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# THE STRUCTURE OF SAMARCANDIN AND SAMARCANDONE, COUMARIN COMPOUNDS FROM FERULA SAMARCANDICA

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From the roots of Ferula samarcandica Kor. we have isolated, in addition to the known farnesiferol [1] and gummosin [2], two new crystalline substances. For one of them, with the composition $C_{24}H_{30-32}O_5$, the name samarcandin is proposed, and for the second, with composition $C_{24}H_{28-30}O_5$, which contains a keto group, the name samarcandone.

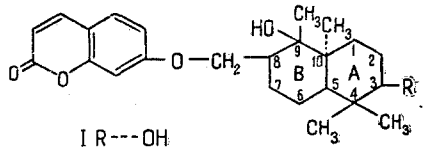
A study of the IR (figure) and UV spectra has shown that both substances belong to the coumarin series. This is also confirmed by the production of umbelliferone by the action of mineral acids on samarcandin. Samarcandin has two hydroxy groups, one of them, possibly secondary, being readily acetylated to give samarcandin monoacetate $C_{26}H_{34}O_6$. The second hydroxy group in samarcandin may be tertiary, since the compound $C_{24}H_{30}O_5$ formed on oxidation with chromic anhydride has maxima in the IR spectra for a keto group and for a hydroxyl and is identical with samarcandone.

Thus, samarcandone is a monoketo derivative of samarcandin. Hydrogenation of the latter gives dihydrosamarcandin $C_{24}H_{34}O_5$. The IR spectrum of this substance has a maximum at 1755 $cm^{-1}$, which can be explained by the disappearance of a double bond in a lactone ring. At the same time, the results of the hydrogenation of samarcandin indicate that it has no double bonds in the nonumbelliferone part of the molecule, but we do not consider that the question of the absence of a double bond from the nonumbelliferone part of the molecule of samarcandin or samarcandone is finally resolved.

The dehydrogenation of samarcandin with selenium gives 1, 2, 5, 6-tetramethylnaphthalene, which shows that it is similar structurally to farnesiferol A [1], gummosin [2], and badrakemin [3]. To elucidate the features of the structure of samarcandin, we dehydrated samarcandone in acetone solution and obtained the keto compound $C_{24}H_{28}O_4$. On exhaustive hydrogenation, this substance formed a diol $C_{15}H_{28}O_2$ with mp 174-175° C, which was identical with the corresponding diol obtained from badrakemone [3].

On dehydration with ethyl hydrogen sulfate, samarcandin is converted into an amorphous substance the hydrogenation of which gives tetrahydrobadrakemin $C_{24}H_{34}O_4$ [3] and, probably, a diol $C_{25}H_{28}O_2$ with mp 158° C. These reactions show that the carbon skeleton and the ether bond linking the umbelliferone with the sesquiterpene triol have the same structure in samarcandin as in badrakemin. The question of the position of the tertiary hydroxyl in samarcandin and samarcandone was resolved on the basis of a study of the NMR spectrum of samarcandin. The position of the tertiary hydroxyl is most probably at a $CH_3$ group of ring B, which is shown by a singlet with $\tau$ 8.8.

Consequently, samarcandin is assigned the probable structure (I) and samarcandone (II).




I R---OH

II R=O

On the basis of biogenetic considerations, it may be assumed that the linkage of rings A and B in samarcandin and samarcandone is the same as in farnesiferol A, although this conclusion still requires experimental confirmation.

We have also detected samarcandin in an acetone extract of the roots of Ferula pseudoreoselinum (Rgl. et Schmal).

The roots of Ferula samarcandica Kor. were collected by an expedition led by the botanist L. P. Markova to the southwestern slopes of Malyi Chimgan of the Tashkent Ala-Tau.

## Experimental

Isolation of samarcandin and samarcandone. The comminuted air-dry roots of F. samarcandica were extracted three times with acetone, each time after five days' steeping at room temperature. The acetone extracts were combined, filtered, and evaporated. The residue—a yellowish viscous liquid (yield 11.5%)—was dissolved in diethyl ether, the acidic products were eliminated by shaking the ethereal solution with 3% aqueous KOH, and the neutral ethereal solution was cooled to −15° C for a long time. A crystalline precipitate of samarcandin deposited with mp 176-177° C (from ethanol or acetone), $[\alpha]_D$ +30° (c 5; ethanol). IR spectrum: 3500 $cm^{-1}$, 3460, 1725, 1708, 1620, 1576, 1552, 1514, 1460, 1417, 1380, 1350, 1325, 1295, 1240, 1200, 1179, 1133, 1080, 1056, 1020, 1000, 986, 942, 926, 914, 900, 878, 828

$cm^{-1}$. UV spectrum: $\lambda_{max}$ 326 mμ (log ε 4.24), shoulder 252 mμ.

