CHEMICAL STUDY OF THE COMPOSITION OF THE POLYPHENOLIC COMPOUNDS OF Hibiscus syriacus

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The flowers and leaves of shrub althea, Hibiscus syriacus L., family Malvaceae, gathered in the Stavropol' botanical garden and in Damascus (Syria) have been investigated. It was established by qualitative chromatographic analysis that the epigeal part of the plant contained five flavonoid compounds, regardless of the growth site.

In order to isolate the flavonoids from the leaves, 100.0 g of air-dry comminuted raw material was exhaustively extracted with 60% ethanol in the boiling water bath in a flask with a reflux condenser. The combined alcoholic extracts were dried, were freed from lipophilic impurities by successive treatment with hexane and chloroform, and were extracted with ethyl acetate. The ethyl acetate extract was concentrated to 1/3 of its initial volume and was poured into a fivefold volume of hexane. A white precipitate deposited, consisting mainly of substance (I). The precipitate was separated off and was purified by recrystallization from aqueous ethanol; the filtrate was evaporated to dryness, the residue was dissolved with heating in 96% ethanol, and this solution was passed through a column filled with cellulose powder. Elution was carried out with water containing increasing amounts of ethanol. The fractions were repurified by gel filtration through Molselekt G-25.

Substances (II) and (III) were obtained in small amount.

The flavonoids from the leaves were isolated by extracting the raw material with acetone, freeing the concentrated acetone extract from lipophilic impurities, and extracting the flavonoid first with ethyl acetate and then with n-butanol. Substances (IV) and (V) were isolated from the butanolic fraction.

Substance (I) was taxifolin 3-O-β-D-glucopyranoside, $C_{21}H_{22}O_{12}$, $[\alpha]_D^{20}$ −40.0° (c 0.01; ethanol). The aglycon was taxifolin (dihydroquercetin), its UV-spectral characteristics corresponding to those described in the literature [1]. The PMR spectrum corresponded to that given in [1]. On oxidation with a mixture of iodine and sodium acetate, the glycoside and the aglycon were converted into isoquercitrin and quercetin, respectively [2].

Substance (II) was herbacetin 7-β-D-glucopyranoside, $C_{21}H_{20}O_{12}$, mp 248°C. The presence of a hydroxyl at C-8 was shown on the basis of the UV spectroscopy of the glycoside and its aglycon and of color reactions [1, 3, 4]. The substance corresponded in its physical and chemical properties to that described in the literature [5].

Substance (III) (isolated in small amount) was kaempferol 3-α-L-arabinoside 7-α-L-rhamnoside. Its structure was shown by UV spectroscopy and by acid hydrolysis under mild and severe conditions. Its properties corresponded to those described in the literature [6].

Substance (IV) was saponaretin, $C_{21}H_{20}O_{10}$, mp 194°C. Under the action of hydriodic acid it was split into apigenin and D-glucose. Under the action of 5% hydrochloric acid it isomerized into vitexin (apigenin 8-C-glucopyranoside [7]. Its correspondence to the substance described in the literature [8] was shown on the basis of the results of UV spectroscopy, cleavage products, and isomerization.

Substance (V) was saponarin (saponaretin 7-O-β-D-glucopyranoside), $C_{27}H_{32}O_{16}$, mp 240-242°C. It corresponded to the substance described in the literature, with respect to UV spectroscopy and the products of cleavage.

This is the first time that substances (I-IV) have been isolated from the plant. Saponarin has been described previously [9].

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SESQUITERPENE LACTONES OF Ferula clematidifolia AND Ligularia alpigena

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Ferula clematidifolia K.-Pol. belongs to the group of species of a typical subgenus including, in addition to this species, *F. penninervis* Regel et Schmalh. (*F. olgae* Regel et Schmalh.) and *F. korshinskyi* Korov. *F. clematidifolia* contains an essential oil [1]. There is no other reliable information on the chemical composition of this species.

We have studied an ethanolic extract of the roots of *F. clematidifolia* gathered in Tadzhikistan (Hissar range, gorge of the R. Shargun') in the flowering phase.

The dried and comminuted roots were extracted with ethanol (by the steeping method), the extract was concentrated, diluted with water and treated with ether, the ethereal extract was dried with sodium sulphate, the solvent was distilled off, and the resin so obtained was chromatographed on a column of silica gel (L 100/250, Chemapol, Czechoslovakia).

Elution with chloroform yielded a crystalline mixture of lactones which was separated by chromatography on a column of silica gel with the use as eluents of mixtures of hexane and ethyl acetate containing increasing concentrations of the latter.

Three crystalline compounds were obtained: (I) – $C_{27}H_{28}O_7$, mp 262-264°C (decomp.); (II) – $C_{29}H_{32}O_9$, mp 212-213°C; (III) – $C_{26}H_{28}O_9$, mp 216-218°C. From their physicochemical and spectral characteristics they were identified as diacylguaianolides, namely: (I) as giferolide, isolated previously from *F. gigantea* [2], and (II) and (III) as malaphyll and malaphyllin, isolated from *F. malacophylla* [3] and *F. gigantea* [2].

Thus, in its chemical composition, *F. clematidifolia* is close to *F. pinninervis*, which has also previously yielded guaianolides – olgin, laferin, olgoferin, talassin A, talassin B, oferin, grilactone [4], ferolide [5], and fegolide [6]. At the same time, it is impossible not to draw attention to the fact that *F. korshinskyi*, assigned by Korovin to the

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