and 340(4 13), IR ν_{max}^{KBr} cm^{-1} 1640 (C = O), 1380 (gem-diMe), 1245, 1120, 920(OCH_2O) and 720(*cis* C = C), ^{1}H NMR (90 MHz, $CDCl_3$) δ7 42 (*s*, H-5), 7 20–7 35 (*m*, H-2′, H-6′), 6 87 (*d*, *J* = 9Hz, H-5′), 6 85 (*d*, *J* = 10 Hz, H-α), 6 58 (*s*, H-3), 6 02 (*s*, OCH_2O), 5 73 (*d*, *J* = 10 Hz, H-β), 3 93 (*s*, OMe) and 1 56 (*s*, gem-diMe)

Synthesis of isopongachromene (**1**) *and 7-benzyloxy-6-methoxy-3′,4′-methylenedioxyflavone* (**4**) 4-Benzyloxy-5-methoxy-2-(3′,4′-methylenedioxybenzoyloxy)acetophenone (**2**) (100 mg) [6] was dissolved in dry pyridine (2 ml) and powdered KOH (450 mg) was added The mixture was heated at 50–60° for 90 min with occasional shaking It was poured into ice and acidified with HCl, pptated diketone (**3**) was filtered, dried and crystallized from $CHCl_3$–MeOH as yellow plates (70 mg), mp 188–189° It gave a greenish blue ferric reaction

The above diketone (3) (70 mg) was dissolved in HOAc (3 ml) and conc HCl (0 2 ml) was added The mixture was refluxed for 3 hr, cooled and poured into ice-cold H_2O The pptated solid (**4**) was filtered and crystallized from MeOH as silky needles (55 mg), mp 199–200° (lit [6] mp 195°), ^{1}H NMR (90 MHz, $CDCl_3$) δ7 48 (*s*, H-5), 7 17–7 45 (*m*, H-2′, H-6′ and $OCH_2C_6H_5$), 6 91 (*s*, H-8), 6 83 (*d*, *J* = 9 Hz, H-5′), 6 53 (*s*, H-3), 5 98 (*s*, OCH_2O), 5 20 (*s*, $OCH_2C_6H_5$) and 3 95 (*s*, OMe)

Isopongachromene (**1**) A soln of **4** (55 mg) in EtOAc (20 ml) was stirred for 3 hr in the presence of 10% Pd–C in a H_2 atmosphere at *ca* 1 atm pres The crude product obtained after removal of EtOAc was chromatographed over Si gel The $CHCl_3$–MeOH eluate on concn afforded a solid (**5**) which crystallized from EtOH as pale-yellow needles (25 mg), mp 278–280°

5 (25 mg) was dissolved in dioxane (5 ml) and refluxed with 2-chloro-2-methylbut-3-yne (0 2 ml), K_2CO_3 (50 mg) and KI (50 mg) for 16 hr The reaction mixture was diluted with H_2O, extracted with EtOAc and dried After evaporation of the solvent, the residue on purification with prep TLC gave a solid, which crystallized from $CHCl_3$–Me_2CO as light yellow crystals (15 mg), identical with **1** in all respects

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C-GLYCOSYLXANTHONES IN THE FERN GENERA *DAVALLIA*, *HUMATA* AND *NEPHROLEPIS*

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Key Word Index—*Davallia*, *Humata*, *Nephrolepis*, Davalliaceae, xanthones, *C*-glycosylation, mangiferin, isomangiferin, biochemical systematics

Abstract—*C*-Glycosylxanthones have been detected in several species of *Davallia*, *Humata* and *Nephrolepis*, while other species lack these compounds This increases the number of fern taxa known to contain *C*-glycosylxanthones from 20 to 33 and the number of xanthone-containing genera from 9 to 11 The taxonomic value of these compounds is still uncertain

