A CHEMICAL STUDY OF THE ROOTS OF Libanotis lehmanniana

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It has been shown previously [1] that the roots of Libanotis lehmanniana Bunge contain about 0.8% of coumarins. Their composition was not studied. We have investigated the roots of this species collected in August, 1969 in the spurs of the Zaravshan range and the upper reaches of the R. Remon and have found that these contain substances reacting with diazotized sulfanilamide having on paper chromatography R_f 0.65, 0.76, 0.40, and 0.28 (traces).

By molecular chromatography on alumina we have isolated three individual substances. A substance with mp 136-137°C (from methanol) is neutral and gives the Liebermann–Burchard reaction for steroids. On the basis of a mixed melting point and its IR spectrum, it was identified as β-sitosterol.

The second component, $C_{21}H_{22}O_7$, mp 78-80°C [from a mixture of carbon tetrachloride and petroleum ether (1 : 30)] was identified by its IR spectrum and a mixed melting point as 3'-acetoxy-4'-angeloyloxy-3',4'-dihydroseselin (pteryxin), which has been isolated from the roots of Libanotis condensata Crantz [2].

We have studied seven other species of Libanotis growing in central Asia by paper chromatography. Pteryxin was found only in the green parts and roots of the species mentioned. The content of pteryxin determined by a chromatospectrophotometric method [3] in the roots of the plant was 3.34% and in the green parts 0.94%. Because of its high content of pteryxin, Libanotis lehmanniana may be regarded as a source of raw material for the production of this lactone.

When the chromatographic column was washed with acetone, a third substance was isolated with the formula $C_{17}H_{18}O_6$, mp 127-128°C, $[\alpha]_D^{20}$ −39.17° (c 0.6, ethanol) which, according to its IR spectrum, was a chromone [λ_{max} 231, 251, 259, 295 nm (log ε 4.20, 4.26, 4.25, 3.92)]. The fact that it is a chromone is also shown by the absorption bands in its IR spectrum (cm^{-1}): 1650 (carbonyl of a conjugated ketone), 3080 (C−H bond of a pyrone ring), 1635, 1590 (aromatic nucleus). Absorption bands at 827, 855, and 880 cm^{-1} show that its molecule contains a 1,2,3,4,5-pentasubstituted aromatic nucleus, and bands at 1380 and 1392 cm^{-1} show the presence of a gem-dimethyl grouping. A narrow band at 1736 cm^{-1} may, in view of the absence of lactone properties, be ascribed to the carbonyl of an ester grouping. The presence of an ester group was confirmed by the formation on alkaline hydrolysis of a hydroxychromone $C_{15}H_{16}O_5$ with mp 199-200°C. On the basis of its physicochemical constants and IR spectrum, the latter was identified as hamaudol, previously isolated from several species of the genus Angelica [4-6]. The isolation of hamaudol in these cases was preceded by the alkaline treatment of the vegetable extracts with caustic alkali according to Späth. In the plants the hamaudol is apparently present in the form of esters, as is shown by the isolation of its methylthioacrylate (seselirin) from Seseli sessiliflorum Schrenk [7].

The composition of hamaudol differs from that of the acylchromone by a C_2H_2O group. Consequently, the latter is the acetate of this hydroxychromone. The acetic acid residue is present in the hamaudol in position 7, since the carbonyl band of the ester in the IR spectrum is in the 1736 cm^{-1} region and the substance gives the reaction for a phenolic hydroxyl with ferric chloride.

In the NMR spectrum of the chromone, singlets at 1.28 ppm (6H) and 2.00 and 2.27 ppm (3H each) are due, respectively, to the protons of a gem-dimethyl, an acetyl, and a C-2 methyl group. A triplet at 5.12 ppm with J = 5 Hz (1H) and a multiplet with a center at 2.82 ppm (2H) are due to the spin–spin coupling of methine and methylene protons in positions 7 and 6. The paramagnetic shift of the first signal is due to the

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electron-accepting influence of the acetyl group present on carbon atom 7. The signal of the sole aromatic proton appears in the form of a singlet at 6.37 ppm. The facts given show that the substance is hamaudol 7-monoacetate, which has been described previously, in 1960 [4].

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