8. J. A. Barltrop and J. D. Coyle, Excited States in Organic Chemistry, Wiley-Interscience, New York, 1977 [Russian translation: Mir, Moscow (1978), p. 246].
9. A. V. Vorob'ev, V. A. Raldugin, S. A. Shevtsov, and Yu. V. Gatilov, Khim. Prir. Soedin., 295 (1986).
10. P. Crews and E. Kho-Wiseman, J. Org. Chem., 42, 2812 (1977).
11. R. B. Bates and D. M. Gale, J. Am. Chem. Soc., 82, 5749 (1960).
12. V. A. Raldugin and V. I. Mamatyuk, Izv. Sib. Otd. Akad. Nauk SSSR. Ser. Khim. Nauk, Series No. 6, Issue No. 17, 71 (1984).
13. E. C. Ashby and T. L. Wieseman, J. Am. Chem. Soc., 100, No. 10, 3101 (1978).
14. R. Stewart and A. Ubbelohde, J. Chem. Soc., No. 10, 2649 (1949).
15. V. Franzen and H. Krauch, Chem. Ztg., 79, 137 (1955).
16. V. A. Raldugin, V. A. Khan, Zh. V. Dubovenko, and V. A. Pentegova, Khim. Prir. Soedin., 609 (1976).
17. J. A. Barltrop and J. D. Coyle, Excited States in Organic Chemistry, Wiley Interscience, New York, 1977 [Russian translation: Mir, Moscow (1978), p. 283].
18. L. Lombardo, Tetrahedron Lett., 23, 4293 (1982).

OBTUSIFOLIN – A NEW COUMARIN FROM ROOTS OF *Haplophyllum obtusifolium*

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From the neutral fraction of a methanolic extract of the roots of *Haplophyllum obtusifolium* Ledeb. (family Rutaceae) have been isolated the lignan diphyllin, the alkaloids skimmianine and γ-fagarine, and a new coumarin with mp 179-180°C the structure of which has been established as 3-(α,α-dimethylallyl)-7-methoxy-8-(3-methylbuta-1,3-diethyl)coumarin.

The isolation of furanoquinoline alkaloids from the basic fraction of a methanolic extract of the roots of *Haplophyllum obtusifolium* Ledeb. (family Rutaceae) has been reported previously [1]. Continuing these investigations, we have studied the neutral fraction obtained from the same methanolic extract. Chromatography of the neutral fraction led to the isolation of a substance with mp 179-180°C (I), the lignan diphyllin, and the alkaloids simmianine and γ-fagarine.

Substance (I) – $C_{20}H_{22}O_3$ – was new, and has been called obtusifol. It dissolved readily in chloroform, less readily in methanol and ethanol, crystallized from ether and acetone, and was revealed by the Dragendorff reagent and in UV light.

The UV spectrum of obtusifolin contained absorption bands of an α-pyrone carbonyl (1710 cm^{-1}) and of aromatic and aliphatic C=C bonds (1624, 1610, 1600, 1569 cm^{-1}). Its UV spectrum had maxima at (nm) 220, 265* (inflection), 276*, 302, 319* (log 4.30, 4.11, 4.19, 4.44 [sic]), which are characteristic for 7-O-substituted coumarins [2].

In the PMR spectrum of obtusifolin three one-proton signals from the protons of the coumarin nucleus appeared at 6.77, 7.20, and 7.42 ppm. According to the literature [2-4], the singlet at 7.42 ppm belonged to a proton at C-4. Its singlet nature indicated the presence of a substitutent at C-3. The other two signals, doublets, at 7.20 and 6.77 ppm were the signals of the protons of a benzene ring present in the ortho-position to one another, as was shown by their spin-spin coupling constant (J = 9 Hz).

The facts given above showed that the coumarin nucleus of obtusifolin has three substituents. One of them is a methoxy group, the protons of which resonated at 3.88 ppm, while the other two were represented by isoprene units. The proton signals observed in the regions of (ppm) 1.42 (6H, singlet; two methyl groups at a quaternary carbon atom); 1.96 (3H broadened

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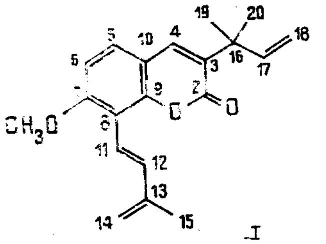
singlet; $=C-CH_3$); 4.92-5.25 (4H, multiplet; two terminal methylene groups); 6.13 (1H, doublet of doublets, J = 10 and 17.5 Hz, $=CH-$ of a vinyl group); 6.82 and 7.47 (doublets; 1H each, J = 16 Hz; trans-olefinic protons) unambiguously showed that one substituent has the structure $-C(CH_3)_2-CH=CH_2$ [2-4] and the other $-CH=CH-C(CH_3)=CH_2$ [2, 5], both being linked to the c coumarin nucleus through C—C bond.

