# FLAVONOL GLYCOSIDES FROM THREE MEMBERS OF THE LYTHRACEAE

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ABSTRACT.—Three members of the Lythraceae were investigated for their flavonoids.

Fresh aerial parts of *Rotala leptopetala* were found to contain quercetin-3-glucoside (major) and quercetin-3-galactoside (minor), while *R. verticillaris* was found to contain quercetin-3-diglucoside (meratin). Free rhamnetin and its 3-rhamnosylglucoside were found to be present in *Ammannia multiflora*. This is the first report of isolation of meratin, rhamnetin and its 3-rhamnosylglucoside from plants belonging to this family.

The Lythraceae, consisting of trees, shrubs, and herbs, are found widely distributed in the tropics, particularly in the New World, while a few members of the family are scattered in the temperate zones (1). Some members of the family are of medicinal value; others, such as *Lawsonia*, yield useful dyes (2).

Three members of the family, two species of *Rotala* and one of *Ammannia*, have been examined for their flavonoids since there appears to have been no reports of such work in the literature. *Rotala leptopetala* Koehne (syn. *Ammannia pentandra* Roxb.), found in wet places, is an herb with unusually erect stems and few branches (3). *Rotala verticillaris* L. (syn. *A. rotala* C. B. Clarke) is a small herb found in rice fields on the east coast of India and is characterized by verticillate, linear leaves (1,3). *Ammannia multiflora* Roxb., found in wet places throughout India, is a small, erect herb with narrow leaves (3,4).

## EXPERIMENTAL[2]

PLANT MATERIAL.—The plants were collected from Narthamalai, about 15 miles away from Tiruchirapalli (S. India) in early February and were identified by a taxonomist. The voucher specimens, 1-3/80, have been deposited in the Department of Chemistry, P. G. Centre.

EXTRACTION AND FRACTIONATION.—Fresh aerial parts (50 g) of *R. leptopetala* were extracted twice by refluxing with hot 85% ethanol. The combined extracts were concentrated *in vacuo*. The aqueous concentrate was successively partitioned into petroleum ether (bp 60–80°), peroxide-free diethyl ether, and ethyl acetate soluble fractions and worked up according to standard procedures (5, 6). The petroleum ether and diethyl ether fractions did not yield any crystalline material. From the ethyl acetate fraction, a yellow solid separated, after chilling in an ice-chest for a few days. After it was recrystallized from methanol, yellow needles, mp 235–237° (decomp.) (15 mg) were obtained. The compound was identified as quercetin-3-galactoside by $R_f$, behaviour in uv light, uv spectra, and direct comparison with an authentic sample. After a few more days, another yellow solid separated from the mother liquor which, on recrystallization from aqueous methanol, was obtained as yellow needles, mp 240–242°, (80 mg). On the basis of uv specta, $R_f$, color reactions, behaviour under uv light, and hydrolytic products (7% sulphuric acid, 100°, 2 hr), the glycoside was identified as quercetin-3-glucoside. The identity was confirmed by mmp and direct comparison with an authentic sample.

Fresh aerial parts (500 g) of *R. verticillaris* were processed as described above. The ether fraction yielded quercetin, mp 314–316°, (30 mg) which was identified by uv spectra, $R_f$ and the preparation and mmp of its penta-acetate. The residue from the ethyl acetate fraction was dissolved in a minimum quantity of acetone and left for a week in an ice chest. A dull yellow solid crystallized, which, on recrystallization from methanol, yielded pale yellow needles, mp 180–182°, (200 mg), $\lambda$ max (MeOH) 257, 366 nm. It gave characteristic shifts with various diagnostic reagents and appeared bluish yellow under uv with and without ammonia. The flavonol glycoside yielded quercetin on acid hydrolysis. A quantitative estimation of the sugar in the glycoside by the Folin-Wu-micro method (7) revealed that two sugar moieties were involved in glycosylation, which was also evident from the chromatographic mobility of the glycoside. Glucose was detected as the sugar present in the glycoside

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[2]Uv spectra were recorded in a Carl Zeiss SPECORD UV VIS double beam recording instrument. Ascending chromatography was carried out on Whatman No. 1, filter paper at 30±2°.

by $R_f$ and by preparation of its osazone. The uv spectral data indicated glycosylation at C-3, and the glycoside was characterized as quercetin-3-diglucoside. The $R_f$ of the glycoside is more in favor of the 3 sophorobioside (8). A comparison with an authentic sample of meratin from *Sterculia pallens* (9) confirmed its identity.

Shale-dried aerial parts (50 g) of *A. multiflora* were processed as described above. The ether fraction afforded a pale yellow solid, mp 290–292°, (15 mg) and λ max (MeOH) 258, 273 sh, 369 nm and characteristic shifts with the diagnostic reagents (5) but no shift on adding NaOAc, dull yellow under uv with and without $NH_3$. On the basis of these results and the $R_f$, it was identified as rhamnetin (quercetin-7-methyl ether).

From the ethyl acetate fraction, a very small quantity of a dull yellow solid separated which had λ max (MeOH) 257, 307 sh, 364 nm giving bathochromic shifts of 52 nm with NaOMe, 25 nm with $AlCl_3$ and 18 nm with NaOAc/$H_3BO_3$ and appeared dull yellow under uv with and without ammonia. It had $R_f$ (X 100): 23 (water), 45 (5% acetic acid), 62 (15% acetic acid), 79 (30% acetic acid), 80 (60% acetic acid), 49 (*n*-butanol-acetic acid-water=4:1:5), 76 (phenol satd. water), 92 (acetic acid-hydrochloric acid-water=30:3:10) and 66 (t-butanol-acetic acid-water=3:1:1) indicative of the presence of a bioside. A methanolic solution of the same, when subjected to hydrolysis (7% $H_2SO_4$, 100°, 2 hr), yielded an aglycone which was identical to that isolated from the ether fraction and gave quercetin on demethylation. The aglycone, thus, must be rhamnetin. Glucose and rhamnose were identified from the aqueous hydrolysate. Partial hydrolysis of an aliquot of the methanolic solution of the same with 1N HCl for 5 min at 100° yielded only rhamnose. The glycoside was, therefore, characterized as rhamnetin-3-rhamnosylglucoside, the position of glycosylation at C-3 being evident from uv spectral data.

## RESULTS

The present study reveals that quercetin-3-glycosides are present in *R. leptopetala* and *R. verticillaris*, while rhamnetin (quercetin-7-methyl ether) and its 3-rhamnosylglucoside occur in *A. multiflora*. This is in general agreement with earlier reports of isolation of flavonol-3-glycosides from *Woodfordia fruticosa* (10, 11). This is the first report of the isolation of meratin, rhamnetin and its 3-rhamnosylglucoside from members of the Lythraceae.

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