Flavonol Glycosides of *Carya pecan* and *Casuarina equisetifolia*

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Carya pecan (Juglandaceae), *Casuarina equisetifolia* (Casuarinaceae), Flavonol Glycosides

The flavonol glycosides of *Carya pecan* and *Casuarina equisetifolia* were isolated and identified. The branches of *C. pecan* were found to contain azaleatin-3-arabinoside, azaleatin-3-rutinoside, quercetin-3-glucoside and caryatin-3′- or -4′-glucoside. From the leaves of *C. equisetifolia* eleven glycosides of kaempferol and quercetin were identified.

Among the trees introduced into Egypt for the purpose of afforestation, the flavonol glycosides of two were studied. *Carya pecan* belongs to the family *Juglandaceae* (walnut family) and *Casuarina equisetifolia* belongs to the family *Casuarinaceae* (beefwood family). Both families belong to the same group, *viz.* Amentiferae, which includes woody plants. The bark of *Carya pecan* (*Carya* species are also known as *Hicoria* [1, 2]) is reported to contain azaleatin (3′,4′,3,7-tetrahydroxy-5-methoxy-flavone) and caryatin (3′,4′,7-trihydroxy-3,5-dimethoxy-flavone) [3, 4]. Kaempferol and quercetin glycosides are also of common occurrence in the *Juglandaceae* [2]. In the present study, the branches of *Carya pecan* were found to contain azaleatin-3-arabinoside, azaleatin-3-rutinoside, caryatin-3′- or -4′-glucoside and quercetin-3-glucoside. The three first glycosides are reported here for the first time. No flavanones could be detected, however catechins were found present. *Casuarina* species have received little attention with regards to their flavonol glycosides. Kaempferol and quercetin were reported in the acid hydrolysate of *C. cunninghamiana* green branches [5]. From *C. equisetifolia* bark, both catechin and gallocatechin were isolated and identified [6, 7]. In the present study, the leaves of *C. equisetifolia* were found to contain the -3-arabinoside, -3-glucuronide, -3-rhamnoside and -3-rutinoside of kaempferol as well as the -3-arabinoside, -3-galactoside, -3-glucoside, -3-glucuronide, -3-rhamnoside, -3-ruinoside and -3-xyloside of quercetin.

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Experimental

Plant material. Carya pecan (Marsh.) Engl. et Graebn. was collected from the yellow mountain, about 10 km north of Cairo. *Casuarina equisetifolia* L. was collected and identified from El-Montazah gardens, Alexandria, by Dr. M. H. El-Lakany.

Extraction and separation. Extraction was carried out with 70% ethanol, and the extracts dried and subjected to column chromatography on polyamide. The column fractions were further separated into single components applying elution techniques.

Identification. Standard methods of identification were followed [8, 9].

(a) Azaleatin-3-arabinoside. m.p. 150 °C, decomp. Mild and strong acid hydrolysis gave rise to arabinose and azaleatin (m.p. 318 °C, demethylation gave quercetin), while methylation followed by acid hydrolysis gave rise to quercetin-3′,4′,5,7-tetramethyl ether. The UV data also confirm that glycosylation is in position 3 (see Table I).

(b) Azaleatin-3-rutinoside. m.p. 200 – 204 °C, decomp. Acid hydrolysis gave rise to azaleatin, glucose and rhamnose, while hydrogen peroxide oxidation [10] gave rise to rutinose. β-Glucosidase failed to effect the rutinoside. The position of glycosylation was also confirmed by complete methylation followed by acid hydrolysis which gave rise to quercetin-3′,4′,5,7-tetramethyl ether, as well as UV spectrophotometry (see Table I).

(c) Caryatin-glucoside. This glucoside was found in trace amounts. It gave rise to caryatin and glucose on acid hydrolysis as well as enzymic hydrolysis (β-glucosidase). R_F values and UV data are outlined in the Table I, and the latter indicate that glucosylation is in position 3′ or 4′. Further studies were not possible due to the trace amounts of the glucoside.

Other flavonoids identified in the branches were quercetin-3-glucoside (m.p. 223 °C), azaleatin (m.p. 318 °C, lit. [2] 317 – 320 °C) and caryatin (m.p. 290 – 292 °C, lit. [2] 299 – 301 °C). R_F values and UV data are outlined in the Table I. No flavanones could be detected, however small amounts of catechins were present as shown by the positive colour with vanillin/HCl.

Applying standard methods of identification [8, 9], the leaves of *C. equisetifolia* proved to contain kaempferol-3-arabinoside, -3-glucuronide, -3-rhamnoside and -3-rutinoside as well as quercetin-3-galactoside, -3-glucoside, -3-glucuronide, -3-rhamnoside, -3-rutinoside and -3-xyloside.

Table I. Paper chromatographic and spectrophotometric data of new glycosides isolated from *Carya pecan*.

	colour under UV [b]	R_F (×100) [c]					MeOH	$\Delta\lambda$			
		1	2	3	4	5	(λ_{max}, nm)	$AlCl_3$ (band II)	NaOAc (band I)	H_3BO_3 (band II)	NaOEt (band II)
quercetin-3-glucoside [a]	brown	14	40	—	61	46	257, 357	45	16	20	53
azaleatin-3-arabinoside	fl.bl.	15	50	66	68	75	252, 348	0	21	21	52
azaleatin-3-rutinoside	fl.bl.	30	63	69	69	73	252, 342	0	14	14	48
caryatin-glucoside	fl.bl.	13	44	42	46	56	264, 340	0	8	0	44
azaleatin	fl.y.	00	9	54	66	61	255, 366	62	21	14	decomp.
caryatin	fl.bl.	4	27	80	82	81	251, 265 §, 346	0	16	21	49

[a] as reference.
[b] fl. = fluorescent, bl. = blue, y. = yellow.
[c] 1 = water, 2 = 15% acetic acid, 3 = n-butanol/ethanol/water (4/1/2.2), 4 = n-butanol/acetic acid/water (4/1/5), 5 = phenol/water (80/20).
§ inflection.

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