Pergamon

PII: S0031-9422(97)00527-X

Phytochemistry, Vol. 47, No. 6, pp. 1161–1162, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

A CAFFEOYL PHENYLETHANOID GLYCOSIDE FROM *PLANTAGO MYOSUROS*

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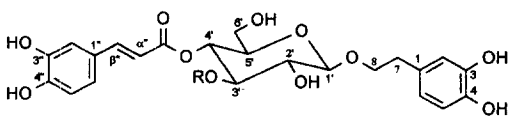
(*Received* 5 *March* 1997)

Key Word Index—*Plantago myosuros*; Plantaginaceae; aucubin; plantalloside; verbascoside; alloside.

Abstract—From *Plantago myosuros*, the iridoid glucoside, aucubin was isolated, together with the caffeoyl phenylethanoid glycosides, plantalloside and verbascoside. Plantalloside is a new verbascoside analogue with a β-allopyranosyl moiety. The structure was elucidated by NMR spectroscopy. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The genus *Plantago* is known to contain iridoids [1] and caffeoyl phenylethanoid glycosides (CPG's) [2–5]. *Plantago myosuros* belongs to subgenus *Plantago* section *Virginica*, which comprises 28 American species of the genus [6]. To our knowledge, this species has not previously been investigated chemically.



1; R = β-Allopyranosyl
2; R = α-Rhamnopyranosyl
3; R = β-Glucopyranosyl

RESULTS AND DISCUSSION

The water-soluble part of the ethanolic extract of *P. myosuros* was fractionated by reversed-phase chromatography to give the iridoid glucoside, aucubin, together with two CPG's, **1** and verbascoside (**2**). The former appeared to be new and we have named it plantalloside.

The ^{13}C NMR spectrum of **1** (Table 1) showed 29 signals and comparison with the spectra of **2** [7] and of plantamajoside (**3**) [4] showed the similarity. Thus, eight signals could at once be assigned to a 3,4-dihydroxyphenylethyl group, nine signals to a caffeoyl moiety and six to a central β-glucopyranosyl moiety carrying an additional sugar at C-3′ (δ 84.7). The remaining six signals fitted well with an auxiliary β-allopyranosyl group when compared with the spectrum of 3,4-dihydroxyphenylethyl β-allopyranoside (**4**), recently reported from the liverwort *Conocephalum conocum* [8]. This suggested the structure shown as **1** for plantalloside. The ^1H NMR spectrum (see Experimental) fitted well with this, in particular, the low field position of H-4′ of the glucopyranosyl group (δ 4.94) showed that this was the point of acylation.

Allose is not commonly found as a sugar in CPG's. It has so far only been found as the core sugar moiety in magnoliosides A–C from *Magnolia obovata* [9, 10] and in sanangoside, a constituent of *Sanango racemosum* and several other species of the Gesneriaceae [11].

EXPERIMENTAL

Plantago myosuros. Lam. was grown at the experimental field of The Botanical Garden, The University of Copenhagen at Tåstrup, Sjælland. The voucher Rahn 669 has been deposited at The Botanical Museum of Copenhagen (C). For NMR, the solvent (methanol-d_4) peaks were used as int. standard.

Extraction and isolation. Frozen whole plants (268 g) were homogenized in EtOH (2 × 600 ml). The extract was concd and partitioned between Et_2O–H_2O. Sepn and evapn of the aq. phase was followed by treatment with activated C (*ca* 1 g) in MeOH to yield the crude extract (2.73 g). This was applied to a Merck Lobar RP_{18} column (size C) and eluted with H_2O–MeOH (25:1 to 1:1). This yielded aucubin (104 mg, 0.04%), plantalloside (321 mg, 0.1%) and verbascoside (73 mg, 0.03%).

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Table 1. ^{13}C NMR data for compounds **1–4** in methanol-d_4

Compound	1	2*	3†	4‡
Aglycone				
C-1	131.5	131.4	131.5	131.5
C-2	117.1	117.0	117.2	117.1
C-3	146.1	145.9	146.0	146.1
C-4	144.6	144.4	144.5	144.6
C-5	116.4	116.2	116.3	116.3
C-6	121.3	121.1	121.2	121.2
C-7	36.5	36.3	36.4	36.5
C-8	72.2	72.0	72.2	72.3
Core sugar				
C-1′	103.9	104.0	103.9	
C-2′	75.8	75.8	75.9	
C-3′	84.7	81.5	84.2	
C-4′	71.1	70.2	70.8	
C-5′	74.9	75.8	75.9	
C-6′	62.3	62.2	62.3	
Caffeoyl				
C-1″	127.7	127.5	127.7	
C-2″	115.3	115.2	115.3	
C-3″	146.8	146.6	146.7	
C-4″	149.7	149.5	149.6	
C-5″	116.7	116.4	116.6	
C-6″	123.2	123.0	123.1	
C-β″	147.5	147.8	147.3	
C-α″	115.2	114.6	115.3	
C=O″	168.5	168.2	168.5	
Auxiliary sugar				
C-1‴	103.7	102.8	105.7	101.9
C-2‴	73.5	72.0	75.9	72.8
C-3‴	72.2	72.0	77.6	72.0
C-4‴	68.3	73.7	71.2	68.9
C-5‴	75.4	70.2	77.7	75.4
C-6‴	62.6	18.2	62.3	63.1

* Data from ref. [7].

† Data from ref. [4]; two signals were reassigned cf. [7].

‡ Data from ref. [8]. The sugar part is formally a 'core' but signals are placed in the 'auxiliary' section for comparison.

Plantalloside. Rechromatography of the above fr. on a size B column with H_2O–MeOH (4:1 to 3:2) and subsequent treatment with activated C gave the analytical specimen as a foam. $[\alpha]_D^{21}$ −51° (*c* 0.13, MeOH). ^1H NMR (500 MHz, methanol-d_4): aglycone: δ 6.71 (*d*, J = 2 Hz, H-2), 6.68 (*d*, J = 8 Hz, H-5), 6.57 (*dd*, J = 8 and 2 Hz, H-6), 4.04 (*m*, H-8a), 3.74 (*m*, H-8b), 2.80 (2H, *m*, 7-CH_2); sugar moieties: δ 4.94 (*t*, J = 9 Hz, H-4′), 4.86 (*d*, J = 8 Hz, H-1‴), 4.42 (*d*, J = 8 Hz, H-1′), 4.03 (*br t*, J = 3 Hz, H-3‴), 3.91 (*t*, J = 9 Hz, H-3′), 3.68–3.45 (8H, unresolved, H-2′, H-5′, 6′-CH_2, H-4‴, H-5‴, 6‴-CH_2), 3.29 (*dd*, J = 8 and 3 Hz, H-2‴); caffeoyl moiety: δ 7.59 (*d*, J = 16 Hz, H-β″), 7.08 (*d*, J = 2 Hz, H-2″), 6.98 (*dd*, J = 8 and 2 Hz, H-6″), 6.79 (*d*, J = 8 Hz, H-5″), 6.32 (*d*, J = 16 Hz, H-α″). ^{13}C NMR (125 MHz): Table 1. (Found: C, 52.2; H, 5.8. $C_{29}H_{36}O_{16}$, 1.5 H_2O requires: C, 52.2; H, 5.9%).

Acknowledgements—We thank Dr K. Rahn, The Botanical Garden, The University of Copenhagen for providing and authenticating the plant material.

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