and the product was extracted with methylene chloride. The residue after the elimination of the solvent in vacuum was recrystallized from ethanol. This gave a substance with mp 202-203°C identical with leucomisin (IV).

SUMMARY

1. A new guaianolide ($C_{15}H_{18}O_4$, mp 201-202°C), which had been called santachin, has been isolated from a chloroform extract of the epigeal part of *Achillea santolina* L.

2. On the basis of spectral characteristics and chemical reactions, the structure of 2-keto-1,10-epox(5,7,11-αH-6-βH)-guai-3,4-en-6,12-olide has been proposed for santachin.

LITERATURE CITED

1. A. Mallabaev, U. Rakhmankulov, and G. P. Sidyakin, Khim. Prirodn. Soedin., 530 (1978).
2. W. Cole and P. L. Julian, J. Org. Chem., 19, No. 2, 131 (1954).

STRUCTURE OF UGAFERIN AND SOME PROPERTIES OF UGAMDIOL DERIVATIVES

A. I. Saidkhodzhaev and V. M. Malikov

UDC 547.992:547.37

Continuing a study of the chemical composition of plants of the genus *Ferula*, from the roots of *Ferula ugamica* Eug. Kor, collected in the upper reaches of the river Angren in the Tashkent oblast we have isolated a new ester with the composition $C_{25}H_{36}O_7$ (M^+ 448) which we have called ugaferin (I).

The UV spectrum of (I) has a maximum at 270 nm (log ε 4.06) due to an aromatic nucleus, and the IR spectrum has absorption bands at 3400-3600 cm^{-1} (hydroxy group), 1735, 1250 cm^{-1} (ester carbonyl group), and 1615, 1560, 1520 cm^{-1} (aromatic nucleus).

When ugaferin was subjected to alkaline hydrolysis with 5% aqueous methanolic caustic potash, the neutral fraction of the hydrolysate yielded a sesquiterpene alcohol with the composition $C_{15}H_{26}O_3$ (II), mp 88-89°C, and the acidic fraction yielded an aromatic acid with the composition $C_{10}H_{12}O_5$, mp 168-169°C (III), which was identified as 3,4,5-trimethoxybenzoic acid [1]. A comparison of the physicochemical constants and spectral characteristics of the alcohol (II), the formation of a mono- and diacetate of (II) and of a mono- and diketone derivative of (II), and also the results of a study of the cyclization product of the monoacetate of (II) showed that (II) was identical with ugamdiol, isolated previously in free form from *F. ugamica* [2, 3]. The same alcohol, under the name of shiromodiol in the form of mono- and diacetates has been isolated from *Parabenzoin trilobum* [4, 5].

Thus, the proof of the structure of ugaferin reduced to determining the position of the acid residue in the ugamdiol molecule. The latter contains two secondary hydroxy groups which differ in the CS values and multiplicities of the hemihydroxylic protons in the PMR spectrum. A comparison of the PMR spectra of guamdiol and ugaferin showed that in the latter there was a downfield shift by 1.11 ppm of the signal from C_8—H in the form of a quartet. Consequently, the trimethoxybenzoic acid residue is present at C_8 and ugaferin has the structure of 8-trimethoxybenzoylugamdiol (I).

Mixed esters of ugamdiol with aliphatic and aromatic acids have been isolated from several species of *Ferula* [6, 7]. In a study of the structure of the mixed diesters of ugamdiol the main difficulty is determining the mutual positions of the acyl residues, since in this case the PMR-spectroscopic method does not always permit an unambiguous conclusion to be drawn. In view of this, we directed our attention to the fact that when the diesters of (I) are hydrolyzed with potassium carbonate in methanol at room temperature some sequence of saponification of the acid residues is observed. Thus, when the diacetate (III) and the dibenzoate (IV) of (II) are saponified under the above-mentioned conditions, the acyl residue at C_8 is split out predominantly, and the ester group at C_6 is not affected. On the other hand, the acetylation and benzoylation of ugamdiol at room temperature form, respec-

---

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 721-724, November-December, 1978. Original article submitted June 29, 1978.

0009-3130/78/1406-0614$07.50

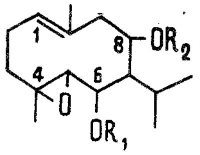
tively, the monoacetate (IX) and the monobenzoate (X) of ugamdiol at the C_6—OH group. Such differences in the reactivities of ugamdiol derivatives are probably due to the steric position of the hydroxy groups and different electron densities on the C_6 and C_8 atoms.