Found, %: C 72.0; 72.16; H 8.22; 8.14. Calculated for $C_{24}H_{32}O_5$, %: C 72.00; H 8.00.

Samarcandin dissolves in chloroform, acetone, ethanol, and, comparatively sparingly, in ether.

Further cooling of the ethereal solution (after the isolation of the samarcandin) gave a crystalline substance—samarcandone—with mp 216-217° C (from ethanol), $[\alpha]_D$ +25.0° (c 2.5; ethanol). IR spectrum: 3547 $cm^{-1}$, 3440, 3350, 1702, 1698, 1615, 1545, 1495, 1395, 1350, 1290, 1242, 1200, 1180, 1152, 1132, 1000, 986, 960, 930, 860, 818 $cm^{-1}$. UV spectrum: $\lambda_{max}$ 322 mμ (log ε 4.05).

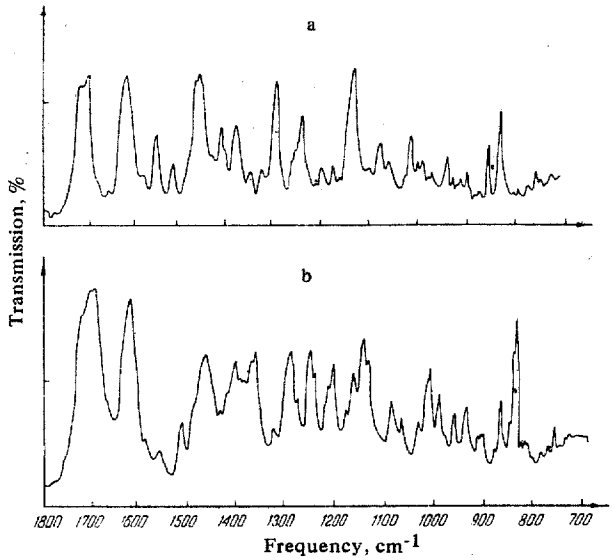
Found, %: C 72.12; 72.27; H 7.44; 7.44. Calculated for $C_{24}H_{30}O_5$, %: C 72.36; H 7.44.

We also isolated samarcandin and samarcandone from acetonic extract of the roots by chromatography on alumina (activity grade III) with chloroform elution. Gummosin and farnesiferol A were found and identified in the first resinous fractions in ethereal solution; the subsequent fractions contained samarcandone, and after this had been eluted samarcandin was obtained. Yield 6.13% of the weight of the resin.

Acid hydrolysis of samarcandin. In drops, 2 ml of concentrated sulfuric acid was added to a solution of 0.5 g of the substance in 4-5 ml of acetic acid.

After 10 min, the mixture was diluted with water and extracted with ether. The ethereal layer was shaken with 5% caustic potash. The alkaline layer was acidified. A precipitate of umbelliferone with mp 233-234° C (from water) deposited. Yield 15%.

Acetylation of samarcandin. A solution of 0.3 g of the substance in 2 ml of acetic anhydride and 2 ml of pyridine was heated in the water bath. The liquid was eliminated to give the monoacetate with mp 152-153° C (from a mixture of ether and petroleum ether), $[\alpha]_D$ +30° (c 1; ethanol). IR spectrum: 3570 $cm^{-1}$, 3500, 1725, 1620, 1553, 1540, 1506, 1460, 1395, 1375, 1350, 1320, 1283, 1262, 1240, 1200, 1175, 1160, 1147, 1132, 1018, 998, 985, 955, 935, 897, 855, 838 $cm^{-1}$. UV spectrum: $\lambda_{max}$ 325 mμ (log ε 4.07).




IR spectra of samarcandin (a) and samarcandone (b) (in paraffin oil).

Found, %: C 70.87; 72.62; H 7.97; 7.87. Calculated for $C_{26}H_{34}O_6$, %: C 70.59; H 7.69.

Saponification of the acetate yielded samarcandin.

Oxidation of samarcandin. A solution of 1 g of chromic anhydride in 2 ml of water was added dropwise to a cooled solution of 1 g of the substance in 15 ml of acetic acid. After 10 min, the mixture was diluted with water until a turbidity appeared and was then extracted with ether. The ethereal layer was washed with sodium carbonate solution until the acetic acid had been eliminated and was then dried with sodium sulfate, and the ether was distilled off. The residue consisted of samarcandone with mp 216-217° C (from ethanol).

