The ease of hydrolysis of the 3'-acyloxy group and of the subsequent esterification of the alcohols formed, and also the use of various amines, provides the possibility of obtaining very diverse acyloxy and amino derivatives.

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6-CHLOROAPIGENIN FROM *Equisetum arvense* L.

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A new compound 6-chloroapigenin, $C_{15}H_9ClO_5$, M^+ 304, mp 305-306°C, λ_{max} 274, 336 (methanol) has been isolated from the ether-soluble fraction of a methanolic extract of the field horsetail. On the basis of the results of UV and PMR spectrosocpy and mass spectrometry, the structure of 6-chloro-4',5,7-trihydroxyflavone has been established for this compound.

From the ether-soluble fraction of a methanolic extract of the herbage of *Equisetum arvense* L. (field horsetail) we have isolated a compound (I) with the composition $C_{15}H_9ClO_5$, M^+ 304, mp 305-306°C, λ_{max} 274, 336 nm (methanol). According to its UV spectra in methanol and in the presence of sodium methanolate, aluminum chloride, and sodium acetate, this compound belongs to the flavone group and has free hydroxy groups in positions 4',5, and 7 of the molecule. The mass spectrum of the compound isolated indicated the presence of chlorine in the molecule of (I).

In the region of the molecular ion of compound (I) two peaks are observed with m/e 304 (100%) and 306 (39%), which is characteristic for chlorine-containing compounds with one chlorine atom in the molecule. The peak of any chlorine-containing ion M is always accompanied by the M + 2 peak with approximately one third of the intensity, since the natural ratio of the isotopes ^{35}Cl and ^{37}Cl is 3:1 [1, 2]. A similar ratio of the peaks is preserved for the chlorine-containing fragments A and A + 2: m/e 186 (41%) and 188 (12%).

The presence of chlorine is also confirmed by the qualitative Stepanov reaction and the Beilstein test [3]. For comparison we used flavones (apigenin, genkwanin, and luteolin), and chlorine-containing organic compounds.

In order to establish the position of the chlorine, we compared the peaks of the fragmentary ions of this compound with the peaks of the fragmentary ions of apigenin, genkwanin, and acacetin. Fragmentation peaks with m/e 121 and 118 confirmed that there is a free OH group in ring B in the 4'-position of the molecule. The position of the chlorine in ring A was confirmed by the presence in the mass spectrum of fragmentation ions with m/e 188, 187,

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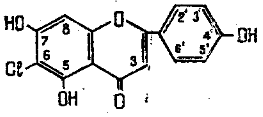
and 186. A positive Gibbs reaction showed a free position 8 of the flavone molecule [4]. Consequently the chlorine can be attached only to position 6 of the molecule. Synthetic 6-, 7-, and 8-chloroflavones obtained by Japanese workers [5, 6] give chlorine-containing fragments as the main peaks of the spectrum, the ratio of the intensities of the ions M^+ and $(M + 2)^+$ again being approximately 3:1.

In all these compounds the high intensity of the peaks of the ions A is observed: 95% in 6-chloroflavone and 100% in 8-chloroflavone. The lowering of the intensity of the peak of ion A in our case (m/e 186, 41%) in obviously connected with the lower stability of this fragment because of the presence of two hydroxy groups in positions 5 and 7 of the molecule of (I).

In the PMR spectrum of compound (I) in deuteromethanol there are the following proton signals: H-3 at 6.36 ppm, H-8 at 6.66 ppm, and two doublets at 6.96 and 7.94 ppm with J = 9 Hz (2 H each) belonging to the 3',5' and the 2',6' protons of ring B. The proton of the 5-OH group appears at 12.9 ppm in deuteroacetone.

On the basis of the facts given, it was established that the compound isolated is new and has the structure of 6-chloro-4',5,7-trihydroxyflavone:



Halogenated flavonoids are found very rarely in nature. The isolation of chlorflavonin (3'-chloro-2',5-dihydroxy-3,7,8-trimethoxyflavonol), of 6-chlorogenistein (6-chloro-4',5,7-trihydroxyflavone) and of 3' 6-dichlorogenistein from microorganisms has been reported previously [7, 8]. Halogenated flavonoids have not been detected previously in higher plants.

EXPERIMENTAL

UV spectra were taken on a Hitachi EPS-3T spectrophotometer, PMR spectra on a Varian HA-100D spectrometer, and mass spectra on a Varian CH-8 spectrometer at 7- eV. The melting point was determined on Kofler block.

