FURTHER FLAVONES AND TRITERPENES AND THE NEW 6-HYDROXYLUTEOLIN 5-β-D-GLUCOSIDE FROM *SALVIA TOMENTOSA*

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ABSTRACT.—In addition to the seven flavones previously isolated from *Salvia tomentosa* (Labiatae), five more, including the new glycoside 6-hydroxyluteolin 5-β-D-glucoside along with cirsilineol, eupatilin, diosmetin and 6-hydroxyluteolin 7-β-D-glucoside have now been obtained. In addition, two known triterpenes, uvaol and β-amyrin, were also isolated from this species.

We previously reported from *Salvia tomentosa* Mill. 5-hydroxy-6,7,3',4'-tetramethoxyflavone, cirsimaritin, jaceosidin, luteolin and its 6-methoxy and 7-glucoside, and 6-methoxyluteolin 7-glucoside (1), and six terpenoids, the new 3-β-hydroxy-8,11,13(14),15-abietatetraen-18-oic acid as well as dehydroabietic, ursolic, oleanolic and crataegolic acids and sitosteryl 3-β-glucoside (2). From this same species, we now describe two additional terpenoids, uvaol and β-amyrin, and five more flavones: 5,7-dihydroxy-6,3',4'-trimethoxyflavone (eupatilin), 5,4'-dihydroxy-6,7,3'-trimethoxyflavone (cirsilineol), 5,7,3'-trihydroxy-4'-methoxyflavone (diosmetin), and the 7- and 5-β-D-glucosides of 6-hydroxyluteolin. The latter compound is new.

EXPERIMENTAL[1]

EXTRACTION AND CHROMOTOGRAPHY.—In our first paper on the chemistry of *S. tomentosa*, we reported that 0.5 kg of leaves collected in Antakya, Turkey, were powdered and extracted successively in a Soxhlet with petroleum ether (bp. 30–60°), benzene, chloroform and ethanol, and that the petroleum ether yielded one flavone and the benzene six flavones (1). The benzene extract also afforded the terpenoids noted above (2). The same silica gel column which yielded these terpenoids has now afforded by elution with benzene-ethyl acetate (85:15) eupatilin (22 mg), cirsilineol (126 mg) and diosmetin (18 mg).

The concentrate from the ethanol extract of the leaf material, when chromatographed over a Polyclar column with 50% aqueous ethanol, afforded a mixture of two flavone glycosides. The mixture was fractionated over a microcrystalline cellulose column (3x50 cm) by elution with *n*-butanol saturated with water to yield the 5- (4 mg) and 7- (25 mg) glucosides of 6-hydroxyluteolin.

EUPATILIN, CIRSILINEOL AND DIOSMETIN.—These three flavone methyl ethers were obtained crystalline, mp 223–4°, 229–31° and 258°, respectively. The compounds were identified by uv, pmr (except diosmetin) and ms spectral methods as well as standard sample comparisons.

6-HYDROXYLUTEOLIN 5- AND 7-β-D-GLUCOSIDES.—Acid and β-glucosidase hydrolyses of these two glycosides afforded 6-hydroxyluteolin (uv, ms and tlc) and glucose (tlc). For the 7-glucoside uv spectral shifts, pmr and ms of the underivatized compound as well as standard sample (3) comparison proved the structure. The color of the new glucoside appeared blue when spotted on paper and viewed under uv light (366 nm) and remained blue when exposed to NH_3 vapor and when sprayed with NA (Naturstoffreagenz-A, Carol Roth, Germany) reagent. These results indicated that the 5-hydroxyl group was substituted. In the uv spectral analysis of this new glucoside, Band I shifted 24 nm in the $AlCl_3$ spectrum relative to Band I in methanol; however, with $AlCl_3$/HCl, Band I was not shifted with respect to Band I in the methanol spectrum. Together with the color reactions, these uv results established a substituted 5-OH.

[1]Spectra were recorded with the following instruments: Uv Varian Techtron model 635; ir, Perkin-Elmer 577 grating model; pmr, Varian 90 MHz; and ms, DuPont 21-491. Adsorbants for tlc and cc were from E. Merck.

Other uv spectral findings established a free 3',4'-dihydroxyl group. Uv spectral data for this 5-glucoside are as follows: uv, λ max (in MeOH) 339, 282, 252 (sh); NaOMe, 387 (higher intensity), 298 (sh), 275; $AlCl_3$, 363, 290 (sh), 275; $AlCl_3$/HCl, 340, 290 (sh), 262; NaOAc, 365, 295 (sh), 260; NaOAc/H_3BO_3, 355, 285 (sh), 260. The ms of the perdeuteriomethyl derivative of this 5-glucoside, while not clean, nevertheless supported the presence of one glucose moiety attached to a 6-hydroxyluteolin skeleton: molecular ion *m/e* 600 (4%); PDM-glucose fragments at *m/e* 230 (13%), 196 (20%) and 161 (13%); and an ion at 352 (20%) for the PDM-aglycone minus CD_3 of the 6-OCD_3 group.

β-AMYRIN AND UVAOL.—When the concentrate from the petroleum ether extract of the leaf material was fractionated over a silica gel column (3x40 cm) with light petroleum ether-benzene (1:1) as eluent, β-amyrin (20 mg), mp 198°, lit 197-200° (4) and uvaol (36 mg), mp 235–, lit 232-3° (5), were obtained. Ir, pmr and ms spectral analysis, acetylation and standard sample comparisons proved their structures.

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