Continuing the study of these plants, we have isolated from the roots a second lactone of the coumarin group with the composition $C_{21}H_{24}O_7$ (I), mp 85–86° C (n-hexane) $[\alpha]_D^{21}$ +48° (c 3.33; dioxane; l 2 dm). On paper chromatography and thin-layer chromatography, compound I forms a spot with the same R_f value as dihydrosamidin.

On the basis of its physicochemical constants, IR spectrum, and the products of alkaline cleavage, compound I has been identified as 4'-acetoxy-2',2'-dimethyl-3'-(1"-methylbutyryloxy)-3',4'-dihydropyrano-5',6':7,8-coumarin (visnadin). Until recently, the only source of this coumarin has been the fruit of Ammi visnaga, family Umbelliferae [2,3]. We have found visnadin for the first time among the wild-growing plants of the USSR.

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THE STRUCTURE OF AGASYLLIN

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We have previously [1] reported the isolation from the fruit of Agasyllis latifolia (M. B.) Boiss, family Umbelliferae, of a new alkylcoumarin—agasyllin, $C_{19}H_{20}O_5$, with mp 78–80° C $[\alpha]_D^{24}$ −44° (chloroform, c 0.91; l 2 dm).

When agasyllin is saponified with 5% methanolic caustic potash, a hydroxylactone $C_{14}H_{14}O_4$ is formed with mp 177–178° C, $[\alpha]_D^{22}$ −13.4° (chloroform; c 0.56; l 2 dm); monoacetate $C_{16}H_{16}O_5$ with mp 137–138° C, which, on the basis of its physicochemical constants and NMR spectra has been identified as (−)-3'-hydroxy-3',4'-dihydropyrano [5',6':7,6]coumarin—a known product of the alkaline saponification of decursin [2].

In the NMR spectrum of agasyllin (spectrum taken on a JNM-4-H-100 spectrometer at 100 MHz with a solution of the substance in carbon tetrachloride), in the weak-field region there are signals characteristic for 6,7-substituted coumarins. Signals at δ = 7.46, 7.08, 6.65, and 6.10 ppm are due, respectively, to the C_4, C_5, C_8, and C_3 protons of the coumarin nucleus [3]. In addition, there are peaks at δ = 1.37 ppm (6 H) (protons of a gem-dimethyl grouping) and at δ = 1.94 and 1.83 ppm (6 H) (protons of two methyl groups in the acid residue). An octet in the δ = 2.4–3.3 ppm region relates to the nonequivalent methylene protons at C'_4, leading to splitting because of spin-spin coupling with the methine proton at C'_3, the resonance signal of the latter appearing at δ = 5.07 ppm. As compared with the spectrum of the hydroxylactone, the signal of this proton in the spectrum of agasyllin has been displaced into the weak-field region by 1.19 ppm. This phenomenon characterizes agasyllin as the ester of a secondary alcohol [4] and, moreover, shows that it belongs to the group of dihydropyranocoumarins [5]. Since the vinyl protons of angelates, tiglates, and esters of the coumarins with senecioic acid may differ from one another [6–8] and the corresponding proton of agasyllin gives a signal at δ = 6.1 ppm, we have identified the acid residue as angeloyl.

Thus, agasyllin is (−)-3-angeloyloxy-3',4'-dihydropyrano-5',6':7,6-coumarin. In its NMR spectrum and the results of alkaline hydrolysis, agasyllin is identical with an acylcoumarin which has been isolated in the form of an oil from the roots of Seseli Libanotis (L.) Koch., family Umbelliferae [9].

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NMR SPECTRA OF SUBSTITUTED PSORALENS

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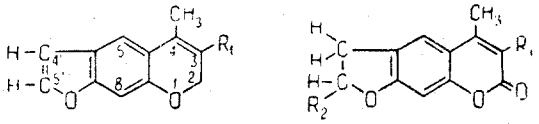
We have studied the NMR spectra of C-substituted derivatives of psoralen and of 4',5'-dihydropsoralen with the general formulas:

I. 4-Methylpsoralen (A; R_1 = H).
II. 3,4-Dimethylpsoralen (A; R_1 = CH_3).
III. 3-Ethyl-4-methylpsoralen (A; R_1 = C_2H_5).
IV. 3,4,5'-Trimethyl-4',5'-dihydropsoralen (B; R_1 = R_2 = CH_3).
V. 3-Ethyl-4,5'-dimethyl-4',5'-dihydropsoralen (B; R_1 = C_2H_5; R_2 = CH_3).



The spectra were obtained on a JNM-4-H-100 instrument at 100 MHz using hexamethyldisiloxane (HMDS) as internal standard, its signal being taken as 0 (δ scale). The spectra of compounds I–III were taken in deuterochloroform and those of compounds IV and V in carbon tetrachloride. The table gives the chemical shifts (in ppm) and the spin-spin coupling constants (J) of the protons of the compounds listed.

Substance	3C–CH_3 (S)*	3C–CH_2–CH_3 (K) (T)	4C–CH_3	5C–H (S)	4'C–H** / 4'C–H***	5'C–H** / 5C'H–CH_3***	8C–H (S)
(I)	—	—	2.40 (D) 1.2****	7.70	6.77 (D) 2.0****	7.60 (D) 2.0****	7.33
(II)	2.15	—	2.40 (S)	7.72	6.77 (D) 2.0****	7.60 (D) 2.0****	7.35
(III)	—	2.61; 1.08 7.4; 7.3****	2.36 (S)	7.67	6.74 (D) 2.0****	7.57 (D) 2.0****	7.27
(IV)	1.93		2.12 (S)	7.06	3.25 (Q); 2.75 (Q)	4.86 (M); 1.42 (D) 6,4****	6.28
(V)	—	2.45; 1.02 7.1; 7.1****	2.18 (S)	7.12	3.25 (Q); 2.75 (Q)	4.87 (M); 1.41 (D) 6.2****	6.33

*S, singlet; D, doublet; T, triplet; Q, quartet; M, multiplet.
**For compounds I–III.
***For compounds IV and V.
****Spin-spin coupling constants, Hz.

It is known that in furocoumarin derivatives the signal of the H_4 proton is shifted to a weaker field (in psoralen it is at 7.93 ppm [1]). Since all the compounds under consideration are substituted by a methyl group at C_4, this signal is lacking for them. The signal for the proton at C_3 (6.14 ppm, not shown in the table) is seen only in the spectrum of 4-methylpsoralen (I).

As in all the furocoumarins, the protons at C_5 and C_8 are nonequivalent and give two singlets at 7.06–7.72 and 6.28–7.35 ppm, respectively. The chemical shift of the proton in the 5 position is affected by conjugation with the α,β-unsaturated carbonyl group of the α-pyrone ring.