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1,3-DI-*O*-GALLOYLQUINIC ACID FROM *GUIERA SENEGALENSIS*

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Key Word Index—*Guiera senegalensis*; Combretaceae; galls; gallotannin; polyphenols; 1,3-di-*O*-galloylquinic acid.

Abstract—A new polyphenol, 1,3-di-*O*-galloylquinic acid, and the known quinic acid gallates, 3-*O*-, 4-*O*-, 5-*O*-, 3,4-di-*O*-, 4,5-di-*O*-, 3,5-di-*O*-, 3,4,5-tri-*O*- and 1,3,4,5-tetra-*O*-galloylquinic acids were isolated from the galls of *Guiera senegalensis*.

INTRODUCTION

The leaves of *Guiera senegalensis* are used in West Africa (Senegal, Guinea and Mali) for the treatment of colds, bronchitis and fever [1]. The antitussive effect confirmed in guinea-pigs has been determined with reference to codeine [2]. The roots have been also used to treat diarrhoea and dysentery [3]. We report herein on the tannin composition of the galls of this species.

Many structural isomers of quinic acid gallates have already been isolated from the Fagaceae [4, 5]. Our continuing work on the polyphenols occurring in the Combretaceae [6] has now resulted in the isolation and characterization of nine gallotanins based on a quinic acid core, one of them, **1**, being a new compound. In this paper, numbering of the quinic acid ring follows the IUPAC nomenclature recommendations [7, 8].

RESULTS AND DISCUSSION

The water-soluble part of the galls of *G. senegalensis* was dried and chromatographed on Sephadex LH-20 to afford the new compound **1**, together with the known 3-*O*-, 4-*O*-, 5-*O*-, 3,4-di-*O*-, 4,5-di-*O*-, 3,5,-di-*O*-, 3,4,5-tri-*O*- and 1,3,4,5-tetra-*O*-quinic acid gallates.

Compound **1** was obtained as an amorphous powder and its structure established on the basis of its spectral data. The positive ion FAB mass spectrum showed a $[M + H]^+$ at m/z 497, in agreement with the molecular formula $C_{21}H_{20}O_{14}$. The ^1H NMR spectrum exhibited signals for two gallic acid moieties (Table 1). The signals for H-3 (equatorial), H-4 (axial) and H-5 (axial) of the quinic acid moiety were assigned according to their multiplicity and spin–spin coupling constants. In [9], the signals for H-2 and H-6 were well separated in the ^1H NMR spectrum. Coupling constant values were measured by irradiation of each quinic acid proton and thus confirmed the structure and conformation of the quinic acid moiety.

The location of the galloyl substitutions at C-1 and C-3 of the quinic acid moiety was deduced from comparison of the ^1H NMR chemical shifts of the protons with those of free quinic acid in CD_3OD [8]. Only the signal for H-3 was shifted downfield by *ca* 1.30 ppm, thus indicating *O*-acylation of C-3. On the other hand, the ^{13}C NMR spectrum of **1** showed lowfield shifts of the C-1 signal (δ 81.3) (Table 1). Long-range correlations were observed in the HMBC spectrum between C-1 (δ 81.3) and H-2, H-3 and H-6, between C-3 (δ 73.1) and H-4ax, between C-4 and H-5ax and H-6ax, and between C-5 and H-4ax and H-6ax. The cross-peak observed between the carbonyl carbon at δ 167.4 was assigned to a galloyl group and the proton at δ 5.39 (H-3eq) confirmed the substitution of a galloyl group at C-3.

From these data, the location of two galloyl groups was concluded to be at C-1 and C-3 positions and, thus, **1** was 1,3-di-*O*-galloylquinic acid. Full assignment of the ^{13}C NMR spectrum was made from heteronuclear 2D NMR spectroscopy (HMQC and HMBC).

EXPERIMENTAL

General. ^1H NMR: 300 MHz. ^{13}C NMR: 75 MHz.

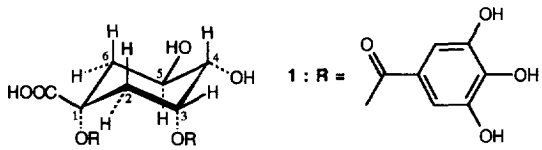
Plant material. Guiera senegalensis J. F. Gmel was collected near Dakar (Senegal) and a voucher specimen is deposited at the Herbarium of the Faculté de

Table 1. NMR spectral data for 1,3-di-*O*-galloylquinic acid (**1**) (CD_3OD)

C	δ_C	δ_H	Multiplicity	*J* (Hz)
Quinic acid moiety				
COOH	174.9	–		
1	81.3	–		
2ax	32.7	2.42	*dd*	−15.6, 3.3
2eq	–	3.01	*ddd*	−15.6, 3.8, 2.1
3	73.1	5.39	*ddd*	3.8, 3.4, 3.3
4	74.8	3.73	*dd*	8.8, 3.4
5	68.3	4.31	*ddd*	9.4, 8.8, 3.3
6ax	40.9	1.97	*dd*	−13.2, 9.4
6eq	–	2.54	*ddd*	−13.2, 3.3, 2.1
Gallic acid moieties				
C=O	168.2	–		
	167.4	–		
1′	121.3	–		
	121.3	–		
2′, 6′	110.3 (2C)	6.87	*s*	
	110.3 (2C)	6.89	*s*	
3′, 5′	145.9 (2C)	–		
	146.1 (2C)	–		
4′	139.7	–		
	139.4	–		

Me_2CO under red. pres., was lyophilized. The brown powder obtained was mixed with Celite 545 (100 g). The mixed powder obtained was packed into a glass column and eluted with $CHCl_3$, $CHCl_3$–Me_2CO (1:1) and Me_2CO. The $CHCl_3$ extract was discarded and the eluate containing Me_2CO was evapd under red. pres. (1.96 g) and subjected to Sephadex LH-20 CC with an aq. MeOH gradient (1:10 to 7:3) and 73 frs collected. Frs 3–4 contained the 4- and 5-*O*-galloylquinic acids, fr. 5 (MeOH–H_2O, 1:10), 1,3-di-*O*-galloylquinic acid (30 mg), fr. 6, a mixt. of 1,3-di-*O*-galloylquinic acid and 3,4-di-*O*-galloylquinic acid, fr. 38 (MeOH–H_2O, 1:5), a mixt. of 3,4-, 3,5- and 4,5-di-*O*-galloylquinic acids, and frs 39–40 (MeOH–H_2O, 3:2), 3,4,5-tri-*O*- and 1,3,4,5-tetra-*O*-galloylquinic acids. Each fr. was further analysed and, where needed, purified by HPLC.

HPLC. Analyt. HPLC was carried out at 20° on a reverse-phase encapped column (RP-18E) (125 × 4 mm; particle size 4 μm, Merck) with a pre-column (4 mm, same phase); the mobile phase was H_2O–THF–*iso*ProH–H_3PO_4, 90:10:5:1) at a flow rate of 1 ml min^{-1}. The injection vol. was 10 μl with UV detection at 280 nm. The R_t of 1,3-di-*O*-galloylquinic acid was 1.7 min, 3,5-di-*O*-galloylquinic acid 5.2 min and 3,4,5-tri-*O*-galloylquinic acid 15.0 min.



1,3-Di-O-galloylquinic acid (**1**). Amorphous powder. IR ν^{KBr} cm^{-1}: 3385, 1710, 1618, 1435, 1354, 1225, 1098, 1032, 762. $[\alpha]_D^{23}$ −30° (MeOH, *c* = 1.0). (+) FAB MS: *m/z* 497 $[M+H]^+$.

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