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Flavonoids Syntheses. VI. Synthesis and Spectral Properties of 4-Arylcourarins (Neoflavones).

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Eight neoflavones (5, 7-dihydroxy-, 5, 7, 2'-trihydroxy-, 5, 7, 3'-trihydroxy-, 5, 7, 4'-trihydroxy-, 5, 7, 2', 5'-tetrahydroxy-, 5, 7-dihydroxy-2'-methoxy-, 7-hydroxy-, and 7, 3'-dihydroxyneoflavone) were prepared by the Pechmann condensation of phloroglucinol or resorcinol with benzoylacetic acid ethyl esters for examination of their spectral properties. In the mass spectra, the neoflavones lacking an O-function at C-2' showed stable fragments of  $(M^+-28)$  caused by decarboxylation. On the other hand, in the case of 2'-oxygenated neoflavones, dehydroxylation or demethylation between  $C_5$ -OH and substituents at C-2' occurred to give  $(M^+-17)$  or  $(M^+-59)$ . Other spectral data showed no specific features that could be used to characterize the structures.

## (Z. Naturforsch., 42c, 1063 (1987))

## Novel Flavonoids from the Fern Notholaena sulphurea.

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The major constituent of the yellow frond exudate of the fern Notholaena sulphurea was identified by spectroscopic methods as 3, 5, 2'-trihydroxy-7-methoxy-8-acetoxyflavone and its structure was confirmed by synthesis. This novel natural flavonoid was also detected in the frond exudate of five other Notholaena species. In the yellow form of N. sulphurea, the rare 5, 2'-dihydroxy-7,8-dimethoxyflavone was also found, along with some trivial flavonoids. The white form of N. sulphurea produces three dihydrochalcones that are accompanies by some kaempferol methyl ethers and apigenin-7-methyl ether. The 3-acetoxy as well as the 3-butyroxy and the 4'-butyroxy derivatives of 7-methyl aromadendrin were also identified in this material.

(Yakugaku Zasshi, 107, 827 (1987))

## Synthesis of Flavonoids in Scutellaria spp. []. Synthesis of 2',6'-Dioxygenated Flavones.

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Five flavones dioxygenated at C-2' and C-6' (5, 7, 2', 6'-tetrahydroxy-(1), 5, 7, 2'-trihydroxy-6'-methoxy-(2), 5, 2'-dihydroxy-7,8,6'-trimethoxy-(3), 5,2', 6'-trihydroxy-7,8-dimethoxy-(4) and 5,7,2'-trihydroxy-8, 6'-dimethoxyflavone (5)) have been isolated from Scutellaris spp.. Among them 1 and 2 were isolated from S. baicalensis, 3 was from S. rivularis, 4 was from both S. baicalensis and S. viscidula, and 5 was from S. discolor, respectively. To confirm these constituents characterized the genus Scutellaria, syntheses of 1-5 were described in this paper. Spectroscopic comparison of the synthetics with the corresponding natural flavones confirmed the respective structures.