4. E. Beloruchev, Gig. Sanit., No. 48 (1950).
5. A. V. Mironenko, Methods of Determining Alkaloids [in Russian], Minsk (1966), p. 11.
6. R. Hegnauer, Chemotaxonomie der Pflanzen, Birkhäuser Verlag, Basel, Vol. IV (1978), p. 289.
7. S. D. Gusakova and A. U. Umarov, Khim. Prir. Soedin., 57 (1978).
8. T. V. Panekina, S. D. Gusakova, E. M. Zalevskaya, and A. U. Umarov, Khim. Prir. Soedin., 618 (1979).
9. J. Sessa, H. W. Gardner, R. Kleiman, and D. Weisleder, Lipids, 12, 613 (1977).
10. S. D. Gusakova and A. U. Umarov, Khim. Prir. Soedin., 27 (1972).
11. F. D. Gunstone and L. J. Morris, J. Chem. Soc., 2127 (1959).
12. C. R. Smith, R. V. Madrigal, and R. D. Plattner, Biochem. Biophys. Acta, (L.), 572, 314 (1979).
13. H. W. Gardner and D. Weisleder, Lipids, 7, 191 (1972).
14. R. Kleiman and G. F. Spencer, J. Am. Oil Chem. Soc., 50, 31 (1973).
15. Handbook on Methods of Investigation, Technical and Chemical Control, and the Accounting of Production in the Oils and Fats Industry [in Russian], Leningrad, Vol. 1, Book 2 (1967).
16. J. A. Fioriti and R. J. Sims, J. Chromatogr., 32, 761 (1968).
17. Houben-Weyl, Methoden der Organishchen Chemie [Russian translation], Moscow, Vol. II (1967), p. 443.
18. F. D. Gunstone and H. R. Shuler, Chem. Phys. Lipids, 15, 174 (1975).
19. T. V. Panekina, S. D. Gusakova, M. Ya. Tabak, and A. U. Umarov, Khim. Prir. Soedin., 44 (1978).
20. M. K. Kates, Techniques of Lipidology, Am. Elsevier, New York (1972).

# ARYLNAPHTHALENE LIGNANS OF *Haplophyllum dauricum*. THE STRUCTURE OF DAURINOL

D. Batsuren, É. Kh. Batirov,
V. M. Malikov, V. N. Zemlyanskii,
and M. R. Yagudaev

UDC 547.99

The arylnaphthalene lignans justicidin B and daurinol I have been isolated from the epigeal part of *Haplophyllum dauricum* (L.) G. Don.

We have previously established the presence of arylnaphthalene lignans in plants of the genus *Haplophyllum* Juss. (family Rutaceae) [1]. In the present paper we report the results of a study of the lignans of *Haplophyllum dauricum* (L.) G. Don.

The plant was collected at the stage of incipient fruit bearing in the Uvurkhangaiskii aimak, Mongolian People's Republic. The roots and epigeal part were studied. From a chloroform fraction of the ethanolic extract of the epigeal part we isolated two individual compounds by adsorption chromatography on a column of silica gel. Both substances exhibited bright blue fluorescence in UV light, and with concentrated sulfuric acid they formed dark brown colorations. These properties are characteristic of arylnaphthalene lignans [2]. The lignan with the composition $C_{21}H_{16}O_6$ (I) mp 234-235°C (methanol) was, according to its IR and PMR spectra, identical with justicidin B [3, 4]. This was confirmed by a direct comparison of (I) with an authentic sample of justicidin B isolated from *Haplophyllum obtusifolium* [1].

Lignan (II) with the composition $C_{20}H_{14}O_6$, $M^+$ 350, $\lambda_{max}^{C_2H_5OH}$ 227, 262, 296, 324, 352 nm (log ε 4.55, 4.68, 4.07, 4.09, 3.41) proved to be new, and we have called it daurinol. The peak of the molecular ion (m/e 350) is the strongest in the mass spectrum of (II). Strong peaks of ions with m/e 321 (M − CHO), 305 (M − $CO_2H$), 292 (M − $C_2H_2O_2$), 291 (M − $CH_3O$ − CO), 277, 263, and others were also observed.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 295-297, May-June, 1981. Original article submitted February 3, 1981.

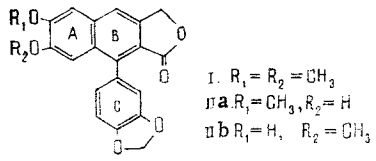
0009-3130/81/1703-0223$07.50  

The IR spectrum of (II) has absorption bands at ($cm^{-1}$) 3390 (hydroxy group), 1762 (C=O), 1623, 1600 (aromatic nucleus), 936 (—$OCH_2O$—), and 777 (1,2,4-trisubstituted benzene ring).

