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**Detection of polyamines by a New Enzymatic Differential Assay
(5) Studies on Polyamine in Blood of Patients with Genitourinary
Malignant Diseases.**

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Diamine, spermidine and spermine in the blood were isolated and determined in 84 patients with genitourinary cancer using the new enzymatic assay. In the early diagnosis, the positive rates of each polyamine were not so high, but relatively high positive rates were demonstrated, when any one of the polyamines were found positive : namely, 85.7% in renal cell cancer 66.7% in renal pelvic and ureteral cancer, 44% in bladder cancers. These results seem to support the usefulness of the new method, and encourage further investigation of polyamines in the blood as tumor markers.

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**Flavonoids Syntheses. I. Synthesis and Spectroscopic Properties of
Flavones with Two Hydroxy and Five Methoxy Groups at C-2',3',4',
5',6,6',7 and C-2',3',4',5,5',6,7**

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Four flavones oxygenated at C-2',3',4' and 6', and seven flavonols oxygenated at C-2',4' and 5', each a 5,6,7-trioxygenated structure in ring A, were synthesized for comparison with brickellin and apulein. The structures of brickellin and apulein were thus confirmed to be 2',5-dihydroxy-3,4',5',6,7-pentamethoxyflavone and 2',5'-dihydroxy-3,4',5,6,7-pentamethoxyflavone. The differences between flavones oxygenated at 2',3',4' and 6', and flavonols oxygenated at 2',4',5' are discussed on the basis of spectroscopic data

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Spectral Properties of 2'-Oxygenated Flavones.

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Many reports dealt with flavonoids possessing hydroxy or methoxy group at C-2' and/or 6' have recently appeared. To clarify the properties of 2'-oxygenated flavones, spectra of UV, ¹H-NMR and MS of 56 relevant flavones were investigated. In the UV spectra, 2'-hydroxyflavone, for example, 2',5,7-trihydroxyflavone, showed a large bathochromic shift of band I by addition of base. In the ¹H-NMR spectra, a characteristic chemical shifts of H-3 were observed. The obtained data were applied to the structure elucidation of naturally occurring flavones.