The presence in the molecule of (I) of an α,α-dimethylallyl and a 3-methylbuta-1,3-dienyl group was confirmed by the formation of a hexahydro derivative (II) on the Adams reduction of obtusifolin.

In the PMR spectrum of (II), in addition to the signals of the protons at C-4, -5, and -6 of the coumarin nucleus at (ppm) 7.36 (1H, singlet) and 7.05 and 6.55 (doublets, 1H each J = 9 Hz), the signals of the protons of the substituents were observed at (ppm); 3.83 (3H, singlet; $-OCH_3$); 2.86-2.66 (2H, multiplet; $Ar-CH_2-$); 1.82 (2H, quartet, J = 7 Hz; $-C\underline{H}_2-CHC_3$); 1.66-1.18 (3H, multiplet; $-C\underline{H}_2C\underline{H}$); 1.26 (6H, singlet, $C(C\underline{H}_3)_2$]; 0.91 [6H, doublet, J = 6 Hz; $-CH-C\underline{H}_3)_2$], and 0.66 (3H, triplet, J = 7 Hz; $-CH_2-C\underline{H}_3$.



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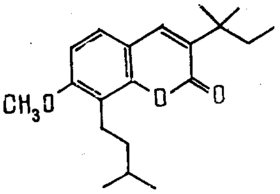

II

The positions of the substituents were established on the basis of the following facts. The value of the chemical shift of the proton at C-4 excluded substitution at C-5 [2]. Consequently, in the light of the facts given above it may be assumed that the substituents in the obtusifolin molecule are present in positions 3, 7, and 8 of the coumarin nucleus. The position of the methoxy group at C-7 suggested on the basis of the UV spectrum of (I) was confirmed by the existence of a NOE (more than 20%) between the protons of the methoxy group and the strong-field doublet at 6.55 ppm in the PMR spectrum of (II). The latter gives grounds for assigning the weak-field doublet at 7.05 ppm to a proton at C-5.

An analysis of the PMR spectra of coumarins containing an α,α-dimethylallyl substituent has shown that when it is located at C-3, the signal of the protons of the $>C(CH_3)_2$ group appears in the 1.42-1.50 ppm intervals [3, 4, 6-8], while when it is present in the benzene ring the signal appears in the 1.56-1.77 ppm interval [8-10].

On the basis of the facts given above, we propose for obtusifolin the structure 3-(α,α-dimethylallyl)-7-methoxy-8-(3-methylbuta-1,3-dienyl)coumarin, and this is confirmed by an analysis of its ^{13}C NMR spectrum.

The chemical shifts (CSs) of the signals of the carbon atoms in the ^{13}C NMR spectrum of obtisufolin are given below:

C atom	Multiplicity	ppm	C atom	Multiplicity	ppm
2	s	169.31	12	d	118.13
3	s	131.77	13	s	143.20
4	d	138.10	14	t	117.45
5	d	126.75	15	q	18.32
6	d	107.40	16	s	40.31
7	s	159.50	17	d	145.56
8	s	112.18	18	t	112.18
9	s	151.00	19	q	
10	s	113.54	20	q	26 07
11	d	137.9	OCH_3	q	56.10

The assignment of the signals of the carbon atoms in the ^{13}C NMR spectrum was made by a comparative study of the CSs and the multiplicities of the signals obtained in experiments with complete and partial suppression of C—H interactions and a comparison with literature figures for the ^{13}C CSs of coumarin derivatives close in structure containing the substituents $-C(CH_3)_2-CH=CH_2$ [11,12] and $-CH=CH-CH(CH_3)_2$ [13]. The ^{13}C NMR of (I) showed 19 signals from the 20 carbon atoms. The CSs of the signals of the carbon atoms of two methyl groups coincided at 26.07 ppm. The CSs of the carbon atoms of the substituted coumarin nucleus and of the substituents were close to those reported in the literature for compounds of similar structure [14].

