KHELLACTONE DERIVATIVES FROM Phlojodicarpus sibiricus

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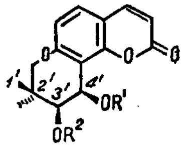
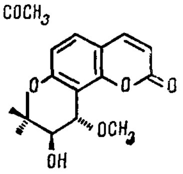
The composition of the coumarin compounds in plants of the genus Phlojodicarpus varies greatly according to the growth site and the time of gathering. Continuing a study of this phenomenon, we have subjected to ethanolic extraction the epigeal part of Phlojodicarpus sibiricus (Steph. ex Speng.) K.-Pol., gathered at the end of flowering in the south of Chita province. When the concentrated extract cooled, it deposited an unresolvable crystalline mixture of two esters of cis-khellactone (about 0.8%) – suksdorfin (I) and 3'-O-acetyl-4'-O-(2"-methylbutanoyl)-cis-khellactone (II). The mother liquor was eluted with water and extracted with ether. The coumarins were isolated from the ethereal extract after its treatment with 0.5% KOH solution. Chromatography on silica gel in the petroleum ether–diethyl ether (9:1) solvent system yielded two stereoisomeric methylated khellactones (III) and (IV) (about 0.01% each).

I. $R' = (CH_3)_2CHCH_2CO; R^2 = COCH_3$
II. $R' = C_2H_5CH(CH_3)CO; R^2 = COCH_3$
III. $R' = CH_3; R^2 = H$





IV

Compounds (I) and (II) were identified on the basis of the following facts. Their coumarin nature followed from the presence of characteristic adsorption bands in the UV and IR spectra (λ_{max} 245, 258, 328 nm; ν_{max} 620, 1670 cm^{-1}). A strong band at 1740 cm^{-1} showed the presence of an ester group. Analysis of the PMR spectrum, taken in $CDCl_3$, and its comparison with literature information showed that (I) and (II) were dihydropyranocoumarins and differed by the acyl residues at C-4'. The positions of the signals of the protons of the coumarin nucleus, and also of H-3' for (I) and (II) were identical with those of pteryxin [1]. However, the methyl group of the acetyl residue at C-3' resonated in the form of two singlets (about 2.1 ppm) and the proton at C-4' in the form of two doublets with J = 4.9 Hz at 6.56 and 6.57 ppm. The acyl residues were identified from the PMR results as an isovaleric acid residue for suksdorfin (I) and an α-methylbutyric acid residue for 3'-O-acetyl-4'-O-(2"-methylbutanoyl)-cis-khellactone (II) [1, 2].

cis-4'-O-Methylkhellactone (III), $C_{15}H_{16}O_5$, M^+ 276, mp 136-137°C (from ether); PMR spectrum in $CDCl_3$, δ, ppm (J, Hz): 6.26 (d, 9.5) H-3; 7.63 (d, 9.5) H-4; 7.32 (d, 8.6) H-5; 6.76 (d, 8.6) H-6; 1.44 and 1.42 (s) 2 CH_3; 3.88 (dd, 5 and 7), H-3'; 4.71 (d, 5) H-4'; 2.95 (d, 7) OH; 3.88 (s) OCH_3.

trans-4'-O-Methylkhellactone (IV), $C_{15}H_{16}O_5$, M^+ 276, mp 161-162°C (from ether) [3]; PMR spectrum in $CDCl_3$, δ, ppm (J, Hz); 6.23 (d, 9.5) H-3; 7.59 (d, 9.5) H-4; 7.31 (d, 8.6) H-5; 6.78 (d, 8.6) H=6; 1.49 and 1.44 (s) $2CH_3$; 3.92 (dd, 3 and 7) H-3'; 4.56 (d, 3) H-4'; 2.15 (d, 7) OH; 3.66 (s) OCH_3.

To establish the structures of the last two substances we used the following facts. The addition of trichloroacetyl isocyanate to (III) caused a shift of the H-3' signal by 1.64 ppm and of the H-4' signal by 0.4 ppm. The corresponding differences for (IV) were 1.53 and 0.2 ppm. Consequently, the methoxy group was located at C-4' [4]. The $J_{3',4'}$ SSCC was 5.0 Hz in (III) and 3.0 Hz in (IV). These values and the resonance of the gem-methyl groups permitted the methylated khellactones to be assigned the stereochemistries (III) and (IV), respectively [5]. So far as we are aware, this is the first time that these compounds have been isolated from natural sources.

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ISOIMPERATORIN FROM Phlojodicarpus sibiricus

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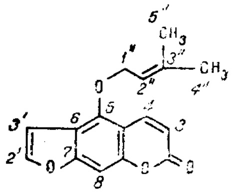
To confirm statements made previously concerning the instability of the chemical composition of plants of the genus Phlojodicarpus, we have investigated an ethanolic extract of Phlojodicarpus sibiricus Steph. ex Speng. K.-Pol., collected in the environs of Yakutsk in the flowering phase.

The whole plant was extracted with ethanol. The ethanolic extracts were concentrated to small volume and cooled, and the crystalline mixture of suksdorfin and 3'-O-acetyl-4'-2''-methylbutanoyl-cis-khellactone that deposited was separated off. It was established by PMR spectroscopy that the mixture of products isolated was quantitatively and qualitatively identical with the mixture of esters isolated from the plant growing in the Chita province [1]. The amount of esters was ∿1.5% on the weight of the dry plant.



The residual extract was diluted with water and was extracted successively with petroleum ether and dimethyl ether. Both extracts were treated with 0.5% KOH and were washed with water. The ethereal extract yielded umbelliferone, which was identified from its physicochemical constants. The petroleum ether extract was chromatographed on SiO_2 using petroleum ether as eluent. This gave a compound with the composition $C_{16}H_{14}O_4$, mp 107-108° (from benzene); λ_{max} (CH_3OH): 220, 248, 260, 267, and 309 nm. These results, and also the PMR spectrum, agreed with the characteristics of imperatorin [2]. The ^{13}C spectrum also agreed with the structure of the latter. The assignment of the signals was made on the basis of a comparison of the spectra of related substances and by the off-resonance method [3, 4]. Below, we give the chemical shifts of the carbon atoms of imperatorin in the ^{13}C NMR spectra taken in DMSO-d_6 (ppm relative to TMS):

C-2	160,1	s	C-6	113,9	s	C-3'	105,5 d
C-3	112,4	d	C-7	157,3	s	C-1''	69,4 t
C-4	139,6	d	C-8	93,6	d	C-2''	119,5 d
C-4a	106,8	s	C-8a	152,1	s	C-3''	139,0 s
C-5	148,6	s	C-2'	146,0	d	C-4''	18,0 q
						C-5''	25,5 q

The evaporated aqueous residue was chromatographed on SiO_2, and chloroform—methanol (9:1) eluted a crystalline compound (yield 0.15%) identical in its melting point and ^1H and ^{13}C

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