The acetylation of daurinol with acetic anhydride in the presence of pyridine yielded a monoacetyl derivative (III) with mp 193-195°C.

The PMR spectrum of (III) showed the signals of protons at (ppm) 2.30 (3 H, s, Ar—$OCOCH_3$), 3.67 (3 H, s, Ar—$OCH_3$), 5.24 (2 H, s, Ar—$\underline{CH_2}O$—), 5.92 and 5.98 (1 H each, dd, $J_{gem} \approx 1.2$ Hz, —$OCH_2O$—), 6.74 (1 H, br. s, H-2'), 6.70 (1 H, q, 8.4 and 1.5 Hz, H-6'), 6.86 (1 H, d, 8.5 Hz, H-5'), 7.08 and 7.46 (1 H, s, each, H-5 and H-8), and 7.62 (1 H, br. s, H-4).

The PMR spectrum shows the presence of subsituting groups in the C-6 and C-7 positions of ring A and the C-3',4'-positions of ring C. The values of the chemical shifts of the signals of the $C_4$—H and Ar—$\underline{CH_2}$—O— protons indicate that the carbonyl group is attached to $C_2$ [5-7]. In order to decide the positions of the substituents —$OCH_3$, —OH, and —$OCH_2O$— in rings A and C we used the methods of double resonance, collapse, and the NOE [8, 9]. On double irradiation with the frequency $\nu_2$ = 762 Hz, corresponding to the resonance transition of the H-4 proton, the signals of the two aromatic protons with δ 7.08 and 7.45 ppm became narrower, obviously because of long-range coupling. Consequently, their assignment to $H_5$ or $H_8$ is difficult. Irradiation of the Ar—$OCH_3$ protons ($\nu_2$ = 367 Hz) led to a rise in the intensity of the signal of the proton with δ = 7.08 ppm by 30%, which shows the position of the $OCH_3$ group in ring A at $C_6$ or $C_7$, and therefore structure (IIa) or (IIb) is proposed for daurinol. A confirmation of this is the fact that the methylation of daurinol with diazomethane led to a methyl ether which proved to be identical with justicidin B.




I. $R_1 = R_2 = CH_3$
IIa. $R_1 = CH_3$, $R_2 = H$
IIb. $R_1 = H$, $R_2 = CH_3$

It must be mentioned that a confirmation of the location of the C=O group at C—2 of the —$CH_2$ group at C—3 is given by the fact that on double irradiation with $\nu_2$ = 524 Hz (Ar—$\underline{CH_2}O$—), the signal of the H-4 aromatic proton at δ 7.62 contracted appreciably and its intensity increased.

Daurinol has also been isolated from the roots of *Haplophyllum dauricum*.

## EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer (tablets with KBr), the UV spectra on a EPS-3T instrument. The NMR spectra in $CDCl_3$ on a JNM-4H-100/100 MHz instrument with HMDS as internal standard (δ scale), and the mass spectra on a MKh-1303 spectrometer. Thin-layer chromatography was performed on Silufol UV-254 plates in the chloroform—ethyl acetate (19:1) system.

Isolation of the Lignans. The comminuted epigeal part of *H. dauricum* (6.5 kg) was extracted ten times with ethanol and then three times with chloroform. The solvents were distilled off in vacuum. The concentrated ethanolic extracted was diluted with water (1:1) and was then extracted successively with petroleum ether (yield of the fraction 261 g), chloroform (126 g), ethyl acetate (20 g), and butanol (258 g). The chloroform fraction was chromatographed on a column of silica gel (1:10). The substances were eluted with benzene—chloroform in various ratios. At a 1:1 composition of the mixture 1.66 g of a mixture of (I) and (II) was eluted. Fractional recrystallization from methanol yielded 0.43 g (0.007%) of justicidin B and 0.82 g (0.013%) of daurinol.

Daurinol. mp 256-257°C (methanol), $R_f$ 0.54. Mass spectrum, m/e (%): $M^+$ 350 (100), 321 (10, m* 350→321, 294, 5), 305 (10), 292 (4), 291 (15), 278 (4), 277 (11), 264 (5), 263 (13), 251 (6), 249 (5), 248 (6), 235 (5), 233 (7), 221 (6), 220 (8), 205 (5), 192 (6), 176 (7), 175 (4), 165 (7), 164 (6), 163 (13), 160 (11), 146 (6).