To confirm the sequence of hydrolysis, we have performed the saponification of the mixed diesters of ugamdiol (VI), VII, and XII). It was found that in all cases the above-mentioned sequence of splitting out of the acyl residues is observed, the nature and molecular weight of the acyl residue having no effect.

The observed differences in the sequence of hydrolysis of ester groups at C_6 and C_8 makes it possible to determine the positions of the acid residues of natural diesters of ugamdiol.

In a study of the properties of ugamdiol esters we also directed our attention to the fact that on passing from ugamdiol to its esters the sign of the optical rotation changes. A comparison of the signs of the specific rotations of ugmadiol esters shows that the C_6 monoesters rotate to the right, like the initial diol, and the C_8 monoesters and C_6, C_8 diesters to the left. This enables us to determine the positions of the acyl groups in ugamdiol monoesters. Below we give the $[\alpha]_D$ values for ugamdiol derivatives:*

Substance	$[\alpha]_D$, deg	Substance	$[\alpha]_D$, deg
I. Ugaferin	−24.5	VII. Fecorin	−29
II. Ugamdiol	+47.5	VIII. Benzoate of (I)	−17.5
III. Diacetate of (II)	−60	IX. C_6-acetate of (II)	+42.5
IV. Dibenzoate of (II)	−12.5	X. C_6-benzoate of (II)	+52.5
V. C_8-acetate of (II)	−78	XI. C_6-angelate of (II)	+37.5
VI. Acetate of (I)	−34.6	XII. C_6-benzoate-C_8-acetate of (II)	−11.6



I. $R_1=H$; $R_2=C_6H_2(OCH_3)_3-CO$
II. $R_1=R_2=H$
III. $R_1=P_2=Ac$
IV. $R_1=R_2=C_6H_5CO$
V. $R_1=H$; $R_2=Ac$
VI. $R_1=Ac$; $R_2=C_6H_2(OCH_3)_3-CO$
VII. $R_1=C_4H_7CO$, $R_2=Ac$
VIII. $R_1=C_6H_5CO$, $R_2=C_6H_2-(OCH_3)_3CO$
IX. $R_1=Ac$, $P_2=H$
X. $R_2=C_6H_5CO$, $P_2=H$
XI. $P_1=C_4H_7CO$, $R_2=H$
XII. $R_1=C_6H_5CO$, $R_2=Ac$

EXPERIMENTAL

The UV spectra were taken on a Hitachi spectrometer (in ethanol, the IR spectra on a UR-20 instrument (tablets with KBr), the mass spectra on an MKh-1303 mass spectrometer, and the PMR spectra on a JNM-4H-100/100 MHz instrument (in $CDCl_3$; 0 — MHDS). The purity of the substances and the course of the reaction were checked by the TLC method on Silufol (in the hexane—ethyl acetate system) using a 1% solution of vanillin in concentrated sulfuric acid as the chromogenic reagent.

Isolation of Ugaferin (I). The comminuted roots of *Ferula ugamica* (3 kg) were treated with ethanol three times. The ethanolic extract was dried, diluted with water (1:2), and treated with ether. After the solvent had been distilled off, 180 g of a light brown viscous mass was obtained. Of this extract, 20 g was placed on a column (60 × 6 cm) filled with silica gel, and it was eluted with petroleum ether—ethyl acetate (3:1). By treatment with ether, fractions 52-71 yielded 0.22 g of crystals with mp 125-126°C and the composition $C_{25}H_{36}O_7$ (M^+ 448), $[\alpha]_D$ −24.5° (c 1.0; chloroform).

Hydrolysis of Ugaferin. The saponification of 0.2 g of the substance was carried out by heating it in 50 ml of 5% aqueous methanolic caustic potash for 4 h. The alkaline solution was extracted with ether, and the extract was washed with water and distilled. This gave 0.08 g of ugamdiol (II), $C_{15}H_{26}O_3$ (M^+ 254), mp 88-89°C (from petroleum ether). The

---

*The specific rotations are given for 1% solutions of the substances in chloroform.

mother alkaline solution was acidified with 5% sulfuric acid and extracted with ether, which gave 0.07 g of 3,4,5-trimethoxybenzoic acid, $C_{10}H_{12}O_5$, mp 168-169°C.

