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SHORT COMMUNICATION

FLAVONOIDS FROM THE ARGENTINE MISTLETOE *PSITTACANTHUS CUNEIFOLIUS*

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Abstract—The four flavonoids of the Argentine mistletoe *Psittacanthus cuneifolius* (Ruiz and Pav.) Blume (Loranthaceae) have been characterized as (+)-catechin, quercitrin (quercetin-3-rhamnoside), reynoutrin (quercetin-3-xyloside) and avicularin (quercetin-3α-arabofuranoside). Neither catechin nor any of the quercetin glycosides could be detected in five different host plants.

INTRODUCTION

IN A PREVIOUS paper[1] we have reported the isolation of tyramine from *Psittacanthus cuneifolius* (Ruiz and Pav.) Blume, a perennial hemiparasite shrub native of Argentine, which grows on different hosts.[2] Under the name of "liga" or "liguilla" it is employed in folk medicine.[3] It is also known and sold in our country as "muérdago" in place of the European mistletoe *Viscum album* L.[4]

We wish now to report the isolation and identification of several flavonoids from the dried leaves of *P. cuneifolius* growing on five different hosts: *Acacia aroma* Gill. ap. H. and A.; *A. caven* Mol.; *Geoffroea decorticans* (Hook and Arn.) Burkart; *Celtis spinosa* Spreng. and *Jodina rhombifolia* Hook and Arn. The following compounds were isolated: (+)-catechin (0·5–1·0%); quercitrin (quercetin-3-rhamnoside, 0·03%); reynoutrin (quercetin-3-xyloside, 0·015%) and avicularin (quercetin-3α-arabofuranoside, 0·01%). Paper- and thin-layer chromatography (PC and TLC) of the crude and purified extracts failed to indicate the presence of any other flavonoids.

The five above-mentioned hosts were investigated in a similar way for flavonoids; neither catechin nor any of the three quercetin glycosides could be detected in any by employing PC and TLC. This is in agreement with recent translocation studies of labelled substances in green mistletoe (*Phoradendron* spp.) growing on conifers and dicotyledonous trees, employing autoradiographic techniques.[5] Phloem-mobile substances did not migrate significantly from

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the endophytic system into the hosts nor did green mistletoes accumulate substances coming from the host via the phloem. It is concluded that the isolated flavonoids are normal metabolites originated in the hemiparasite (*P. cuneifolius*) and not in the host.

EXPERIMENTAL

Plant material. The fresh leaves from each sample of *P. cuneifolius* were collected in Córdoba Province, Argentina. The material was air dried and then ground to a coarse powder in a Wiley mill.

Chromatography. Solvents used for paper chromatography on Whatman No. 1 and Whatman No. 3 MM paper were: distilled water; 10 and 15% acetic acid; BAW, *n*-butanol:acetic acid:water (4:1:5) and Forestal, acetic acid:conc. HCl:water (30:3:10).[6] Thin-layer chromatography was carried out on Polyamide Merck with ethanol:water (6:4)[7] and on Polyamide +20% cellulose MN 300 with $CHCl_3$—MeOH—MeCOEt (9:4:2) as mobile phase.[8] The flavonoids were detected by their colours in u.v. light and by spraying with 2% ferric chloride solution. Column chromatography was performed following the method of Seikel *et al.*[9]

Spectroscopy. U.v. spectra were determined in a Beckman, model DK-2, spectrophotometer by the usual procedures[10] and i.r. spectra were determined in potassium bromide, using a Perkin Elmer Model 21 spectrophotometer.

Melting points and optical rotation. Melting points are uncorrected and were determined using a Fisher-Johns melting point apparatus. Optical rotations were measured in a Carl Zeiss Circle polarimeter.

Isolation and identification of flavonoids. Powdered dried leaves were extracted repeatedly with hot methanol until the extracts were colorless. The filtered combined methanolic extracts were concentrated at 40° *in vacuo* until methanol had been removed and the aqueous residue extracted three times by shaking with portions of light petroleum (60–80°). The aqueous fraction was concentrated *in vacuo* and further purified by column chromatography on Nylon.[9] The column was first washed with water and then eluted by increasing methanol-water mixtures. All fractions were concentrated *in vacuo* at 40°. From the eluates with water-methanol (70:30 v/v) crystallized (+)-catechin, recrystallized from water to give m.p. 173–174°. (Found: C, 60·25; H, 4·96. Calc. for $C_{15}H_{14}O_6$. 1/2 H_2O: C, 60·20; H, 5·05%); $[\alpha]_D^{29}$ +18° (*c* 2·0 acetone–water); pentacetate, m.p. 129–130°, $[\alpha]_D^{27}$ +39° (*c*, 3·6 tetrachloroethylene); pentamethyl ether, m.p. 89–90°.

From the eluates of water–methanol (50:50 v/v), quercitrin m.p. 181–183° was obtained. Further elution (15:85 v/v water-methanol) gave a mixture of two flavonoids which only could be separated by ascending chromatography on Whatman No. 3 MM paper[11] and 10% acetic acid as mobile phase; two bands were obtained (red-brown colour in u.v. light). Elution of the band with R_f 0·26 gave reynoutrin m.p. 202–203°. The other band, R_f 0·20 yielded avicularin m.p. 215–216°. The melting points, optical rotations and u.v. spectra of all compounds isolated were in agreement with those described in the literature.[12,13] They were further identified by mixed melting point, i.r. spectra, R_f on TLC and PC employing the solvent systems described above (see Table 1).

Acid hydrolysis. Flavonoid glycosides were hydrolysed by heating at 100° in 2 N HCl-ethanol (1:1) in stoppered tubes for 60 min.[14] After cooling, the reaction mixture was made up to 10 ml with ethanol and the concentration of aglycone was determined spectrophotometrically.[15] When the solvent was removed *in vacuo*, the solid was dissolved in water and the quantitative determination of sugars was carried out[16] on Whatman No. 1 paper with *n*-butanol:pyridine:water (6:4·3). The sugars were revealed with aniline hydrogen phthalate, the colored spots being eluted with 0·7 N HCl in 80% ethanol (v/v) and absorbances being measured with a Hitachi–Perkin Elmer Model 139 spectrophotometer. All three flavonoids gave quercetin and the appropriate monosaccharide in the following ratios: quercetin:rhamnose 1·1·1, quercetin:xylose 0·90, 1·05 and quercetin:arabinose 1·26:0·97.

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TABLE 1. CHROMATOGRAPHIC PROPERTIES OF FLAVONOIDS ISOLATED FROM ARGENTINE MISTLETOE

Solvent system	Support	R_f value of				
		Quercetin	(+)-catechin	Quercitrin	Reynoutrin	Avicularin
Water	Whatman No. 1 paper	—	0·33	0·19	0·08	0·07
BAW (4:1:5)		0·78	0·67	0·80	0·78	0·80
15% HOAc		—	0·52	0·47	0·30	0·31
Forestal		0·40	—	—	—	—
10% HOAc	Whatman No. 3 MM paper	—	0·49	0·35	0·26	0·20
EtOH:H_2O (6:4)	Polyamide	—	0·64	0·25	0·25	0·20
$CHCl_3$:MeOH:MeCoEt (9:4:2)	Polyamide+ 20% cellulose	—	0·68	0·38	0·45	0·36

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