UDC 577.15/17:582.89

LIBANORIDIN—A NEW COUMARIN FROM LIBANOTIS SCHRENKIANA

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 1, pp. 52–53, 1969

From the roots of Libanotis schrenkiana by extraction with methanol followed by chromatography on a column of alumina, we have isolated a new coumarin $C_{16}H_{16}O_5$ with mp 125–126° C (from a mixture of petroleum and diethyl ether), which we have called libanoridin. The IR spectrum of this substance (Fig. 1) is typical for coumarins [1]. The

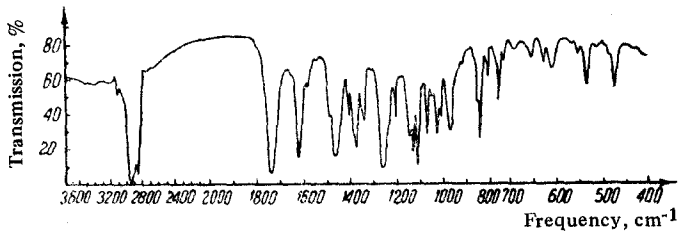


Fig. 1. IR spectrum of libanoridin in paraffin oil (UR-10).

values of the chemical shifts and the spin-spin coupling constants in the NMR spectrum of libanoridin (Fig. 2) and also the assignments of the signals are given in the table. The assignments were made on the basis of a previous study of the NMR spectra of natural coumarins [2].

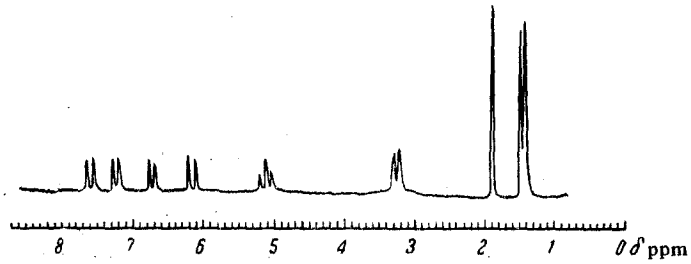
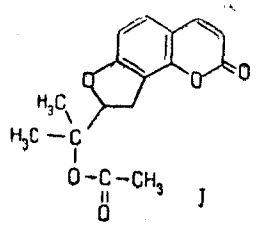


Fig. 2. NMR spectrum of libanoridin in deuterochloroform (JNM-4H-100, O-tetramethylsilane).

On the basis of the empirical formula and the features of the NMR spectrum, libanoridin can be ascribed the structure 5'-(1-acetoxy-1-methylethyl)-4',5'-dihydrofuro-2',3':7,8-coumarin (I).



I

Chemical shift, δ ppm	Multiplicity	J, Hz	Intensity	Assignment
1.49	Singlet	—	3H	CH_3
1.56			3H	CH_3
1.97			3H	CH_3—C—O—
3.30	Doublet	8.5	2H	CH—CH_2—Ar
5.14	Triplet	8.5	1H	
6.17	Doublet	10.0	1H	H_3 ring protons
6.72		8.5	1H	H_6 of the cou-
7.25		8.5	1H	H_5 marin nu-
7.62		10.0	1H	H_4 cleus

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27 May 1968

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UDC 577.15/17:582.89

COUMARINS OF THE ROOTS OF HERACLEUM SOMMIERI AND THE FRUIT OF H. ASPERUM

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 1, pp. 53-54, 1969

In the roots of Heracleum sommieri Manden., collected in the Mestia region of the Georgian SSR, by chromatography on paper in the petroleum ether—formamide system [1] we have found eight compounds of a coumarin nature from which, by means of column chromatography on acidic alumina, we have isolated pimpinellin $C_{13}H_{10}O_5$ with mp 117-119° C, isopimpinellin $C_{13}H_{10}O_5$ with mp 148-149° C, bergapten $C_{12}H_8O_4$ with mp 188-189° C, and sphondin $C_{12}H_8O_4$ with mp 189-192° C.

In the fruit of H. asperum M. B. prepared in the Kazbek region of the Georgian SSR using the system given above we have found six coumarin substances. From them, on a column of alumina, we have obtained bergapten and a furocoumarin fluorescing brownish yellow in UV light with mp 148-151° C, $[\alpha]_D^{21}$ +24.5° (chloroform), which is readily acetylated (mp 105-108° C) and oxidized and forms a number of derivatives under the action of acids. It has not yet been possible to identify this substance. A third substance was eluted from the column together with the bergapten. It was possible to isolate this compound only by means of column partition chromatography on silica gel (stationary phase formamide, mobile phase a 1:1 mixture of petroleum ether and benzene). This substance, $C_{17}H_{16}O_5$, with mp 100-102° C, proved to be phellopterin [2].

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29 July 1968

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UDC 547.972

FLAVONOIDS OF SERRATULA INERMIS

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 1, p. 54, 1969

We have studied the flowers of S. inermis Gilib. [1,2] and S. tinctoria (dyers sawwort) ssp. eu-tinctoria Br.-Bl. By chromatography on Kapron [3] of a methanolic extract, we have isolated two substances of a flavonoid nature.

Substance (I), $C_{15}H_{10}O_5$, forms bright yellow acicular crystals with mp 348-350° C. Its acetyl derivative $C_{21}H_{16}O_8$ with mp 186-187° C has three acetyl groups.

Substance (II), $C_{15}H_{10}O_6$, forms yellow acicular crystals with mp 330-331° C (from 50% ethanol). Its acetyl derivative $C_{23}H_{18}O_{10}$ with mp 226-227° C has four acetyl groups.