methyl groups (0.86 ppm, J = 6.7 Hz, 6 H) of a C_{28} methyl group (2.01, s, 3 H), of C_{27} and C_{29} methyl groups (1.14 ppm, s, 6 H), and of a C_{26} methine group at 1.95 ppm (septet, J = 2.1 Hz, 1 H). Irradiation at 0.86 ppm converted the septet at 1.95 ppm into a singlet.

In the structure of its side chain, compound (Ia) that we have obtained has no analogs among natural steroids.

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KAEMPFEROL DERIVATIVES FROM THE FRUIT OF THE JAPANESE PAGODA TREE

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UDC 547.972

Buds of *Sophora japonica* L. (Japanese pagoda tree) are an industrial source of rutin — a valuable drug with a vitamin P action. The fruit of the plant contains an insignificant amount of rutin [1-3]. We have isolated the two quantitatively predominating glycosides from the fruit of the Japanese pagoda tree.

Compound (I), $C_{27}H_{30}O_{16}$, mp 198-201°C (from methanol) $[\alpha]_D^{20} - 69.1°$ (c 1.01; methanol). $\lambda_{max}^{CH_3OH}$: 267, 352.5 nm.

The acid hydrolysis of substance (I) in 0.5% sulfuric acid gave an aglycone with mp 275-277°C (M^+ 286), which was identified from its mobility on TLC and by spectral characteristics as kaempferol [4]. D-Glucose was detected as the sugar component. The GLC method [5] showed the presence of two D-glucose residues in compound (I).

The PMR spectrum of the trimethylsilyl ether of the diglycoside (I) (100 MHz, CCl_4, 0 — HMDS) showed signals of the protons of the aglycone: H-2', H-6' — 7.85 (2 H, d, J = 8 Hz); H-3', H-5' — 6.67 (2 H, d, J = 8 Hz); H-8 — 6.30 (d, J = 2Hz); H-6 — 5.97 (d, J = 2 Hz). The anomeric protons of the sugar resonated at 5.33 ppm (d, J = 7 Hz) and 5.94 ppm (d, J Hz). The 12 protons of the carbohydrate moiety were represented by signals in the 2.92-4.01 ppm region.

On the basis of the UV spectrum of the diglycoside (I) with diagnostic reagents ($\lambda_{max}^{CH_3OH}$: 275, 352.5; $\lambda_{max}^{CH_3ONa}$: 275, 330, 399; $\lambda_{max}^{AlCl_3}$: 275, 352.5, 400; $\lambda_{max}^{AlCl_3 + HCl}$: 275, 352.5, 400; λ_{max}^{NaOAc}: 263, 350; $\lambda_{max}^{H_3BO_3 + NaOAc}$: 263, 350 nm), it may be concluded that in the compound under consideration the hydroxy groups at C-5 and C-4 are free and those in positions 3 and 7 are substituted by D-glucose residues. According to the facts given, compound (I) is kaempferol 3,7-diglucoside.

This kaempferol glucoside has been isolated previously from peony [6] and guelder rose [7] flowers. The amount of (I) in the fruit of the Japanese pagoda tree amounts to from 5 to 7%.

Substance (II), $C_{32}H_{38}O_{20}$, mp 173-175°C (from methanol), $[\alpha]_D^{20} + 21.8°$ (c 0.45; methanol) was also a kaempferol glycoside and it contained two D-glucose and one L-rhamnose residues. The amount of (II) in the fruit was about 1%.

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DAURINE — A NEW ALKALOID FROM *Haplophyllum dauricum*

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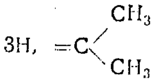
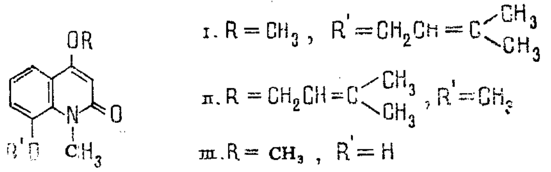
From the total alkaloids of the roots of *Haplophyllum dauricum* (L.) G. Con., collected in Mongolia, by column chromatography we have isolated an optically inactive base with mp 117-118°C, which has been called daurine. The base is soluble in ethanol and chloroform and crystallizes from acetone.

The IR spectrum of daurine has intense absorption in the 1650 cm^{-1} region (2-quinoline system); there is no absorption band corresponding to active hydrogen. The UV spectrum has absorption maxima at (nm) 215, 235, 254, 268 shoulder, 276 shoulder, 286 shoulder, 328, which are characteristic for alkaloids of the 4,8-dialkoxy-N-methyl-2-quinoline series [1].

The PMR spectrum of daurine ($CDCl_3$, 0 — TMS, taken on a Varian XL-200 instrument) contains signals characterized by the following values (δ, ppm): 1.73 and 1.80 (singlets, 3 H each,  $3H, =C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$) : 3.91 and 3.93 (singlets, 3 H each, NCH_3 and OCH_3); 4.57 and 5.52 (doublet, 2 H, $^3J = 6.8$ Hz; triplet, 1 H, $^3J = 6.8$ Hz; protons of a $-O-CH_2-CH=$fragment forming a three-spin system of the A_2X type); 6.05 (singlet, 1 H, H-3); 7.09 (quartet, 1 H, $J_{ortho} = 7.9$ Hz and $J_{meta} = 2.4$ Hz, H-7); 7.13 (triplet, 1 H, $J_{ortho} = 7.8$ Hz and 7.2 Hz, H-6); 7.60 (quartet, 1 H, $J_{ortho} = 7.2$ Hz and $J_{meta} = 2.4$ Hz, H-5) — aromatic protons forming a system of the ABC type; a similar pattern is observed in the spectrum of edulitine [2].

What has been stated above and also the presence in the mass spectrum of the alkaloid of intense peaks of ions with m/z 273 (M^+, 33%), 205 (M − 69, 100%), and 69 (M − 205, 18%) gives grounds for the assumption that daurine may have a 4-methoxy-8-(γ,γ-dimethylallyloxy)-N-methyl-2-quinolone (I) or an 8-methoxy-4-(γ,γ-dimethylallyloxy)-N-methyl-2-quinolone (II) structure.



I. $R = CH_3$, $R' = CH_2CH = C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$

II. $R = CH_2CH = C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$, $R' = CH_3$

III. $R = CH_3$, $R' = H$

The choice between these structures was made on the basis of the following facts. In an alkaline medium, the UV spectrum of daurine did not change, while on the addition to an ethanolic solution of the base of a drop of concentrated hydrochloric acid it became identical with the spectrum of folifidine (III) taken under similar conditions. An examination of the sample obtained from the acidified ethanolic solution showed its identity with (III) (GLC, IR spectra).

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