidation of Isoridentin (VII). A cooled solution of CrO_3 in pyridine was added to 100 mg of the lactone in pyridine. The mixture was kept at —6°C for 3 h and was then evaporated in vacuum, after which water was added to the residue and it was shaken with chloroform. The chloroform extract was washed with water, the solvent was distilled off, and the residue was chromatographed on silica gel with elution by benzene and then by benzene—ether (10:1). This gave 40 mg of the hydroxy compound (VII) with the composition $C_{15}H_{18}O_4$, mp 155-157°C (hexane—ethyl acetate), $[\alpha]_D^{22}$ + 130.4° (c 0.46; MeOH).

Dihydroisoridentin (VI). A solution of 150 mg of the lactone in ethanol was treated with 200 mg of $NaBH_4$. The reaction took place slowly, and methanol was added dropwise to accelerate it. The reaction was followed by TLC on silica gel in the chloroform—methanol (30:1) system with a 0.5% solution of vanillin in concentrated H_2SO_4 as the chromogenic agent. The excess of $NaBH_4$ was decomposed with water. The mixture was neutralized with 10% CH_3COOH, and the reaction product was extracted with chloroform. This yielded crystals with the composition $C_{15}H_{22}O_4$, mp 187-188°C (ethanol), M^+ 266.

Tetrahydroisoridentin. A solution of 100 mg of isoridentin in 5 ml of glacial acetic acid was treated with 10 mg of PtO_2 and hydrogenated for 2.5 h. From the reaction products

by chromatography on silica gel with hexane—acetone (7:3) were isolated crystals with the composition $C_{15}H_{24}O_4$, mp 228-230°C (ethanol), 20 mg, M^+ 268.

SUMMARY

1. A new lactone, isoridentin, with the composition $C_{15}H_{20}O_4$, has been isolated from the epigeal part of *Achillea biebersteinii*.

2. On the basis of chemical and spectral information it has been established that isoridentin has the structure of 1,3-dihydroxygermacra-4,10(14),11(13)-trien-6,12-olide.

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UV-SPECTROPHOTOMETRIC DETERMINATION OF GLYCYRRHIZIC ACID IN *Glycyrrhiza glabra*

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The analysis of glycyrrhizic acid in licorice has been discussed in the literature [1-5]. The methods proposed by the authors of these papers are based on the gravimetric, titrimetric, or photocolorimetric determination of glycyrrhetic acid (genin), isolated in the hydrolysis of glycyrrhizic acid [1, 4-8]. These methods are associated with considerable expenditure of time, laboriousness, and nonspecificity, since accompanying substances are analyzed in addition to the glycyrrhizic acid. The authors of these methods are faced with the necessity of choosing the optimum conditions and for checking the completeness of hydrolysis.

Gravimetric methods in which the determination is effected from the weight of the crude glycyrrhizic acid have also found practical use (State Pharmacopoeia of the USSR, Tenth ed., 1968; Pharmacopoeia of the German Democratic Republic, Seventh ed., 1970) [1-3].

Recently, chromatographic methods of determining glycyrrhizic acid with the aid of chromatography in a thin layer of sorbent (TLC) have been developed which permit this acid to be analyzed without the accompanying components [9, 10].

We have developed a method for analyzing glycyrrhizic acid in roots and in the thick extract and dry licorice powder produced industrially. The proposed method is based on the chromatographic separation of glycyrrhizic acid from the accompanying substances followed by its spectrophotometric determination. For comparison, a thick licorice extract and a dry licorice powder were analyzed gravimetrically and by the methods developed (Tables 1 and 2).

As can be seen from Tables 1-2, the results obtained by the gravimetric method are high. A qualitative chromatogram in the system of solvents given below of the crude glycyrrhizic acid obtained by the gravimetric method showed the presence of four unidentified substances in addition to glycyrrhizic and glycyrrhetic acids. The R_f value of glycyrrhizic acid is 0.33 and those of the closest unknown substances 0.23 and 0.45.

The chromatographic separation of the glycyrrhizic acid from the accompanying substances was effected in a fixed layer of silica gel in the chloroform—methanol—water (80:35:7) solvent system with a 1% solution of vanillin in sulfuric acid as the chromogenic agent; the sensitivity of the chromatographic method is 5 μg.

The UV spectrum of ammonium glycyrrhizate has one intense band with λ_{max} 252 nm (log ε 4.04, $E^{1\%}_{1cm}$ = 130 ± 3.84). The intensity of this extremum enables it to be used as the analytical band. The absorption of solutions of the acid in the region of working concentrations (D = 0.1-0.6) obeys Beer's law.

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