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FLAVONOL GLYCOSIDES OF *CARYA PECAN**†

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Key Word Index—*Carya pecan*; Juglandaceae; flavonol glycosides.

Abstract—The flavonol glycosides characterized from the branches of *Carya pecan* include three new compounds, azaleatin 3-glucoside azaleatin 3-diglycoside and caryatin 3′- (or 4′-) rhamnoglucoside, together with azaleatin 3-rhamnoside. In the leaf tissue, quercetin 3-glucoside, quercetin 3-galactoside, quercetin 3-rhamnoside, quercetin 3-arabinoside and a small amount of kaempferol 3-monomethyl ether were identified.

Azaleatin and caryatin have been previously identified from the bark of *Carya pecan* [1, 2]. Five glycosides of azaleatin have been reported from other plant sources [3]. Two new azaleatin glycosides, the 3-arabinoside and the 3-rutinoside together with caryatin 3′- (or 4′-) glucoside, have been recently characterized in the branches of *C. pecan* [4]. Trace amounts of a number of other glycosides were also detected, but could not be identified at that time. In the present study, a larger sample of branch tissue has been reinvestigated, and the flavonols of the leaves also studied. In addition to the previously mentioned glycosides [4], the branches were also found to contain the following glycosides: azaleatin 3-glucoside, azaleatin 3-rhamnoside, azaleatin 3-diglycoside and caryatin 3′- (or 4′-) rhamnoglucoside. This is the first report of azaleatin 3-glucoside and caryatin 3′- (or 4′-) rhamnoglucoside in nature. In the leaf tissue quercetin 3-glucoside, 3-galactoside, 3-arabinoside and 3-rhamnoside, and a trace amount of kaempferol 3-monomethyl ether were characterized.

EXPERIMENTAL

Plant material. Carya pecan (Marsh.) Engl. et Graebn. was collected from the yellow mountain, *ca* 10 km N. of Cairo.

Extraction and separation. Branch and leaf tissue were extracted with 70% EtOH and the conc extracts dried and subjected to column chromatography on Polyamide. The column fractions were further separated into single components applying elution techniques.

Identification. Known compounds were identified by standard procedures [5, 6].

Azaleatin 3-glucoside. Acid hydrolysis of this glycoside gave azaleatin and glucose. The position of glycosylation was determined by UV data and H_2O_2 oxidation. R_f values and colour reactions are recorded in Table 1. This is the first report of this glycoside in nature.

Azaleatin 3-diglycoside. It was very sensitive to solvents containing acids, and during purification by PC was mostly converted to free azaleatin. The compound must be carefully treated during elution. The instability of azaleatin glycosides

Table 1. Chromatographic and UV data of new flavonol glycosides from *Carya pecan*

	Colour under UV*	R_f(×100)†					MeOH (λ_{max}, nm)	Δλ			
		1	2	3	4	5		$AlCl_3$ band I	NaOAc band II	H_3BO_3 band I	NaOMe band I
Azaleatin 3-glucoside	sh. bl.	11	35	47	44	69	248, 260,‡, 292‡, 344	2	8	16	50
Azaleatin 3-rhamnoside	sh. bl.	25	45	60	56	68	248, 296‡, 336	10	12	16	37
Azaleatin 3-diglycoside	sh. bl.	21	48	30	24	9	250, 256, 262‡, 300‡, 338	88	7	24	37
Caryatin 3′- (or 4′-) rhamoglucoside	sh. bl.	11	28	45	34	42	261, 298, 338	5	7	0	42

* sh. = shiny, bl. = blue.

† 1 = H_2O, 2 = 15% HOAc, 3 = *n*-BuOH–EtOH–H_2O (4 : 1 : 2.2), 4 = *n*-BuOH–HOAc–H_2O (4 : 1 : 5), 5 = PhOH–H_2O (4 : 1).

‡ Inflection.

* This paper is dedicated to the memory of the late Dr. Wadie Tadros, Professor of Chemistry, Cairo University.

† Part II in the series "Flavonol Glycosides of *Carya pecan*". For Part I see [4].

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has previously been noted [7, 8]. Acid hydrolysis with 0.1 N HCl gave azaleatin, glucose and galactose. The mild acid hydrolysis did not give an intermediate monoglycoside. The UV data indicates that glycosylation is in position 3. The addition of $AlCl_3$ showed a large shift which can only be explained by the immediate breakdown of the glycoside due to the acidity of $AlCl_3$ so that this shift is due to the aglycone rather than the glycoside. Free azaleatin showed a shift on the addition of $AlCl_3$ to 425 nm. R_f values confirm that it is a diglycoside (Table 1).

Caryatin 3′- (*or* 4′-) *rhamnoglucoside.* Acid hydrolysis gave caryatin, glucose and rhamnose. The UV data (Table 1) indicated that positions 3 and 5 are occupied as no shift with $AlCl_3$ was observed. The positive shift with NaOAc proved that position 7 was free. The absence of a shift with H_3BO_3 indicated that either the 3′- or 4′-position is glycosylated. Addition of HCl to the $AlCl_3$ complex also showed no change. From the above data, the glycosylation is either in position 3′ or 4′. The spectrum with NaOMe seems to indicate a free 7,4′-hydroxylation pattern [6] and consequently glycosylation might be in the 3′- rather than the 4′-position.

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