C-Glycosylxanthones have previously been reported from the following fern genera *Asplenium* (one species and its hybrids), *Athyrium* (1), *Cardiomanes* (1), *Ctenitis* (1), *Davallia* (1), *Elaphoglossum* (5), *Hymenophyllum* (5), *Marsilia* (3) and *Trichomanes* (2) [1, 2] This paper reports the occurrence of *C*-glycosylxanthones in several additional *Davallia* species as well as in several species of the closely related genera *Humata* and *Nephrolepis*, all members of the Davalliaceae *sensu* Crabbe *et al* [3]

The results of the present survey of 27 fern species for *C*-glycosylxanthones are presented in Table 1 Mangiferin and isomangiferin were found in five of nine species of *Davallia*, one of three species of *Humata* and five of eleven species of *Nephrolepis* Mangiferin alone

Table 1 Members of the Davalliaceae examined for *C*-glycosylxanthones

Taxon	NYBG numbers	Mangiferin	Isomangiferin
Araiostegia sp	919/79	—	—
Davallia bullata Wallich ex Hooker	472/77	—	—
D canariensis (L) Smith	633/76, 145/79	—	—
D epiphylla (Forster) Sprengel	289/77	—	—
D. mariesii Moore ex Baker	286/77	+	+
D plumosa Baker	119/81	+	+
D pyxidata Cavanilles	3329/78, 1375/76	+	+
D solida (Forster) Swartz	244/66, 273/77 151/79, 328/79	+	+
D tasmanii Field	?	—	—
D trichomanoides Blume	578/42, 1127/76 138/79	+	+
Davallodes hirsutum (Smith) Copeland	306/77	—	—
Humata heterophylla (Smith) Desvaux	1310/76	—	—
H tyermanii Moore	181/69, 3294/78	+	+
H vestita (Bl) Moore	1290/78	—	—
Nephrolepis acuminata (Houtt) Kuhn	1173/76	+	+
N biserrata (Sw) Schott	1162/76	+	+
N cordifolia (L) Presl	876/77, 3977/77 717/79	—	—
N dryeri hort	?	+	—
N exaltata (L) Schott	119/79	+	+
N occidentalis Kze	?	+	+
N pectinata (Willd) Schott	300/76	—	—
N pendula Smith	383/77	—	—
N rivularis (Vahl) Mett ex King	304/76, 1286/76	—	—
N rufescens Wawra	302/76	+	—
N waimea hort	187/79	+	+
Oleandra bradei Christ	308/76	—	—
Scyphularia pentaphylla Fee	2/63	—	—

+, Present, —, not detected, ?, number not known *Nephrolepsis dryeri* may be a synonym for *N exaltata* but the absence of isomangiferin in *N dryeri* is the reason for its retention as a separate taxon in the table

was detected in another two species of *Nephrolepis* Neither mangiferin nor isomangiferin were detected in the related taxa *Araiostegia* sp , *Davallodes hirsutum, Oleandra bradei* or *Scyphularia pentaphylla*

Hoshizaki [4, 5] has recently reviewed some of the cultivated genera of the Davalliaceae and the occurrence of xanthones may be relevant to some of her views on the taxonomy of the genus *Davallia* Thus, she suggests that *Davallia bullata* has such strong affinities with *D mariesii* that it should be reduced to a subspecies of *D mariesii* However, in the present study xanthones were found in *D mariesii* but appear to be absent from *D bullata* Hoshizaki further describes the connection between *D fejeensis* and *D solida* as so very close that some botanists question the separation of the two species This view is supported by the presence of xanthones in both species

In *Nephrolepis occidentalis* both mangiferin and isomangiferin were found, although it has previously been reported as not containing *C*-glycosylxanthones [1] This may be a further example of infraspecific variation in xanthone occurrence, as previously reported in *Ctenitis decomposita* [6] and several *Asplenium* hybrids [7] Another species of *Nephrolepis, N acuminata*, contained two other compounds on the two-dimensional chromatogram which had the characteristic colour reactions of *C*-glycosylxanthones Their crude *Rf* values in 15% acetic acid suggested that they may have been mangiferin or isomangiferin *O*-glycosides These compounds will be further investigated when larger amounts of material are available None of the other taxa gave any indication of containing xanthones other than mangiferin or isomangiferin

