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Flavonoids Syntheses. V. Synthesis of Flavonoids with Three Hydroxy and Four Methoxy Groups and Their Spectral Properties.

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Twelve flavonoids with three hydroxy and four methoxy groups located at C-5, 6, 7, 2′, 3′, 4′, 6′, C-5, 7, 8, 2′, 3′, 4′, 6′, C-3, 5, 6, 7, 2′, 4′, 5′ aud C-3, 5, 7, 8, 2′, 4′, 5′ were synthesized to confirm of the structure of NAS-3 and to investigate the spectral properties of the heptaoxygenated flavonoids. In the UV spectra, the absorptions based on band I are characteristically observed at 330 nm. In the case of the flavonols, these bands are at 350 nm. The conspicuous UV absoption of the flavonoids oxygenated at C-2′ and/or C-6′ can be explained as follows; when C-3 and C-2′ and/or C-6′ are oxygenated, the mesomeric effects between the B ring and C ring diminish because of steric hindrance. The fact was supported by the X-ray analysis of a model compound.

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Flavonol Glycosides from *Epimedium sagittatum*.

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The aerial parts of *Epimedium* spp. have been used as crude drug in China and Japan. The species are distributed in China (16 species), Japan (9 species), Europe, the Middle East and the Himalayas. For the chemotaxonomy of the genus *Epimedium*, chemical constituents of *E. saggitatum* (SIEB. et ZUCC.) MAXIM. were investigated. In the present study, two new flavonol glycosides were isolated besides the known flavonol glycosides, icariin and icarisid I. On the basis of spectral analyses, the structures of the compounds were determined to be anhydroicaritin-3-O-α-rhamnopyranoside and icaritin-3-O-α-rhamnopyranoside.

〔Yakugaku Zasshi, **107**, 315 (1987)〕

Syntheses of Flavonoids in *Scutellaria baicalensis*. (1).

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5, 7, 2′-Trihydroxy- (**1**), 7, 2′, 3′, 5′-tetrahydroxy- (**2**), 5, 2′-dihydroxy-6, 7, 8-trimethoxy- (**4**), 5, 2′, 5′-trihydroxy-6, 7, 8-trimethoxyflavone (**5**) and 5, 7, 2′, 6′-tetrahydroxyflavanone (**3**) isolated from *Scutellaria baicalensis* were synthesized to confirm their proposed structures. Condensations of 2-hydroxy-3, 4, 5, 6-tetramethoxyacetophenone or phloacetophenone diisopropylether with 2-isopropyloxy-, 2, 3-diisopropyloxy- or 2, 6-diisopropyloxy benzaldehyde in the presence of alkali medium (KOH or piperidine) gave the corresponding chalcones, which were led to the flavones by oxidation and deisopropylated with BCl_3 to afford the desired flavones (**1**, **2**, **4** and **5**). The flavanone (**3**) was also prepared by the same method of cyclization of the chalcone. The respective synthetic flavonoids were in good agreement with the natural flavonoids.