Ugamdiol Diacetate (III). A solution of 0.15 g of the substance in 3 ml of pyridine was treated with 2 ml of acetate anhydride, and the mixture was heated at 80°C for 4 h. The resulting acetyl derivative $C_{19}H_{30}O_5$ had mp 91-93°C (from ether).

Ugamdiol Dibenzoate (IV) was obtained by heating 0.2 g of ugamdiol in 3 ml of pyridine and 3 ml of benzoyl chloride; $C_{29}H_{34}O_5$, mp 157-158°C (from ether).

Ugamdiol C_8-Acetate (V). A solution of 1 g of ugamdiol in a mixture of 5 ml of pyridine and 3 ml of acetate anhydride was left at room temperature. The reaction product was separated on a column of silica gel. This yielded the monoacetate $C_{17}H_{28}O_4$ with mp 79-80°C (from ether).

Ugaferin Acetate (VI). The acetylation of 0.1 g of ugaferin was performed as described above. This gave the acetate (I), $C_{27}H_{38}O_8$, mp 133-134°C (from ether).

Ugaferin Benzoate (VIII). Ugaferin (0.1 g) was dissolved in a mixture of benzoyl chloride (2 mg) and pyridine (3 ml). This gave (VIII) with mp 210-211°C (from ether).

Ugamidiol C_6-Acetate. A solution of 0.3 g of ugamdiol diacetate in 15 ml of methanol was treated with 10 ml of a 5% solution of potassium carbonate in water. The mixture was left at room temperature for 90 min. The reaction product was separated on a column of silica gel, and the monoacetate $C_{17}H_{28}O_4$ with mp 130-131°C (from petroleum ether—diethyl ether) was isolated. The same monoacetate was obtained by the acetylation of ugamdiol at room temperature.

Ugamdiol C_6-Benzoate (X). A solution of 0.7 g of ugamdiol in 5 ml of pyridine was treated with 4 ml of benzoyl chloride and the mixture was left at room temperature for 1 h. The reaction product showed three spots with R_f 0.42 (dibenzoate) and 0.33 and 0.30 (monobenzoates). Separation on a column of silica gel yielded 0.22 g of the dibenzoate (IV) of (II) and 0.13 g of the C_6-monobenzoate of (II) with mp 164-165°C (from ether). The C_6-monobenzoate of (II) is also formed by the hydrolysis of the dibenzoate of (II) with potassium carbonate in methanol.

Ugamdiol C_6-Angelate (XI). A solution of 0.3 g of fecorin in 10 ml of methanol was treated with 3 ml of 5% aqueous potassium carbonate solution and the mixture was left at room temperature for 1 h. This gave the C_6-angelate (XI) of (II) with mp 116-117°C (from hexane).

The C_6-Benzoate-C_8-Acetate (XII) of (II). Ugamdiol C_6 benzoate was acetylated with acetic anhydride in pyridine. This gave the diester (XII) with mp 151-152°C (from ether).

Hydrolysis of the Acetate and Benzoate of (I). The acetate and benzoate of ugaferin (VI, VIII) (0.2 g in each case) were saponified with potassium carbonate in methanol at room temperature. Ugaferin (I) with mp 123-124°C was isolated from the reaction products.

SUMMARY

A new ester ugaferin has been isolated from the roots of *Ferula ugamica*, and the structure of 8-trimethoxybenzoylugamdiol has been established for it.

By a study of the physicochemical properties of the mono- and diesters of ugamdiol the possibility has been shown of determining the positions of acyl residues by stepwise hydrolysis and from the sign of the specific rotation.

LITERATURE CITED

1. Beilsteins Handbuch der organischen Chemie, 10, 1407 (1971).
2. N. P. Kir'yalov, Trudy BIN SSSR, 15, 129 (1969).
3. N. P. Kir'yalov, Abstracts of the Third Indo—Soviet Symposium on the Chemistry of Natural Compounds [in Russian], Tashkent (1973), p. 87.
4. K. Wada, Y. Enomoto, K. Matsui, and K. Munakata, Tetrahedron Lett., 4613 (1968).
5. K. Wada and K. Munakata, Tetrahedron Lett., 4617 (1968).
6. Kh. M. Kamilov, V. M. Potapov, and G. K. Nikonov, Khim. Prirodn. Soedin., 132 (1976).
7. A. Sh. Kadyrov, A. I. Saidkhodzhaev, and G. K. Nikonov, Khim. Prirodn. Soedin., 152 (1975).