In the cyanidin reaction, substance (I) forms an orange pigment which is extracted completely by octanol [4], which shows its aglycone nature. With a solution of ferric chloride it gives a green coloration, which may be an indication of the presence of a free 5-hydroxy group in it. The products of the alkaline fusion of the flavonoid are phloroglucinol and p-hydroxybenzoic acid.

In the cyanidin reaction, substance (II) forms an orange-red pigment which can be extracted from aqueous solutions with octanol. With ferric chloride it gives a green color and it reduces an ammoniacal solution of silver nitrate [5]. The products of alkaline fusion are phloroglucinol and protocatechuic acid.

From the results of a spectroscopic investigation in the UV region with ionizing and complex-forming reagents [6], a chromatographic comparison in several systems of solvents, and the absence of depressions of the melting points of substances (I) and (II) in admixture with apigenin and luteolin, respectively, flavonoid (I) can be characterized as 5,7,4'-trihydroxyflavone or apigenin and flavonoid (II) as 5,7,3',4'-tetrahydroxyflavone or luteolin.

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SCROPHULEIN—A NEW FLAVONOID FROM *SCROPHULARIA GROSSHEIMII*

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From the herb *S. grossheimii* Schischk. we have isolated apigenin, luteolin, diosmetin, and a substance of a flavone nature which we have called scrophulein.

Scrophulein has the composition $C_{17}H_{14}O_6$, mol. wt. 314 (mass spectrometrically), mp 266–268° C (from 50% ethanol), λ_{max} 345, 280 mμ, R_f 0.05 (15% CH_3COOH), 0.51 (60% CH_3COOH), 0.31 [benzene—ethyl acetate—acetic acid—formamide (24.5 : 73.5 : 2 : 1)]. In the cyanidin reaction, the substance forms an orange pigment which can be extracted by octanol. On acid hydrolysis no cleavage was observed.

From the results of IR spectroscopy, scrophulein contains a hydroxy group (3400 cm^{-1}), a methoxy group (2960 and 2850 cm^{-1}), the carbonyl group of a γ-pyrone (1670 cm^{-1}), an aromatic system (1620, 1580, 1520, and 1510 cm^{-1}) and also 1,4- (820, 840 cm^{-1}) and 1,2,3,4,5-substitution (865 cm^{-1}) in benzene rings [1,2].

In the UV spectra, the maxima of bands I and II are of almost the same intensity, which is characteristic for flavones [3]. The functional groups were determined spectrophotometrically in the UV region, using diagnostic reagents. The following results were obtained: λ_{max} with sodium acetate 350 and 290 mμ ($\Delta\lambda_1$ 5 mμ), λ_{max} with sodium ethoxide 400 and 245 mμ ($\Delta\lambda_1$ + 55 mμ), λ_{max} with zirconyl nitrate 365 and 300 mμ ($\Delta\lambda_1$ + 20 mμ).

Thus, the results of UV spectroscopy show that scrophulein contains free phenolic hydroxy groups in positions 5 and 4'.

On demethylation with hydriodic acid, scrophulein gave scutellarein. A spectroscopic investigation showed that with zirconyl nitrate scutellarein gives a bathochromic shift of +34 mμ, while apigenin gives one of 55 mμ. Consequently, there is probably a methoxy group in position 6 of scrophulein and a second methyl group substitutes the 7-hydroxy group.

By analyzing literature information on the various methoxy derivatives of scutellarein—hispidulin (6-methoxy-), pectolinarigenin (6,4'-dimethoxy-), and micanin (6,7,4'-trimethoxy-) [4]—it may be concluded that scrophulein is a new natural methoxy derivative of scutellarein—5,4'-dihydroxy-6,7-dimethoxyflavone.

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NEW FLAVONOID COMPOUNDS FROM GALEOPSIS LADANUM

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By recrystallizing the total flavonoids of Galeopsis ladanum L. (red hempnettle) [1] from methanol we have isolated a glycoside fraction the acid hydrolysis of which under mild conditions (1% hydrochloric acid, 95° C, 1 hr) has given one and under more severe conditions (10% sulfuric acid, 95° C, 8 hr) two substances of a flavonoid nature. With magnesium and hydrochloric acid, both substances form an orange pigment soluble in octanol. Consequently, they are aglycones.

Aglycone (I) is a bright yellow crystalline substance with mp 310-313° C (ethanol—water) and R_f 0.72 [butanol—acetic acid—water (4 : 1 : 2)], 0.32 (40% acetic acid) and 0.60 [benzene—ethyl acetate—acetic acid—formamide (24.5 : : 73.5 : 2 : 1)]. According to its IR spectrum, this flavonoid has a free hydroxy group (3400 cm^{-1}), methoxy groups (2850 and 2980 cm^{-1}), the carbonyl group of a γ-pyrone participating in the formation of a hydrogen bond with neighboring hydroxy groups (1665 cm^{-1}), and also substitution of the hydrogen atoms of benzene rings in positions 1, 2, 3, 4, and 5 (880 cm^{-1}) and 1 and 4 (845 cm^{-1}) [2, 3]. The UV spectrum exhibits maxima at 335, 282, and 255 and a shoulder at 300 mμ. The distance between the main maxima (335 and 282 mμ) is 53 mμ, which is characteristic for flavones [4]. However, the low intensity of the long-wave maximum (about 10%) gives grounds for assuming that the aglycone (I) is a flavone in which hydroxy groups are either not present in the B ring or are substituted. Spectroscopic investigations in the UV region with diagnostic reagents showed the presence of only one free hydroxy group at C_5 in the aglycone (I) from the bathochromic shift of the maximum of the long-wave band (20 mμ) of the complex of the flavonoid with zirconyl nitrate [5]. The low value of this shift may be due to the steric influence of substituents present in position 6.

Aglycone (II) is a yellow crystalline substance with mp 190-192° C, R_f in the systems given above 0.60, 0.20, and 0.50, respectively and λ_{max} 342 and 285 mμ. The maximum of the long-wave band has a considerably greater intensity than that of the short-wave band, which is generally observed for flavone compounds with a hydroxy group in position 4'. By means of a spectroscopic study with diagnostic reagents, the aglycone (II) was found from the bathochromic shift of 30 mμ with sodium ethoxide to contain a 4'-hydroxy group in addition to a 5-hydroxy group.

Both substances were rapidly decomposed on being heated with sodium acetate in an aqueous medium. Such properties are probably explained by the presence in the molecules of 5,6-dihydroxy groupings, which are readily oxidized in a weakly alkaline medium.

The demethylation of the substances led to the formation of scutellarein (mp 345° C, decomp., λ_{max} 338 and 285 mμ, R_f in the above-mentioned systems 0.70, 0.30, and 0.60, respectively) with free hydroxy groups in positions 5, 6, 7, and 4'. Consequently in the aglycone (I) the 7- and 4'-hydroxy groups are methylated and in the aglycone (II) only the 7-hydroxy group.

Thus, on the basis of chemical and spectroscopic investigations substance (I) has been characterized as 5,6-dihydroxy-7,4'-dimethoxyflavone and substance (II) as 5,6,4'-trihydroxy-7-methoxyflavone. These substances proved to be new, and we have called them, respectively, ladanein and ladanetin.

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