10-Hydroxymajoroside, an Iridoid Glucoside from *Plantago cornuti* Gouan L.

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Iridoids, *Plantago cornuti*

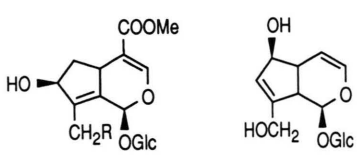
10-Hydroxymajoroside, a second representative of the rare majoroside type iridoid glucosides, along with the well known aucubin, has been isolated from *Plantago cornuti*.

Introduction

Recently we reported the isolation of iridoids from different *Plantago* species [1–4]. As a part of our continuing studies on *Plantago* plants, we report the isolation of a new iridoid glucoside, 10-hydroxymajoroside, as well as the known aucubin, from *Plantago cornuti* Gouan. The new iridoid is the second representative of the rare majoroside type iridoids. The iridoid composition of *P. cornuti* has not been investigated till now.

Results and Discussion

Separation of the methanol extract of *P. cornuti* by sequential charcoal treatment, vacuum liquid chromatography (VLC) and column chromatography on silica gel, yielded the new iridoid glucoside, 10-hydroxymajoroside (**1**), as well as aucubin (**2**). The latter compound was identified as aucubin by ^{1}H and ^{13}C NMR spectra.



1: R=OH
3: R=H

2

The molecular formula $C_{17}H_{24}O_{11}$ of **1** was determined by ^{13}C, DEPT NMR analysis (Table II) and DCI/MS(NH_3) [5] (*m/z* 422 $[M+NH_4]^+$). The absorption maximum at 235 nm in the UV spectrum showed the presence of an iridoid enol ether system conjugated with a C-4 carbomethoxy group.

The ^{1}H and ^{13}C NMR data of **1** (Tables I and II) were very similar to those of majoroside (**3**), an iridoid isolated previously from *P. major* [3], thus suggesting the same skeleton. The strong deshielding of H-1 and its appearance as a singlet due to the absence of the typical 1,9-coupling confirmed the unusual position of the double bond in the 8,9-position in the five membered ring. The main difference in the ^{1}H NMR of **1** were the presence of signals for two protons at δ 4.45 (1H, *d*, $J_{10a,10b}$ = 14.1, 10a-H) and 4.26 (1H, *dd*, $J_{10a,10b}$ = 14.1, $J_{5,10}$ = 2.6, H-10b) indicating a $-CH_2OH$ group as well as the absence of the singlet at δ 1.85 for Me-10. The signal for H-7 was deshielded (**1:** δ 5.05; **3:** δ 4.61). The long-range coupling of H-5 with H-3 (J = 1.8 Hz) and H-10b (J = 2.6 Hz), absence of coupling between H-7 at

Table I. ^{1}H NMR data of compounds **1** and **3.**

H	**1** (D_2O)	**3*** (D_2O)
1	6.40 *s*	6.23 *s*
3	7.45 *d* (1.8)	7.44 *d* (1.9)
5	3.76 *m*	3.75 *m*
6a	1.83 *m*	1.85 *m*
6b	2.46 *dd* (7.0/14.3)	2.40 *dd* (7.2/14.5)
7	5.05 *d* (7.0)	4.61 *brd* (7.1)
10a	4.26 *dd* (2.6/14.1)	1.85 *d* (2.5)
10b	4.45 *d* (14.1)	
OMe	3.76 *s*	3.75 *s*
1′	4.89 *d* (8.2)	4.88 *d* (8.1)
2′	3.29 *t* (9.0)	3.29 *t* (9.1)
3′		3.53 *m*
4′	3.36–3.56	3.45 *t* (9.5)
5′		3.53 *m*
6′a	3.76 *m*	3.75 *m*
6′b	3.95 *dd* (1.5/11.9)	3.96 *dd* (2.0/12.3)

* Ref. [3].

