

# SUMMARY

The mass spectra of four guaianolides with epoxy groups at C<sub>1</sub>-C<sub>2</sub> have been studied. A mechanism is suggested for the formation of the fragmentary ions. The origin of the second-degree fragments has been confirmed by measurements of elementary compositions.

## LITERATURE CITED

1. S. M. Kupchan, J. M. Cassady, and J. E. Kelsey, J. Am. Chem. Soc., **88**, 5292 (1966).
2. L. Tsai, R. J. Highet, and W. Herz, J. Org. Chem., **34**, 945 (1969).
3. P. I. Zakharov, R. I. Evstratova, and K. S. Rybalko, Khim. Prir. Soedin., 587 (1971).
4. M. A. Irwin and T. A. Geissman, Phytochemistry, **12**, 863 (1973).
5. T. Asawa and D. Taylor, Tetrahedron Lett., **13**, 1169 (1977).
6. M. I. Yusupov, Sh. Z. Kasymov, G. P. Sidyakin, and U. Rakhmankulov, Khim. Prir. Soedin., 579 (1979).
7. M. S. Yusupov, A. Mallabaev, Sh. Z. Kasymov, and G. P. Sidyakin, Khim. Prir. Soedin., 580 (1979).
8. U. A. Abdullaev, Ya. V. Rashkes, and S. Yu. Yunusov, Khim. Prir. Soedin., 125 (1975).
9. U. A. Abdullaev, Ya. V. Rashkes, S. Z. Kasymov, and G. P. Sidyakin, Khim. Prir. Soedin., 636 (1980).

## COUMARINS OF THREE SPECIES OF THE GENUS *Haplophyllum*

A. Z. Abyshev, N. Ya. Isaev,  
and Yu. B. Kerimov

UDC 577.15/17.582.89

The results are given of an investigation of three species of the genus *Haplophyllum*: *H. villosum*, *H. kowalenskyi*, and *H. tenue*, from which five substances of coumarin nature have been isolated. Of them, two substances (I and II) have been identified as scopoletin and lomatin isovalerate, respectively, while suitable structures have been established for the new compounds tenuidin, villosin, and tenudiol. It has been shown that the coumarin composition of the plants changes with the growth site.

We have studied the coumarin composition of the epigeal part of three species of plants of the genus *Haplophyllum* (family Rutaceae): *H. villosum*, *H. kowalenskyi*, and *H. tenue*, collected in the Nakhichevan ASSR from various growth sites in the full-flowering stage (see Table 1). Five substances have been isolated (I, C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>, mp 204-205°C; II, C<sub>19</sub>H<sub>22</sub>O<sub>5</sub>; III, C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>, mp 74-75.5°C; IV, C<sub>20</sub>H<sub>24</sub>O<sub>5</sub>; V, C<sub>20</sub>H<sub>26</sub>O<sub>6</sub>) all possessing the properties characteristic for compounds of the coumarin series.

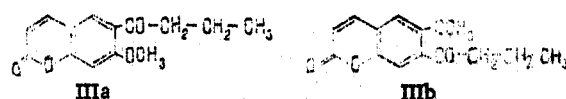
In their physicochemical constants and IR and PMR spectra, substances (I) and (II) corresponded to the known coumarins scopoletin [1] and lomatin isovalerate [2]. Substances (III-V) proved to be new, not previously described in the literature. We have called them tenuidin, villosin, and tenudiol.

The IR spectra of tenuidin (III) showed absorption bands at (cm<sup>-1</sup>) 1725 (C=O of an  $\alpha$ -pyrone), 1700 (keto group), and 1655, 1610, and 1515 (-CH=CH bond in an aromatic ring).

