

FLAVONOID GLYCOSIDES IN *AMMANNIA COCCINEA* (LYTHRACEAE)

SHIRLEY A. GRAHAM,¹ BARBARA N. TIMMERMANN and TOM J. MABRY

The Department of Botany, The University of Texas at Austin, Texas 78712

Only a few flavonoids are known from the Lythraceae, including quercetin and kaempferol glycosides from *Cuphea ignea* DC. (1) and the C-glycosides vitexin and orientin from *Lythrum salicaria* L. (2, 3).

We describe the first chemical investigation of the Lythraceous genus *Ammannia*. Four flavonol and three flavone glycosides were isolated and characterized from *Ammannia coccinea* Rottb., a herbaceous annual widely distributed in temperate and tropical regions of the New World (4). An extract of 99 g of dried leaves collected in Austin, Texas, yielded quercetin 3- β -D-glucoside (90 mg), rutin (60 mg), luteolin 7- β -D-glucoside (35 mg), isorhamnetin 3-rutinoside (50 mg), apigenin 7- β -D-glucoside (30 mg), vitexin (15 mg) and kaempferol 3-rhamnoglucoside (18 mg). Additional populations of *A. coccinea* from California, Illinois, Kansas, Oklahoma, Alabama, Florida, and Costa Rica exhibited essentially this same pattern of flavonoids. The predominance of flavonols in *A. coccinea* is consistent with their occurrence as the major flavonoid type reported for the Lythraceae and for the order Myrtales, generally (5).

EXPERIMENTAL²

PLANT MATERIAL.—Plants were collected in Austin, Texas, October, 1979. Voucher

¹Permanent address: c/o A. Graham, Department of Biological Sciences, Kent State University, Kent, Ohio 44242.

²Uv spectra were recorded on a Beckman DB spectrophotometer; pmr spectra on a Varian EM 390; ms data in a DuPont 21-491 instrument. Adsorbants used were polyclar powder (GAF) for cc, microcrystalline cellulose and pre-coated cellulose plates (E. Merck), and pre-coated polyamide plates (Macherey-Nagel) for tlc.

specimens, *Graham 700*, are deposited in the herbaria of the University of Texas at Austin and the University of Michigan.

EXTRACTION AND ISOLATION.—Air-dried and powdered leaves of *A. coccinea* (99 g) were extracted with 85% and 50% aqueous methanol until the extract was colorless. The combined extracts were concentrated under reduced pressure until only water remained. The aqueous layer was extracted successively with *n*-hexane, chloroform, and ethyl acetate. Tlc and two-dimensional paper chromatography showed identical flavonoid patterns in the ethyl acetate and water fractions and no flavonoids in the hexane and chloroform extracts. The ethyl acetate fraction was chromatographed separately over two polyclar columns (7.5×60 cm, 200 g each) packed in the elution solvent. One of the columns was eluted first with chloroform-methanol-methyl ethyl ketone, 9:4:1, and the other with ethyl acetate-methanol, 1:1. The polarity of the solvents was increased in both columns by the addition of methanol and water until the columns were finally eluted with 50% aqueous methanol. Similar flavonoid fractions from both columns were combined and purified over Sephadex LH-20 columns using MeOH or 80% aqueous methanol.

IDENTIFICATION OF FLAVONOIDS.—All structural assignments employed both β -glucosidase and acid hydrolyses. In addition, quercetin 3- β -D-glucoside, rutin, luteolin 7- β -D-glucoside and isorhamnetin 3-rutinoside were also determined by uv, pmr and ms. Apigenin 7- β -D-glucoside, kaempferol 3-rhamnoglucoside and vitexin were identified by uv spectra data. The aglycones from all the O-glycosides as well as the O- and C-glycosides (except for kaempferol 3-rhamnoglucoside) were co-chromatographed with authentic standards on cellulose tlc plates using 15% and 40% aqueous acetic acid; ethyl acetate-methanol, 1:2, and 50% aqueous methanol. Sugars obtained upon acidic hydrolyses were identified by co-chromatography with standard sugars using pyridine-ethyl acetate-acetic acid-water, 36:36:7:21 on cellulose tlc plates.

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