EXPERIMENTAL

For general observations, see [1]. The PMR spectra of (I) and (II) were obtained on a Tesla BS-567 A spectrometer with ν_0 =100 MHz in $CDCl_3$, 0 – GMDS, and the ^{13}C NMR spectra on BS-567 A and XL-200 (Varian) spectrometers with ν_0 = 25.142 and 50 MHz in $CDCl_3$; 0 – TMS.

Isolation. The neutral fraction (18 g) of the methanolic extract of the roots of Haplophyllum obtusifolium (for its preparation, see [2]) was chromatographed on a column of silica gel L 100/250 μ (Czechoslovakia). Ethereal eluates yielded substances in the following sequence: obtusifolin (159 mg), diphyllin (230 mg) with mp 286-288°C (decomp.), skimmianine (90 mg) with mp 176-177°C, and γ-fagarine (105 mg) with mp 139-140°C. The known substances were identified by comparison with authentic samples.

Obtisufol. Crystals in the form of needles with mp 179-180°C (from ether), yellowing in the air; R_f 0.8 in the toluene–ethyl acetate–formic acid–methanol (5:4:1:1) system. Mass spectrum, m/z (%): M^+310(100), 295(55), 279(48), 267(15), 254(12), 237(10), 223(11), 211(14), 209(11), 165(11), 105(12), 69(15).

Hexahydroobtusifolin. A solution of 38 mg of obtusifolin in 15 ml of ethanol was treated with 25 mg of PtO_2 and the mixture was shaken in a current of hydrogen for 3 h. Then it was filtered, and the filtrate was evaporated in vacuum. The residue was dissolved in chloroform and was passed through a layer of alumina (0.5 g). After the solvent had been distilled off, 32 mg of (II) was obtained: $C_{20}H_{28}O_3$, mp 97-98°C, ν_{max}^{KBr} (cm^{-1}) 1720 (C=O of an α-pyrone), 1618, 1580, 1500 (aromatic C=C bonds); $\lambda_{max}^{ethanol}$ (nm) 235 (inflection), 248.5, 259, 303, 342 (inflection). Mass spectrum, m/z (%): M^+ 316(64), 301(22), 288(89), 287(100), 285(19), 273(62), 259(33), 229(10).

SUMMARY

The new coumarin obtusifolin has been isolated from the roots of Haplophyllum obtusifolium Ledeb. and its structure has been established on the basis of chemical and spectroscopic studies as 3-(α,α-dimethylallyl)-7-methoxy-8-(3-methylbuta-1,3-dienyl)coumarin.

LITERATURE CITED

1. I. A. Bessonova and S. Yu. Yunusov, Khim. Prir. Soedin., 736 (1986).
2. M. E. Perel'son, Yu. N. Sheinker, and A. A. Savina, The Spectra and Structure of Coumarins, Chromones, and Xanthones [in Russian], Moscow (1975).
3. A. D. Matkarimov, É. Kh. Batirov, V. M. Malikov, and E. Seitmuratov, Khim. Prir. Soedin., 173 (1982).
4. N. F. Gashimov, A. Z. Abyshev, A. A. Kagramanov, and L. I. Rozhkova, Khim. Prir. Soedin., 15 (1979).
5. H. R. Arthur and W. D. Ollis, J. Chem. Soc., 3910 (1963).
6. M. M. Ballantyne, P. H. McCabe, and R. D. H. Murray, Tetrahedron, 27, 871 (1971).
7. A. V. Rama Rao, K. S. Bhide, and R. B. Mujumdar, Indian J. Chem., 19B, 1046 (1980).
8. A. G. Gonzalez and L. F. Rodriguez, Herba Hung., 10, 95 (1971).
9. S. K. Garg, S. R. Gupta, and N. D. Sharma, Planta Med., 38, 186 (1980).
10. R. D. H. Murray and M. M. Ballantyne, Tetrahedron, 26, 4667 (1970).
11. É. Kh. Batirov, A. D. Matkarimov, V. M. Malikov, and E. Seitmuratov, Khim. Prir. Soedin., 780 (1982).
12. M. Nicoletti, F. D. Monache, and G. B. Marini-Bettolo, Plant Med., 45, 250 (1982).
13. V. Kumar, J. Reisch, D. B. M. Wickremaratne, R. A. Hussain, K. S. Adesina, and S. Balasubramaniam, Phytochemistry, 26, 511 (1987).
14. H. Duddek and M. Kaiser, Org. Magn. Reson., 20, 55 (1982).