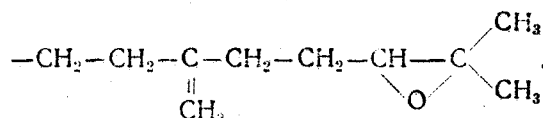
In the PMR spectrum of (III), in addition to the signals of the protons of a 6,7-disubstituted coumarin ring (one-proton doublets at 6.26 and 7.66 ppm, J = 10 Hz, H-3 and H-4, and singlets at 6.80 and 6.91 ppm, H-8 and H-5), the signals of the protons of a methoxy group are observed at 3.95 ppm (singlet, 3 H) and those of a normal butyryl radical (triplet at 1.28 ppm, 3 H, and multiplet with its center at 2.88 ppm, 4 H). On the basis of these results, two structures are possible for compounds (III) -  $\alpha$  and  $\beta$ . From biogenetic considerations, (IIIa) is the more probable:

---

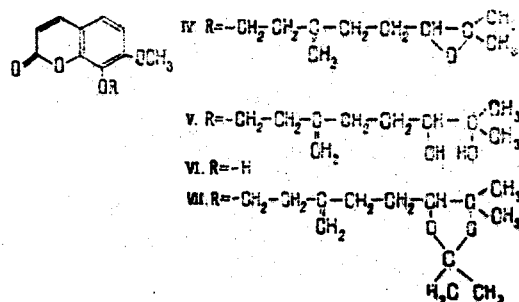
Leningrad Sanitary-Hygienic Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 800-803, November-December, 1980. Original article submitted March 24, 1980.



Villosin (IV) and tenudiol (V) are optically inactive liquid substances and, unlike tenuidin (III), belong to the group of 7,8-disubstituted coumarins, since their PMR spectra show the signals of the H-3-H-6 protons (doublets at 6.33 and 7.73 ppm,  $J = 10$  Hz; 7.37 and 6.91 ppm,  $J = 9$  Hz, 1 H). The PMR spectrum of (IV) also has the signals of the protons of a methoxy group (singlet at 3.91 ppm, 3 H), of a methylene group on a double bond (unresolved signals at 5.11 and 5.28 ppm, 2 H), of methyl groups on a quaternary carbon atom with a hydroxy group (singlets at 1.17 and 1.25 ppm, 3 H each), and of an Ar-O-CH<sub>2</sub>- grouping (multiplet at 4.37 ppm, 2 H). The signals of the protons of three methylene groups and of a methine proton appear in the form of a multiplet in the 2.06-2.80 ppm interval (7 H). The facts given permit the following structure to be suggested for the side chain of compound (IV):



The position of the substituents in compound (IV) were established from the results of acid hydrolysis, which formed two substances; one of them was identified as 8-hydroxy-7-methoxycoumarin (VI), C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>, mp 170-171.5°C, and the other, according to PMR spectra, corresponded to (V). Thus, the methoxy groups in (IV) and (V) occupy position 7 in each case, and the terpenoid moiety is attached at position 8, (IV) being 8-(6',7'-epoxy-3'-methylene-7'-methyloctenyloxy)-7-methoxycoumarin and (V) the corresponding diol, since the IR spectrum of the latter has an absorption band in the IR spectrum at 3550 cm<sup>-1</sup> (hydroxy groups).



A proof of the presence of two neighboring hydroxy groups in the side chain of (V) was the production by the usual method of its acetonide (VII) with the composition C<sub>23</sub>H<sub>30</sub>O<sub>6</sub>, the IR spectrum of which lacked the absorption band of a OH group while its PMR spectrum showed signals of the protons of four methyl groups (singlets at 1.09 and 1.40 ppm, 3 H each, and at 1.25 ppm, 6 H).

As can be seen from Table 1, the coumarin compositions of plants gathered from different growth sites were different, even if the plants were collected in the same phase of development.

#### EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrometer (in paraffin oil), and PMR spectra on an HX-90 spectrometer (in CDCl<sub>3</sub>, 0 - TMS). Melting points were determined on a Kofler block.