This report increases the number of fern species known to contain *C*-glycosylxanthones from 20 to 33, and the number of xanthone-containing genera from 2 to 11 As suggested by Wallace *et al* [1], *C*-glycosylxanthones may be useful characters at the subfamily or subgenus level of fern classification A survey of further fern genera may be of interest to pteridologists, but at the present moment it appears unlikely that *C*-glycosylxanthones will be of great value in determining the phylogeny of the ferns as a whole

EXPERIMENTAL

Fresh frond material was obtained from the living collections maintained at the New York Botanical Garden Voucher specimens are in the New York Botanical Garden Herbarium A small amount (0 5–1 0 g) was extracted in 80% MeOH by the use of a Polytron homogenizer [8] After 1 hr the solns were spotted onto Whatman No 1 paper for 1 D-PC in H_2O and 15% HOAc After drying, the *C*-glycosylxanthones were detected in UV light (360 nm) as orange spots, becoming fluorescent yellow on fuming

with NH_3, at R_f values of 4–20 (H_2O) and 16–50 (HOAc) The species with *C*-glycosylxanthones were subjected to 2D-PC in TBA and 15% HOAc [9] The compounds were eluted in 80% MeOH for R_f comparison in TBA, BAW, 15% HOAc and H_2O with authentic mangiferin and isomangiferinfrom *Asplenium montanum* [10]

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FLAVONE *C*-GLYCOSIDES OF *PHORADENDRON TOMENTOSUM* FROM DIFFERENT HOST TREES

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Key Word Index—*Phoradendron tomentosum*, mistletoes, Loranthaceae, flavones, apigenin mono- and di-*C*-glycosides

Abstract—Apigenin, three known apigenin *C*-glycosides, vitexin, schaftoside and isoschaftoside together with apigenin 4′-*O*-glucoside have been identified in leaves of *Phoradendron tomentosum* growing on different hosts

Mistletoes are semi-parasitic plants which in modern botanical taxonomy are classified into two families, the Loranthaceae and Viscaceae [1] In an earlier paper Becker and Exner [2] reported the isolation of eight flavonoids from *Viscum album* all of which were methylated quercetin derivatives The present paper describes the characterization of apigenin *C*-glycosides from plants of *P tomentosum* (DC) Gray, growing on three different host trees *Ulmus crassifolia* Nutt, *Prosopis glandulosa* Torr and *Celtis laevigata* Willd

Ethyl acetate and water extracts of air-dried leaf material of *P tomentosum* resulted in the isolation of the previously known flavonoids vitexin [3, 4], schaftoside (6-*C*-glucosyl-8-*C*-arabinosylapigenin) and isoschaftoside (6-*C*-arabinosyl-8-*C*-glucosylapigenin) [5] together with lesser amounts of apigenin 4′-*O*-glucoside and apigenin Colour reactions in UV light before and after fuming with ammonia (olive) and spraying with Naturstoff reagent (NA) (green) [6] are in accordance with those of apigenin derivatives Isomerization with 0 1 N trifluoracetic acid indicated the presence of *C*-glycosides Cochromatography with authentic samples and UV, ^1H- and ^{13}C NMR data were in agreement with reported values [3, 7–9]

The present investigation has revealed that apigenin mono- and di-*C*-glycosides are the predominant compounds in *P tomentosum*, the distributional pattern being uniform irrespective of the host plant It is interesting to note that the methylated quercetin derivatives of *Viscum album* [2] also show a quite uniform pattern However further investigations on the flavonoids of other mistletoe species are needed before any conclusions on their value in systematic differentiation can be drawn

EXPERIMENTAL

P tomentosum leaves were collected by J Exner near Austin, Texas, U S A Voucher specimens are deposited in the Herbarium of the Botany Dept, University of Texas at Austin

Extraction and isolation Air dried leaves (200 g) were ground and extracted with 80% MeOH (1 l × 3), filtered and evaporated

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