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COUMARINS FROM *Phlojodicarpus sibiricus*

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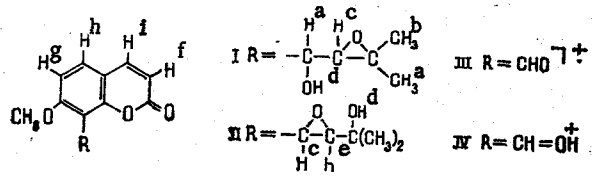
Phlojodicarpin [8-(2,3-epoxy-1-hydroxy-3-methylbutyl)-7-methoxycoumarin, $C_{15}H_{16}O_5$, mp 143-145°C, $[\alpha]_D^{25}$ − 37.5°], and isophlojodicarpin [8-(1,2-epoxy-3-hydroxy-3-methylbutyl)-7-methoxycoumarin, $C_{15}H_{16}O_5$, mp 132-134°C, $[\alpha]_D^{25}$ − 102.5°] have been isolated from the epigeal part of *Phlojodicarpus sibiricus*. The results of the IR, UV, PMR, and mass spectrometry of these compounds are given.

Phlojodicarpus sibiricus is used in folk medicine for the treatment of tumors. In order to isolate and identify the active principle, we have fractionated an alcoholic extract of the epigeal part of the plant, being guided by the results of biological control. The test used was a determination of cytotoxic activity *in vitro* with respect to four lines of cells: sarcoma-37, and Fisher, Ehrlich, and NK/Ly tumors according to the literature [1]. This showed that the biological activity was localized in the ethereal solution obtained on partitioning the alcoholic extract between water and ether (ED_{50} < 10 μg/ml). The main components of this solution were coumarins. By crystallization and preparative thin-layer chromatography, from the total coumarins we isolated two substances which we have called Phlojodicarpin (I) and isophlojodicarpin (II). Another coumarin was also present, in trace amounts.



Substances (I) and (II) had the same molecular weight of 276 and the same elementary composition, $C_{15}H_{16}O_5$. Strong absorption in the IR spectrum at 1610 and 1705 cm^{-1} showed the presence of a coumarinic lactone ring. Each compound contained a hydroxy group (3430 and 3410 cm^{-1}, respectively) and an epoxide ring (3000, 1246, and 947 cm^{-1}). Isophlojodicarpin had a fourth epoxide band at 863 cm^{-1}. In phlojodicarpin this was masked by the absorption of two adjacent aromatic C–H bonds at 825 cm^{-1}. The two compounds had the same UV spectrum with maxima at 260 and 328 nm which did not shift on the addition of sodium methanolate. This permitted them to be assigned to the 7-OR-substituted coumarins [2].

The M − 30 ion in the mass spectra of (I) and (II) showed the presence of a methoxy group attached to an aromatic ring. More intensive fragments with m/e 204 and 205 we ascribe to structures (III) and (IV), from which it follows that one of the oxygen atoms is attached to a benzene carbon atom. Other intensive ions are formed by the loss of HCO and CH_2O from

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(III) and (IV). The mass spectra of (I) and (II) were almost identical, with the exception of the fact that single signals of phlojodicarpin ions were replaced by clusters in the spectrum of (II).

In the PMR spectrum of (I), the signals of protons a, b, c, and d were represented in the form of complex multiplets. We explain this by the fact that (I) can exist as various conformers stabilized by intramolecular hydrogen bonds of the hydroxyl with the oxygen atoms of the epoxide, lactone, or methoxy groups. On the addition of Eu(dpm)$_3$ and heating, the corresponding signals acquired the spin–spin splitting and the paramagnetic shift expected for structure (I). However, each of the protons g, i, and f then appeared in the form of two doublets of equal intensity and the proton h in the form of a triplet. The ratio of the intensities within these multiplets changed on heating. Cases of the splitting of signals of protons remote from the center of coordination of a paramagnetic ion have been observed repeatedly (see, for example, [3]) and can be explained by conformational features of the complex.

The PMR spectrum of isophlojodicarpin did not contain these complicating features. The assignment of the signals is given in the Experimental part. The spin–spin coupling constant J_{bc} = 5 Hz, which permits the Z configuration to be assigned to the substituents in the oxirane ring. In this respect, (II) differs from its analog phebalosin for which the structure of an E-epoxide has been adopted [4]. In an isomer of (II), lophopterol, the side chain is attached at position 6 of the coumarin nucleus [5].

A third coumarin was found in trace amounts. Its mp was 92-93°C. Its UV spectrum had a maximum at 322 nm showing no displacement under the action of ionizing additives. Its IR spectrum was similar to those of (I) and (II) but there were two differenences: There was no absorption of an OH group and there was an additional peak at 1730 cm^{-1}. We assumed that this substance was an acyl derivative of (I) or (II). However, it proved to be stable to alkaline hydrolysis. Its structure has not been determined.

The pure coumarins (I) and (II) possessed no cytotoxic properties.

The epigeal part of the plant used in this work was collected in the mountains of the Gobi-Altai in the region of Lake Orog-nur (Mongolian Peoples' Republic) in the flowering stage. Other coumarins — visnadin and dihydrosamidin — have been isolated previously from the roots of *Phlojodicarpus sibiricus* of unknown provenance [6].