TABLE 1

Compound	H. villosum		H. Kowalenskyi		H. tenue	
	Dagri	Sirab	Azna-byurt	Milakh	Lisbirt	Nakhi-chevan
Scopoletin	+	—	+	+	—	—
Lomatilin isovalerate	—	—	—	+	—	+
Tenuidin	—	+	—	—	+	—
Villosin	—	+	—	—	—	+
Tenudiol	—	—	—	—	+	—

The purity of the substances obtained was checked on Silufol plates in the benzene-acetone (10:3) system. The elementary analyses of the compounds studied corresponded to the calculated figures.

Isolation of the Coumarins. The combined epigeal parts of *H. villosum*, *H. kowalenskyi*, and *H. tenue* (1000 g, 575 g, and 132 g, respectively) were extracted with methanol, and then the extracts were concentrated to small volume, diluted with water, and re-extracted with diethyl ether. After the ethereal extracts had been evaporated, resins were obtained (254 g, 127 g, and 58 g, respectively), which were separated on columns containing neutral alumina (L 40/250) of activity grade III. Elution was performed with petroleum ether, petroleum ether-chloroform, and chloroform. As a result of a study of the fractions obtained and re-chromatography of the mixture of substances in suitable systems the following compounds were isolated:

from *H. villosum* - scopoletin (I),  $C_{10}H_8O_4$ , mp 204-205°C (from ethanol),  $R_f$  0.27 (bright blue); tenuidin (III),  $C_{14}H_{14}O_3$ , mp 74-75.5°C (from ether),  $R_f$  0.85 (blue); and villosin (IV),  $C_{20}H_{24}O_5$ ,  $R_f$  0.76 (blue);

from *H. kowalenskyi* - (I) and lomatin isovalerate (II),  $C_{20}H_{24}O_5$ ,  $R_f$  0.70 (violet); and

from *H. tenue* - (I-IV) and tenuidol (V),  $C_{20}H_{26}O_6$ ,  $R_f$  0.17 (blue).

Acid Hydrolysis of Villosin (IV). A solution of 0.85 g of (IV) in 20 ml of 10% sulfuric acid was boiled for 5 h. The hydrolysate was diluted with water and extracted with chloroform. When the chloroform was concentrated, crystals (0.42 g) deposited which were filtered off and washed with hot chloroform. This gave substance (VI) with the composition  $C_{10}H_8O_4$ , mp 170-171.5°C;  $R_f$  0.26 (blue), identical with 8-hydroxy-7-methoxycoumarin. The mother solution after the evaporation of the solvent was separated preparatively on Silufol plates in the benzene-acetone (10:3) system. About 0.1 g of viscous substance corresponding from its PMR spectrum to tenuidiol (V) was isolated.

Tenuidiol Acetonide (V). A solution of 0.28 g of (V) in 10 ml of acetone was treated with five drops of concentrated sulfuric acid and the mixture was left at room temperature for 3 h. Then it was worked up in the usual way. This gave the liquid acetonide (VII), with the composition  $C_{23}H_{30}O_6$ , in the IR spectrum of which there was no absorption band of hydroxy groups while its PMR spectrum contained, in addition to other signals, the signals of the protons of four methyl groups (singlets at 1.09 and 1.40 ppm, 3 H each, and at 1.25 ppm, 6 H).

#### SUMMARY

The coumarin compositions of three species of the genus *Haplophyllum* have been determined; five substances (I-V) of coumarin nature have been isolated from them.

On the basis of chemical and spectral properties, (I) and (II) have been identified as the known compounds scopoletin and lomatin isovalerate, while appropriate structures have been established for the new substances (III-V) - tenuidin, villosin, and tenuidiol.

#### LITERATURE CITED

1. A. A. Kagramanov, N. F. Gashimov, A. Z. Abyshev, and L. I. Rozhkova, *Khimiya Prir. Soedin.*, 88 (1979).
2. F. Bohlmann and K. M. Rode, *Chem. Ber.*, 101, 2741 (1968).