Isolation of 6-Chloroapigenin. The ether-soluble fraction (18 g) of a methanolic extract obtained from the herbage of the field horsetail [9] was chromatographed on silica gel L (100/250 μ) (Czechoslovakia). Elution of the column with benzene–acetone (9:1) yielded 6-chloroapigenin. It was purified additionally on microcolumms of polyamide and was recrystallized from methanol. Yield ∿17 mg.

Chromatographic monitoring was carried out by TLC (Silufol) in the chloroform–acetone–methanol (16:4:1) system (R_f 0.53) and the chloroform–acetone (4:1) system.

6-Chloroapigenin. The yellow were soluble in ethanol, pyridine, and acetone, mp 305-306°C. In the course of a determination of the melting point the compound underwent recrystallization at 220°C but, according to GLC, this did not correspond to a change in the nature of the product. UV spectrum, λ_{max} (nm): (CH_3OH) 274, 336; (+CH_3ONa) 283, 328, 402; (+$AlCl_3$) 280, 310, 354, 392; (+$AlCl_3$ + HCl) 282, 308, 348, 390; (+CH_3COONa) 284, 313, 400; (+CH_3COONa + H_3BO_3) 280, 313, 343.

Mass spectrum at 120°C, m/e (J, %): $(M + 2)^+$ 306 (30), M^+ 304 (100), (M – 28) 276 (10), (A + 2) 188 (12), (A + 1) 187 (34), 186 (41),(A – 28), 158(11), 138 (20), C 121 (9), B 118 (15).

PMR spectrum in deuteromethanol (ppm): 6.36 (s, H-3), 6.66 (s, H-8), 6.96 and 7.94 (d, J = 9 Hz, H-3',5' and H-2',6'); in deuteroacetone: 6.44 (s, H-3), 6.7 (s, H-8), 7.0 and 8.0 (d, J = 9 Hz, H=3',5' and H-2','), and 12.9 (s, 5-OH).

SUMMARY

A new compound has been isolated from the herbage of the field horsetail for which the structure of 6-chloro-4',5,7-trihydroxyflavone has been established.

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CHEMICAL COMPOSITION OF THE ESSENTIAL OILS OF MONGOLIAN WORMWOODS

Artemisia xerophytica and *A. xantaphora*

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The chemical compositions of the hydrocarbon fractions of the essential oils of endemic wormwoods of Mongolia, *Artemisia xerophytica* (xerophytic wormwood) and *Artemisia xantaphora* (yellow wormwood), have been investigated. In the essential oil of *A. xerophytica* 22 hydrocarbons out of 26 have been identified and in that of *A. xantaphora* 18 out of 27.

The plant world of Mongolia is an inexhaustible source of natural compounds and, in particular, of essential oils. Particular interest is presented by the *Artemesia* genus which in Mongolia numbers more than 58 species, some of them being endemic [1]. Many species of wormwood (*Artemisia xerophytica, A. scoparia, A. adamsis, A. sieversiana*) form the main plant coverage of the steppe, semidesert, and desert.

The present paper gives the results of an investigation of the terpene and sesquiterpene hydrocarbons of the essential oils of the wormwoods *A. xerophytica* and *A. xantaphora* (xerophytic wormwood and yellow wormwood), which are endemic plants of Mongolia and have not been studied previously.

In the essential oil of *A. xerophytica* we found 43% of terpene hydrocarbons and 25% of sesquiterpene hydrocarbons (Fig. 1), and in that of *A. xantapora* 40% of terpene hydrocarbons and 12% of sesquiterpene hydrocarbons (Fig. 2).

We attempted to investigate the biogenetic link between the terpene and sesquiterpene hydrocarbons in the essential oils considered. Some workers consider that monoterpene hydrocarbons of a definite structure presuppose the presence in an essential oil of the corresponding sesquiterpene hydrocarbons differing from the former by one isoprene group [3]. This hypothesis is confirmed in the oils that we have investigated as examples. Thus, in the essential oil of *A. xerophytica* there is the monoterpenoid camphene and the sesquiterpene hydrocarbon β-santalene, the structures of which are similar. In addition, the simultaneous presence of α-santalene, longifolene, β-santalene, and logicyclene suggest that their biogenesis from a common precursor is possible. β-Santalene probably undergoes cyclization through one of the unsaturated centers of the molecule, leading to the formation of α-santa-

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