LATILOBINOL – A NEW TERPENOID COUMARIN FROM Prangos latiloba

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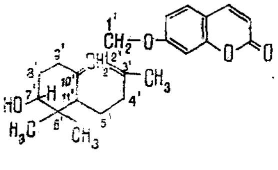
In an investigation of the chemical composition of Prangos latiloba Eug. Kor., in addition to other coumarin derivatives, we have isolated a new terpenoid coumarin with the composition $C_{24}H_{30}O_4$, mp 121-122°C, $[\alpha]_D^{18}$ $-63°$ (c 0.92; chloroform), which we have called latilobinol (I).

The IR spectrum of (I) has the following characteristic absorption bands (cm^{-1}): 3460 (OH group), 1700 (α-pyrone C=O), 1610, 1560, and 1510 ($-CH=CH-$ bond in an aromatic ring). The presence of one secondary hydroxy group in the molecule of (I) was confirmed by the production of a monoacetate (II), $C_{26}H_{32}O_5$, with mp 191-192°C. The IR spectrum of (II) lacked the absorption band of a hydroxy group.

When compound (I) was treated with a mixture of acetic and sulfuric acids, umbelliferone (III), $C_9H_6O_3$, mp 232-233°C, and a sesquiterpene alcohol (IV) with the composition $C_{15}H_{26}O_2$ were formed. The structure of the latter and, consequently, that of (I) were determined unambiguously from the PMR spectrum of (I) (HX-90, $CDCl_3$, TMS) which showed the signals of the following protons: H_3 and H_4 (doublets, 6.20 and 7.60 ppm, J = 10 Hz), H_5 and H_6 (doublets, 7.31 and 6.81 ppm, J = 8.5 Hz), H_8 (singlet 6.75 ppm), $-CH=$ (triplet, 5.40 ppm, J = 6 Hz), $=CH_2$ (singlets, 4.63 and 4.84 ppm), $-O-CH_2-C=$ (doublet, 4.60 ppm, J = 6 Hz), $-CH-O-$ (quartet, 3.35 ppm, J_1 = 10 Hz, J_2 = 5 Hz), $=C-CH_3$ (singlet, 1.77 ppm), $>C<^{CH_3}_{CH_3}$ (singlets, 0.75 and 1.02 ppm). In addition, in the interval of 1.60-2.40 ppm there is a series of signals due to the protons of aliphatic and cyclic methylene groups, of a methine group in a ring, and of a hydroxy group (totalling 10 H).

The PMR spectrum of (II) shows an additional signal from $-OCO-CH_3$ groups (singlet, 2.05 ppm) and a paramagnetic shift of the signal from the hemihydroxylic proton that was observed at 4.64 ppm. Likewise, the chemical shifts of the signals of the gem-dimethyl groups have changed very slightly, one of them undergoing a diamagnetic (0.08 ppm) and the other a paramagnetic (0.05 ppm) shift. This indicates that the hydroxy group in the molecule of (I) is close to the gem-dimethyl grouping, i.e., in position 7', which agrees well with the features of the PMR spectrum of (I) taken with the addition of $Eu(DPM)_3$, in which the signals of the gem-dimethyl groups undergo a pronounced paramagnetic shift and appear at 1.27 and 1.57 ppm.

Thus, it follows from the PMR spectra of (I) and (II) that the terpenoid part of the molecule of (I) has the same structure as that of farnesiferol B (V), i.e., it consists of two fragments, one of which is a six-membered ring and the other is an open chain, and the latter is attached to the coumarin nucleus in position 7; moreover, it is most likely that the exocyclic methylene group in (I) occupies the same position as that in (V), namely position 10'. Hence the following structure is suggested for latilobinol:



Consequently, (I) is a stereoisomer of (V) [1]. The study of the stereochemistry of (I) is continuing.

LITERATURE CITED

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