Fractionation of the Saccharinic Anilides on a Cellulose Column.—A concentrated ethanol solution containing the saccharinic anilides formed from 1 g. of sugar was applied to the top of a 2 by 22 inch cellulose column (Whatman Cellulose powder) and washed with about 2 liters of 9:1:2 acetone–water–benzene during a period of 20 hours. The first 500 cc. of effluent were discarded, and then 12-cc. fractions taken every 7.5 minutes. The anilides were eluted very rapidly, the slowest fraction, of R_f 0.60, being found in fractions 48 to 56. The **C_6-saccharinic anilide**, isolated from a mixture prepared from D-glucose, was obtained in 150 mg. crude and 60 mg. purified yield, m.p. 120–121° cor. (crystallized from ethyl acetate and ligroin), $[\alpha]^{23}D$ −23.9° (95% EtOH, *c* 3.3). Calcd. for $C_{12}H_{17}O_6N$: C, 56.50; H, 6.70; N, 5.48. Found: C, 56.41; H, 6.74; N, 5.38. The **C_5-saccharinic anilide**, isolated from a mixture prepared from L-arabinose, was obtained in 10 mg. yield, m.p. 108–110° cor. (crystallized from ethyl acetate–benzene, and then benzene–ligroin). It is quite soluble in ether. No rotation was taken. Calcd. for $C_{11}H_{15}O_4N$: C, 58.70; H, 6.70; N, 6.22. Found: C, 59.30; H, 7.33; N, 5.68.

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Glucoluteolin Isolated from the Leaves of *Sophora angustifolia*

BY SHIZUO HATTORI AND HIROAKI MATSUDA

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Sophora angustifolia Siebold et Zuccarini is a perennial herbaceous plant of the family *Leguminosae* which is very common in Japan. Its root contains the alkaloid matrin.[1]

From the concentrated aqueous extract of the leaves of this plant, ethyl acetate extracted a pale yellow glycoside, which was purified by recrystallization from pyridine–water and melted at 254°. On hydrolysis, it yielded the luteolin (5,7,3′,4′-tetrahydroxyflavone) and the sugar glucose. By direct comparison, this glycoside proved to be identical with glucoluteolin which we had isolated from the leaves of *Humulus japonicus* Siebold et Zuccarini[2] and has the structure luteolin-7-glucoside.

Experimental

Twelve kg. of fresh leaves, collected in June, was extracted with 10 l. of boiling water; the decoction was concentrated to 1 l. and after extraction with ether repeatedly extracted with ethyl acetate. On concentration of the combined yellow ethyl acetate solution by distillation a yellow residue was obtained.

Pale yellow needles, m.p. 233–234°, yield 0.02%, resulted on recrystallization several times from ethanol. The crystals were further purified by recrystallization from water on addition of pyridine and obtained as somewhat lustrous, pale yellow needles of m.p. 254°. An ethanolic solution of this substance gave a greenish-brown coloration, was easily oxidized by means of pentamminecobaltic chloride, showed strongly positive Molisch reaction, and, when reduced with magnesium powder and concd. hydrochloric acid, gave an orange-yellow color. The R_f is 0.47 in *n*-butyl alcohol–acetic acid–water (4:1:1). All of these properties were the same as those exhibited by authentic glucoluteolin ($C_{21}H_{20}O_{11}$) and no lowering occurred in a mixed melting test with the authentic sample.

The crystals are very difficultly soluble in hot water and dilute ethanol, and contain 6% (1.5 moles) of water of crystallization.

It is very difficult to hydrolyze glucoluteolin completely. The hydrolysis was achieved by heating it with 30% sulfuric acid for 6 hours. After cooling, the precipitated aglycone was filtered (yield, about 55% of the glycoside used) and when recrystallized from ethanol, yellow needles gradually separated. These crystals of the aglycone did not melt under 300°, showed a dark greenish-brown coloration and, when reduced with magnesium powder and concd. hydrochloric acid, gave an orange color.

Part of the aglycone was acetylated by the usual method and the purified acetate consisted of white long needles of m.p. 222°. This melting point did not alter when the acetylated product was mixed with authentic tetraacetylluteolin. Further, the methylated aglycone, which was obtained by methylating with dimethyl sulfate and potassium carbonate in acetone, consisted of colorless needles and melted at 144°. When mixed with authentic tetramethylluteolin, the methylated product did not lower the melting point.

By means of osazone formation, glucose was identified as the only sugar in the hydrolysate.

The methylated glucoside, which was obtained by methylating the glucoluteolin with dimethyl sulfate and potassium carbonate in acetone, gave, on hydrolysis with boiling 30% sulfuric acid, colorless needles of m.p. 284°. These were identical with authentic 5,3′,4′-trimethylluteolin by mixed melting test.

Not only the leaves, but also the pale yellow flowers of this plant contain glucoluteolin. In this latter case, however, 50% ethanol was found to be more convenient than hot water for its extraction. The yield was a little higher, that is, 0.06% of the fresh material.

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Derivatives of Reserpine. Communication on the Rauwolfia Alkaloids. XIII

BY CHARLES F. HUEBNER

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We wish to report some new derivatives of reserpine[1] prepared with the object of determining the effect of chemical change on pharmacological activity. Chemical modifications of reserpine (I) resulted in compounds obtained from alkylation of the indole nitrogen (II and III) and by conversion of the carbomethoxy group to the corresponding amide IV.

Methyl reserpate, in the form of its N-potassium derivative, readily undergoes alkylation in liquid ammonia with methyl iodide and with allyl bromide according to an adaptation of the method recently described for the preparation of N-methylharman.[2] The N-alkyl methyl reserpates are then esterified with 3,4,5-trimethoxybenzoyl chloride (II and III). Reserpine itself, can be directly N-alkylated; however, this is the less convenient of the two alternative methods because of the relative insolubility of reserpine and its N-potassium derivative in liquid ammonia. The amide of reserpic acid results from the action of a large excess of sodium amide on reserpine in liquid ammonia, ammonolysis occurring at both its ester linkages. Reesterification of reserpamide with 3,4,5-trimethoxybenzoyl chloride gives the amide corresponding to reserpine (IV).

Pharmacological investigation of these reserpine derivatives by Dr. Plummer and his associates showed that they are devoid of the tranquillizing and hypotensive properties characteristic of the

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