Hydrogenation of samarcandin. One gram of the substance in solution in 20 ml of acetic acid was hydrogenated with 0.28 g of platinum oxide. The amount of hydrogen consumed was 292 ml. The catalyst was filtered off, and the filtrate was diluted with water and extracted with ether. The ethereal layer was washed with water and alkali and the ether was distilled off. The residue consisted of dihydrosamarcandin (0.44 g) with mp 182-184° C (from ethanol). On a plate coated with alumina (activity grade II) the substance gave a single spot on elution with chloroform. IR spectrum: 3483 $cm^{-1}$, 3460, 1755, 1627, 1508, 1465, 1430, 1390, 1370, 1350, 1325, 1300, 1290, 1270, 1260, 1235, 1160, 1115, 1080, 1070, 1010, 1000, 990, 970, 960, 935, 930, 905, 875, 860, 835, 810 $cm^{-1}$. UV spectrum: $\lambda_{max}$ at 324 and 290 mμ (log ε 1.87 and 3.73).

Found, %: C 71.59; 71.68; H 8.51; 8.38. Calculated for $C_{24}H_{34}O_5$, %: C 71.64; H 8.46.

Dehydrogenation of samarcandin. A mixture of 0.2 g of the substance and 0.2 g of selenium was heated to 250-300° C for 1 hr. The reaction product was dissolved in petroleum ether and filtered through a layer of alumina (activity grade II). The solvent was distilled off. The colorless crystals had mp 112-113° C (from ethanol) and gave no depression of the melting point in admixture with a sample of 1, 2, 5, 6-tetramethylnaphthalene.

Dehydration of samarcandone. A solution of 1.5 g of the substance in 100 ml of acetone containing 4 ml of sulfuric

acid was heated for 20 min, diluted with water, and extracted with ether, and the product was chromatographed on alumina (activity grade II). Elution was performed with ether. The first fractions consisted mainly of an oil. The subsequent fractions consisted of a crystalline substance—a keto compound with mp 142–143° C (from ether). IR spectrum: 1709 $cm^{-1}$, 1616, 1580, 1560, 1459, 1400, 1380, 1357, 1318, 1285, 1275, 1240, 1200, 1160, 1130, 1000, 895, 830 $cm^{-1}$. UV spectrum: $\lambda_{max}$ 323 mμ (log ε 4.6), shoulder 250 mμ.

Found, %: C 75.62; 75.72; H 7.56; 7.57. Calculated for $C_{24}H_{28}O_4$, %: C 75.79; H 7.36.

Hydrogenation of the keto compound. In 20 ml of acetic acid, 0.65 g of the substance was hydrogenated with 0.2 g of platinum oxide. After 3 hr, 306 ml of hydrogen had been added. The solution was diluted with water and extracted with ether. The neutral ethereal layer was dried, and the solvent was distilled off. This gave a colorless oil (0.53 g) which was heated in the water bath with 0.5 g of caustic potash in 15 ml of ethanol for 1 hr; after cooling, the mixture was diluted with water and ether. Extraction yielded 0.26 g of a diol $C_{15}H_{28}O_2$ with mp 174–175° C (from ether).

The substance gave no depression of the melting point in admixture with the diol $C_{15}H_{28}O_2$ from badrakemone [3].

Dehydration of samarcandin. A solution of 0.4 g of the substance in 4 ml of 10% ethyl hydrogen sulfate was heated in the water bath for 20 min and was then diluted with water and extracted with ether. The amorphous residue (0.34 g) with $R_f$ 0.71 (in a thin layer of alumina, activity grade II), on elution with ether, was hydrogenated in 10 ml of acetic acid with 0.1147 g of platinum oxide. The amount of hydrogen consumed was 170 ml. The mixture was diluted with water, and ethereal extraction yielded tetrahydrobadrakemin with mp 196–197° C (from ethanol). IR spectrum: 3520 $cm^{-1}$, 1763, 1632, 1585, 1515, 1485, 1420, 1395, 1350, 1325, 1302, 1280, 1240, 1203, 1165, 1132, 1101, 1080, 1070, 1020, 998, 970, 930, 901, 870, 848, 806, 770, $cm^{-1}$.

The ethereal solution contained traces of a substance having the same $R_f$ value as the diol $C_{15}H_{28}O_2$ with mp 158° C isolated from badrakemin.

The microanalyses were carried out by E. A. Sokolova; the UV, IR, and NMR spectra were recorded by T. V. Bukreeva and T. N. Timofeeva.

Summary

From an acetonic extract of the roots of Ferula samarcandica Kor. have been isolated farnesiferol A, gummosin, and two new coumarin substances, samarcandin $C_{24}H_{30-32}O_5$ and samarcandone $C_{24}H_{28-30}O_5$. Samarcandin has been converted into samarcandone and their probable structures—I and II—have been established.

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