EXPERIMENTAL

Melting points were determined on a Kofler instrument and are uncorrected. UV spectra were taken on an SF-4A spectrophotometer in ethanol, IR spectra on a UR-10 instrument in KBr tablets and in paraffin oil, mass spectra on an MKh-1303 mass spectrometer with a system for direct introduction at an energy of 50 eV and a temperature of 100°C, and PMR spectra on a BS 487C spectrometer in deuterochloroform or deuteroacetone at temperatures of 20 and 60°C with HMDS as internal standard. The results of elementary analysis corresponded to the calculated values.

Isolation of the Coumarins. The dried and comminuted plant (2.3 kg) was extracted three times with 10-liter portions of 96% ethanol. The extract obtained was filtered, evaporated in vacuum to a volume of ~1 liter, and diluted with water. The precipitate that deposited was separated off and was dissolved in 300 ml of ether, and the solution was washed with 0.5% caustic potash solution and with distilled water. After drying with sodium sulfate and evaporation of the ether, 75 g of an oily liquid was obtained which, on standing in the refrigerator, deposited 4.3 g of pale yellow crystals of combined coumarins. Preparative thin-layer chromatography on silica gel in the solvent system benzene–ethyl acetate (2:1) separated the material into fractions containing a mixture of (I) and (II) and the pure minor ketone. The first fraction was crystallized several times from benzene. In this process, the crystals became enriched in compound (I) and the mother liquid in (II). For the complete separation of (I) and (II) we used preparative thin-layer chromatography on silica gel in the solvent system chloroform–methanol (10:1). This gave 1.04 g of (I), 92 mg of (II), and 3 mg of the minor coumarin.

Phlojodicarpin (I), $C_{15}H_{16}O_5$. mp 143-145°C, $[\alpha]_D^{25}$–37.5° (c 8.64; methanol), mol. wt. 276. UV spectrum, λ_{max} (log ε), nm: 260 (3.37), 328 (4.25). IR spectrum, cm^{-1}: 3440 (OH), 3000, 1249, 937 (epoxide), 2925 (OCH_3), 1705 (CO), 1612 (C=C), 843 (arom.). Mass spectrum,

m/e (%): 276, M(70); 246, M–CH_2O (62); 206 (40); 205, III (95); 204, IV (100); 191 (33); 189 (92); 176, III–COH (95); 175, IV–COH (94); 161 (30); 148 (23); 147 (47); 146 (52); 78 (21); 73 (24); 71 (20); 43 (47). PMR spectrum, δ, ppm (paramagnetic shift)*: 1.34 s, $3H^a$ (Δ 20 Hz); 1.41, s, 3 H^b (Δ 31 Hz); 2.90, d, H^c, J_{ce} = 3 Hz (Δ 43 Hz); 3.65, s, OCH_3 (Δ 10 Hz); 3.84, m, H^d (Δ 70 Hz); 4.50, d, H^e, J_{ce} = 3 Hz (Δ 54 Hz); 6.09, two d, H^f, J_{fi} = 10 Hz (Δ 11 Hz); 6.69, two d, H^g, J_{gh} = 9 Hz (Δ 10 Hz); 7.15, tr, H^h (Δ 5 Hz), 7.49, two d, H^i, J_{if} = 10 Hz (Δ5 Hz).

Isophlojodicarpin (II), $C_{15}H_{16}O_5$, mp 132-134°C, $[\alpha]_D^{25}$ – 102.5° (methanol), M 276. UV spectrum, λ_{max} (log ε, nm): 260 (3.87); 328 (4.25). IR spectrum, cm^{-1}: 3430, 3000, 1246, 930, 860. 1714, 1610, 835. PMR spectrum, δ, ppm: 1.31, m, 6 H^a; 3.68, s, OCH ; 3.80, d, H^b, J_{bc} = 5 Hz; 4.11, s, H^d; 4.55, d, H^c, J_{bc} = 5 Hz; 6.11, d, H^f, J_{fi} = 10 Hz; 6.61, d, H^g, J_{gh} = 8 Hz; 7.34, d, H^h, J_{gh} = 8 Hz; 7.73, d, H^i, J_{fi} = 10 Hz.

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*The chemical shifts are given for a solution in deuterochloroform at 20°C, and the spin–spin coupling constants are taken from the spectrum recorded with the addition of $Eu(dpm)_3$ at 60°C.

ESSENTIAL OIL OF *Blumea mollis*

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The alkanes n-triacontane and n-hentriacontane, 2,3-dimethoxy-p-cymene, chrysanthanone, 2,4,5-trimethoxyallylbenzene, methyl 5-isopropyl-2-methylcyclopentenecarboxylate, and caryophyllene oxide have been isolated from the essential oil of *Blumea mollis* by chromatographic methods. The identities of these terpenoids have been established by physicochemical and spectral methods.

Blumea mollis DC [1] (family Compositae) is a common weed growing in India and Sri Lanka. Its leaves are used in Indian medicine [2]. The antimicrobial activity of the oil of the plant has been investigated [3]. Related species of plants have been studied previously [4, 5], but there is no information on the essential oil of *Blumea mollis* in the literature. This induced us to begin a chemical study of the plant the results of which are given below.

From the essential oil of *Blumea mollis* by chromatographic methods we have isolated the alkanes n-triacontane and n-hentriacontane, 2,3-dimethoxy-p-cymene, chrysanthanone, 2,4,5-trimethoxyallylbenzene, methyl 5-isopropyl-2-methylcyclopentenecarboxylate, and caryophyllene oxide. The identities of these terpenoids have been established by physicochemical and spectral methods.

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