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Table II. ^{13}C NMR spectral data of compounds **1** and **3.**

C	**1** (D_2O)	**3*** (D_2O)
1	93.80 *d*	94.56 *d*
3	153.85 *d*	153.98 *d*
4	115.26 *s*	115.60 *s*
5	38.08 *d*	37.72 *d*
6	42.11 *t*	41.92 *t*
7	78.72 *d*	82.54 *d*
8	143.88 *s*	142.75 *s*
9	137.59 *s*	134.07 *s*
10	58.24 *t*	13.64 *q*
11	172.48 *s*	172.42 *s*
OMe	54.66 *q*	54.62 *q*
1′	101.19 *d*	101.20 *d*
2′	75.44 *d*	75.53 *d*
3′	78.38 *d*	78.48 *d*
4′	72.33 *d*	72.42 *d*
5′	79.17 *d*	79.20 *d*
6′	63.48 *t*	63.58 *t*

* Ref. [3].

δ 5.05 and H-5 at δ 3.76 and strong coupling of H-5 with H-6b ($J = 7.0$ Hz) were proven by selective decoupling.

The ^{13}C NMR data and DEPT NMR analysis of **1,** compared with those of **3,** clearly confirmed the occurrence of a $-CH_2OH$ at C-8 (Table II). Instead of a signal at δ 13.64 *q* for Me-10, the presence of a signal at δ 58.24 *t* for C-10 was observed. The signal of C-7 (**1:** δ 78.72; **3:** δ 82.54) was shielded while that of C-9 (**1:** δ 137.59; **3:** δ 134.07) deshielded. Hence, **1** is 10-hydroxymajoroside.

Materials and Methods

DCI/MS (NH_3) were recorded with JEOL JMS D-300 (ion source temp. 130 °C). The ^1H and ^{13}C NMR spectra were measured on a Bruker 250 MHz spectrometer: 250 MHz; 62.9 MHz. TSPA-d_4 int. standard. The normal and selective-decoupled proton spectra were measured with presaturation of solvent. ^{13}C NMR spectra were obtained by use of DEPT sequence for multiplet selection. The chemical shifts are accurate within δ ± 0.005 (^1H) and ± 0.02 (^{13}C), and the coupling constants within ± 0.3 Hz.

Plant material

Above ground parts of *Plantago cornuti* were collected in Tsarevo along the beach in June 1991 when plants were in flower. Voucher specimen SOM 151024 is deposited in the Herbarium of the Institute of Botany with Botanical garden, Bulgarian Academy of Sciences, Sofia.

Isolation

Dried above ground parts of *P. cornuti* (120 g) were exhaustively extracted with MeOH. The combined extract was evaporated *in vacuo* below 45 °C and fractionated with dichlorethane and water. The water layer was chromatographed on active charcoal (19 g) and eluted with H_2O. H_2O–MeOH (9:1), MeOH, MeOH–Me_2CO (1:1) and MeOH–$Cl(CH_2)_2Cl$ (1:1). The MeOH fr (1.2 g) contained almost only 2. The last two frs (600 mg) after VLC on silica gel (36 g) and elution with $Cl(CH_2)_2Cl$ with increasing MeOH content and further purification on a silica gel column (15 g) of fr 4 (148 mg) afforded frs 12–13 (17 mg) of pure 1 and frs 17–19 (12 mg) of pure **2.**

10-Hydroxymajoroside (**1**)

Amorphous powder, $[\alpha]_D^{20}$ −21.78° (MeOH); UV λ_{max}^{MeOH} nm: 235; DCI/MS(NH_3): *m/z* (rel. int.) 422 $[M+NH_4]^+$ (53), 404 $[M+NH_4-18]$ (10), 242 [Agl] (28), 224 [Agl−18] (46), 207 [Agl−18−17] (78), 189 [Agl−2 × 18−17] (100). ^1H and ^{13}C NMR data ara given in Table I and II.

Acknowledgements

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