Daurinol Monoacetate. A mixture of 50 mg of (II), 0.5 ml of pyridine, and 2 ml of acetic anhydride was kept at room temperature for 24 h. The acetyl derivative was isolated by the usual method. mp 193-195°C (ethanol), $R_f$ 0.77.

Daurinol Methyl Ether. An ethereal solution of diazomethane was added to a suspension of 40 mg of (II) in 5 ml of anhydrous chloroform. After 6 h, the solvent was distilled off. The reaction product was separated from the initial substance by chromatography on a column of alumina. mp 231-233°C (methanol), $R_f$ 0.68. A mixture with justicidin B gave no depression of the melting point, and their IR spectra were identical.


## SUMMARY

Justicidin B and a new arylnaphthalene lignan daurinol have been isolated from *Haplophyllum dauricum*. On the basis of chemical and spectral characteristics using double resonance it has been ascribed the structure (IIa or b).


## LITERATURE CITED


1. É. Kh. Batsuren, A. D. Matkarimov, and V. M. Malikov, Khim. Prir. Soedin., No. 3, 386 (1981).
2. S. Ghosal, R. P. S. Chauhan, and R. S. Srivastava, Phytochem., 13, 2281 (1974); 13, 1933 (1974).
3. M. Okigawa, T. Maeda, and N. Kawano, Tetrahedron, 26, 4301 (1970).
4. K. Munakata, Sh. Marumo, K. Ohta, and Y.-L. Chen, Tetrahedron Lett., 3821 (1967).
5. L. H. Klemm, K. W. Gopinath, D. Hsu Lee, F. W. Kelly, E. Trod, and T. M. McGuire, Tetrahedron, 22, 1797 (1966).
6. Z. Horii, M. Tsujiuchi, and T. Momose, Tetrahedron Lett., 1079 (1969).
7. T. L. Holmes and R. Stevenson, J. Org. Chem., 36, 3450 (1971).
8. R. A. Bell and J. K. Saunders, Can. J. Chem., 48,1114 (1970).
9. G. E. Bachers and T. Schaefer, Chem. Rev., 71, 617 (1971).


# MICRANTHOSIDE — A NEW GLYCOSIDE FROM *Eupatorium micranthum*


T. G. Sagareishvili, M. D. Alaniya, V. G. Tsitsishvili, and É. P. Kemertelidze



UDC 547.972



From the epigeal parts of the plant *Eupatorium micranthum* Less., introduced into the Sukhumi Botanical Garden, a new glycoside has been isolated which has been called micranthoside and which has the structure of 4',5-di-O-β-glucosyl-7-O-methyldihydrokaempferol or 4',5-di-O-β-D-glucosyl-7-O-methylaromadendrin.


The epigeal part of *Eupatorium micranthum* Less. syn. *E. ligustrinum* DC., family Asteraceae (Compositae), introduced into the Sukhumi Botanical Garden (Georgian SSR) [1], has proved to be rich in flavonoid compounds [2] (Scheme, following page, top).

From an aqueous alcoholic extract of the plant we have quantitatively isolated the main substance, a flavonoid glycoside which has been named micranthoside (I).

Micranthoside (I), $C_{28}H_{34}O_{16}$, gives the reactions specific for flavonoids. In the UV spectrum $\lambda_{max}^{C_2H_5OH}$ 280 nm (log ε 4.4). The IR spectrum shows the absorption bands characteristic for a hydroxy group (3420 $cm^{-1}$), for the carbonyl of a γ-pyrone ring (1680 $cm^{-1}$), for aromatic rings (1615, 1580, 1520 $cm^{-1}$), and for a methoxy group (2920 $cm^{-1}$).

The assignment of the PMR spectrum of compound (I) taken in deuteropyridine (Fig. 1a) permitted it to be ascribed to the group of flavonol diglycosides.

A complex multiplet in the 3.8-4.4 ppm region has an integral intensity corresponding to the protons of the two glucose residues. At 5.30 ppm there is the signal of one anomeric proton in the form of a doublet with a constant of 6.5 Hz (the use of double resonance showed that on suppression of the resonance at 4.20 ppm the doublet splitting was eliminated). Such


I. G. Kutateladze Institute of Pharmocochemistry, Academy of Sciences of the Georgian SSR, Tbilisi.


Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 298-303, May-June, 1981. Original article submitted March 2, 1981.

0009-3130/81/1703-0225$07.50