

## ISOLATION AND CHARACTERIZATION OF TAXIFOLIN 6-C-GLUCOSIDE FROM *GARCINIA EPUNCTATA*

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**ABSTRACT.**—*Garcinia epunctata* is an indigenous medicinal plant of Cameroon from which taxifolin 6-C-glucoside was isolated and characterized. The nmr assignments obtained from COSY and INAPT experiments are reported for the first time.

During the course of our study of the Cameroonian medicinal plant *Garcinia epunctata* Staff (Guttiferae), we have isolated and characterized taxifolin 6-C-glucoside. Reports of related compounds are rare, with seven C-glucosides of 3-hydroxyflavanonols having been reported to date (1-5), all from the genus *Zelkova*. The lack of nmr data on the parent compound (5), as well as the somewhat ambiguous assignment of the position of the glucose moiety on the flavonoid nucleus, prompted us to study the molecule in some detail. We now report the  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr assignments below, as well as the unambiguous position of the C-glucoside.

The flavanone C-glucoside **1** was isolated from the extract of the stem bark of *G. epunctata*. The ir spectrum (KBr disc) exhibited broad bands between 3552-3116  $\text{cm}^{-1}$  (hydroxyl and chelated hydroxyl) and 1646  $\text{cm}^{-1}$  (carbonyl); uv  $\lambda$  max (MeOH) 291 nm  $\epsilon$  max 19645, 325 nm (sh) 4112. The  $^1\text{H}$ -nmr (DMSO- $d_6$ ) and  $^{13}\text{C}$ -nmr data are shown in Table 1. The  $^1\text{H}$  nmr was assigned using the 2D

homonuclear chemical shift correlation experiment COSY (6) and clearly established the presence of a glucose moiety in the molecule via coupling and chemical information (Table 1). The upfield  $^1\text{H}$ -nmr chemical shift of H-1'' in the glucose moiety ( $\delta$  4.88) is consistent with a C-glucoside rather than an O-glucoside. The  $^{13}\text{C}$ -nmr spectral data were consistent with that reported for taxifolin itself (7), with differences at C-6 (taxifolin C-6  $\delta$  96.1, C-8  $\delta$  95.1; **1** C-6  $\delta$  106.1, C-8  $\delta$  94.8). A series of 1D long-range heteronuclear nmr experiments [INAPT (Insensitive Nuclei Assignment thru Polarization Transfer)] (8,9) showed the H-2 proton coupled with C-3, C-4, C-9, C-1', C-2', and C-6'; the 5-OH coupled with C-5, C-6, and C-10; H-8 coupled with C-6, C-7, C-9, and C-10; and the 3-hydroxylated proton coupled with C-2, C-3, and C-4. This clearly established that the C-6 position was substituted, as well as making carbon assignments. The upfield  $^{13}\text{C}$ -nmr chemical shift of C-6 ( $\delta$  106.1) also indicates C substitution rather than O substitution, confirming

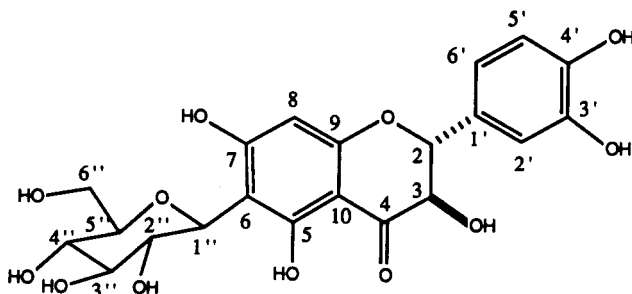


TABLE 1.  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr Spectral Data of Compound **1** (DMSO- $d_6$ ) at 300 MHz and 75 MHz, respectively.

Atom	$^1\text{H}$ (ppm)	multiplicity	$J$ (Hz)	$^{13}\text{C}$ (ppm)
2 . . . . .	4.96	d	11.01	83.0
3 . . . . .	5.82-OH, 4.47	d,d	6.13, 6.81	71.7
4 . . . . .				198.1
5 . . . . .	12.48	s		162.7
6 . . . . .				106.1
7 . . . . .				166.4
8 . . . . .	5.92	s		94.8
9 . . . . .				161.4
10 . . . . .				100.3
1' . . . . .				128.1
2' . . . . .	6.75	s		115.4
3' . . . . .				145.9
4' . . . . .				145.1
5' . . . . .	6.88	s		115.2
6' . . . . .	6.75	s		119.5
1'' . . . . .	4.88	br		73.0
2'' . . . . .	3.13	m		70.8
3'' . . . . .	3.49	m		79.2
4'' . . . . .	3.67	m		70.3
5'' . . . . .	4.88	br		81.6
6'' . . . . .	4.48	br		61.7

the structure as shown. The peracetate of **1** had  $^1\text{H}$ -nmr spectral data in agreement with those published (5).

## EXPERIMENTAL

**GENERAL EXPERIMENTAL PROCEDURES.**—Ir spectra were obtained on a Nicolet 20 DBX and uv spectra on a Varian Techtron model 635 spectrophotometer. All nmr experiments were performed on a Nicolet NT-300 WB spectrometer equipped with 5 mm  $^1\text{H}$  and  $^{13}\text{C}$  probes operating at 300.06 and 75.45 MHz, respectively. Compound **1** was run in DMSO- $d_6$  and its peracetate in  $\text{CDCl}_3$ ; all chemical shifts were referenced to internal TMS (0.00 ppm) for  $^1\text{H}$ -nmr and  $^{13}\text{C}$ -nmr spectra.

**PLANT MATERIAL.**—The stem bark of *G. epunctata* was collected in August 1986 at Mankii in Fouban, Cameroon. The plant was identified at the site by a botanist of the Centre for the Studies of Medicinal Plants, Yaounde, and later at the National Herbarium, Yaounde, Cameroon, where a voucher specimen documenting the collection is on deposit.

**EXTRACTION AND ISOLATION.**—The dried and ground stem bark of *G. epunctata* (1.0 kg) was placed in a flask containing EtOH (4 liters) and heated with occasional stirring in an  $\text{H}_2\text{O}$  bath at  $55^\circ$  for 6 h. After filtration, the powder was again

extracted with EtOH ( $2 \times 4$  liters at  $55^\circ$ ). The combined EtOH extracts were concentrated to 2 liters and left to stand at room temperature. After 3 weeks a precipitate was filtered and washed several times with EtOH to give a solid (3.4 g) which showed one major spot at  $R_f$  0.63 on tlc [Si gel, *n*-BuOH-EtOAc-HOAc- $\text{H}_2\text{O}$  (3:1:1:10)]. Repeated recrystallization from EtOH gave pure compound **1** (2.0 g):  $^1\text{H}$  and  $^{13}\text{C}$  nmr see Table 1.

## ACKNOWLEDGMENTS

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