SHIKONIN FROM LITHOSPERMUM OFFICINALE

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According to literature data [1] the roots of Lithospermum officinale L. (common gromwell) contain a red pigment which so far has not been studied.

The roots used for the investigation were collected in September 1965 in the Botanical Garden of the All-Union Scientific Research Institute for Medicinal and Aromatic Plants (Moscow Oblast). Qualitative reactions showed that they contained a pigment with similar properties to alkanin and shikonin [2, 3, 6, 7].

The pigment was isolated by Brockmann's method [4, 5]. 4.2 kg of the roots was extracted twice with petroleum ether (bp 40°-70° C) in a ratio of 1 : 6 for 18 hr. The red extracts were combined and evaporated in vacuum. This gave 7.95 g of a resinous substance. 2 grams of this substance was dissolved in 800 ml of petroleum ether and extracted with 1 *l* of 1 N aqueous potassium hydroxide, the pigment passing into the alkaline aqueous layer with a blue coloration. The alkaline solution was washed with petroleum ether (2 × 200 ml) and left to stand for 48 hr at room temperature. Then the solution was acidified with 50% acetic acid until a red color appeared (pH 6). This gave a precipitate of 1.1 g (yield on the raw material ~0.1%) of a dark red crystalline substance having the composition $C_{16}H_{16}O_5$, mp 143°-146° C (from benzene) which proved to be the known shikonin isolated from the roots of Lithospermum erythrorhizon Sieb. et Zucc.

The IR spectrum of the compound obtained had bands at 1622 cm^{-1} (C=O- OH of a carbonyl group linked by an intramolecular hydrogen bond to a neighbouring hydroxy group, 3150 (OH group), 1579 cm^{-1} (C=C double bond); and the IR spectrum had λ_{max} 215, 277, 515, 554 mμ (log ε 4.561, 3.960, 2.866, 3.661). The IR and UV spectra were identical with those of an authentic sample of shikonin. A 1% solution in benzene was dextrorotary.

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OSTRUTHOL FROM XANTHOGALLUM PURPURASCENS

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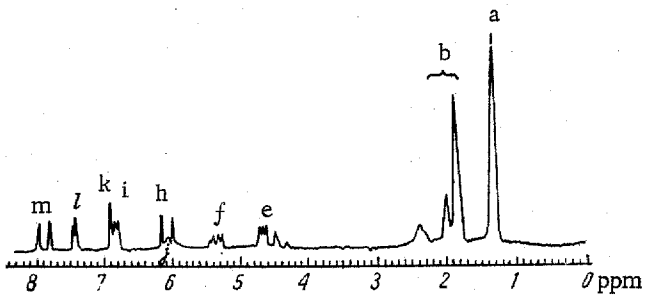
The dihydropyranocoumarin xanthogallin has been isolated previously [1, 2] from the roots of X. purpurascens Lallem.

By chromatography on alumina with elution by benzene we have obtained from the mother liquor an additional amount of xanthogallin (0.82%) and a lactone of the composition $C_{21}H_{22}O_7$ with mp 141°-143° C (0.11%). The UV spectrum of the lactone has the following absorption maxima: λ_{max} 220, 250, 260, 267, 310 mμ (log ε 4.14, 4.16, 4.11, 4.14, 4.05); these are characteristic for furocoumarins substituted in position 5. Its IR spectrum (taken on a UR-10 spectrograph) exhibits absorption bands at 3505 cm^{-1} (hydroxyl), 3170, 3128 (C - H bond of a furan ring), 1697, 1630 (vibrations of furan and α-pyrone rings), and 1609, 1585 cm^{-1} (skeletal vibrations of a benzene ring) which also shows that the lactone belongs to the furocoumarin group.

The NMR spectrum (figure) shows that the lactone is a 5-monosubstituted furocoumarin (the spectrum was taken

on a JNM-C-60 NMR spectrometer as a solution in CCl_4, and the chemical shifts were calculated in parts per million with respect to tetramethylsilane as internal standard taken as 0). The doublets m and h (δ = 7.89 and 6.08) [3] relate to the protons in positions 4 and 3 of the coumarin nucleus; the doublets *l* (δ = 7.41, J = 2 c/s) and i (δ = 6.82, J = 2 c/s) are due to the presence of protons in positions 5 and 4 of the furan nucleus; the singlet k (δ = 6.90) may be assigned to a proton in position 8. The two peaks b (δ = 2.01 and 1.84) with an intensity of six proton units indicate the presence in the molecule of two olefinic methyl groups, one of which is present in the neighbourhood of a proton (multiplet 6.15 ppm) and the other on a completely substituted carbon atom. The singlet a (δ = 1.32), also with an intensity of six proton units, shows the presence of two equivalent methyl groups. The position of the signal at 1.32 ppm is characteristic for the grouping $(CH_3)_2-\overset{|}{C}-OH$. The single-proton quadruplet f and the two-proton multiplet e indicate the presence of a $-\overset{H}{O}C-\overset{H}{C}-$ grouping.



NMR spectrum of ostrutol

These features of the NMR spectrum and also the fact of the presence of one hydroxy group in the furocoumarin molecule with seven oxygen atoms altogether makes it possible to assume that the latter is apparently an ester of oxypeucedanin hydrate and angelic or tiglic acid. In actual fact, saponification of the lactone with 5% caustic soda solution in methanol gave a diol of the composition $C_{16}H_{16}O_6$ with mp 133° C identical from its IR spectrum and a mixed melting point test, with oxypeucedanin hydrate.

As was mentioned above, the signal of the ethylene proton of the acid of ostruthol absorbs at 6.15 ppm, while the ethylene proton of the angelate in deltoin, according to our results [2], absorbs at 6.15 ppm and in xanthogallin at 6.05 ppm. Fraser [6] has shown that the ethylene proton in methyl angelate absorbs at 5.97 ppm, and in methyl tiglate at 6.72 ppm. On this basis, Seshadri et al. [7] have shown that the acid in the selinidin that they have studied is angelic and not tiglic acid (absorption at 5.98 ppm but not at 6.57).

The results obtained permit the conclusion that the lactone that we have isolated is an ester of angelic acid and oxypeucedanin hydrate and corresponds to ostruthol. This conclusion is confirmed, in particular, by the melting point of the substance which, by a well-known analogy [4, 5, 8] should be much lower for a tiglate.

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