Bull. Pharm. Sci., Assiut University, Vol. 20, Part 1, June 1997, pp. 23-26.

TWO PHENYLPROPANOID GLUCOSIDES FROM *GLINUS LOTOIDES* L. VAR. DICTAMNOIDES

Arafa Hamed[1], Irina Springuel[1], Nasr El-Emary[2], Hidemichi Mitome[3], Hiroaki Miyaoka[3] and Yasuji Yamada[3]

1 *Faculty of Science, South Valley University, Aswan 81528, Egypt*
2 *Faculty of Pharmacy, Assiut University, Assiut 71526, Egypt*
3 *Tokyo College of Pharmacy and Life Sciences, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan*

من خلاصة الكلوروفورم المحضرة من خلاصة الميثانول الكلية لأجزاء نبات الجلينس المعروف بإسم حشيشة العقرب ، أمكن الحصول على مركبين جلوكوزيديين أحدهما معروف بإسم "سيتروزين-سي" والأخر جديد يفصل لأول مرة من مصدر طبيعى وقد سمى "ديكتامنوزيد-أ".

A new phenylpropanoid glucoside (dictamnoside A) and another known one (Citrusin C) were isolated from the chloroform-soluble fraction of Glinus lotoides L. var. dictamnoides extract. Their structures were determined by means of spectroscopic methods.

INTRODUCTION

Glinus lotoides L. = *Glinus dictamnoides* Burm. (= *Mollugo glinus* A. Rich.)[1] known in Arabic as Hashishet El-Aqrab or Moghera,[2] is widely distributed in Allaqi area, south of Aswan.[3] Various species of the genus *Glinus* (Molluginaceae), are used as green vegetables. They are bitter in taste and used in Indian system of medicine as antiseptic, anthelmintic, anti-dirrhoeal, in bilious attacks and for curing boils, wounds and pains.[4] The juice of these plants is taken internally to strengthen weak children.[4,5] The genus is generally known to produce saponin compounds of variable structures, which may be important for the chemotaxonomy of this genus.

EXPERIMENTAL

Melting points were taken on Yamazawa micro-melting point apparatus; Optical rotations were measured on a JASCO-360 digital polarimeter; UV spectra were obtained on a Hitachi 200-10 spectrophotometer; IR spectra were taken on a JASCO IR-A-2 spectrometer; ^{1}HNMR, ^{13}CNMR, NOESY, HMQC and HMBC spectra, were taken on a Bruker AM-400, Bruker AM-500; MS, were obtained on Hitachi RMU-7M spectrometer.

Extraction and isolation of the compounds from *Glinus lotoides* L. var. Dictamnoides

The herb *Glinus lotoides* L. var. dictamnoides (Fam. Molluginaceae), was collected on April 1993 from Allaqi area, south of Aswan and it was identified by Prof. Dr. Irina Springuel, Prof. and Head of Botany Department, Faculty of Science, South-Valley University, Aswan. The air-dried total herb (1.6 kg) was powdered and extracted at room temperature with methanol (95%) by maceration (3 times). The methanol extract was concentrated under reduced pressure to a syrupy consistency.

Fractionation of the dried extract

The solvent-free extract (80 g) was mixed with 100 ml methanol, 150 ml water, transferred to a separating funnel and partitioned between hexane (**A**), chloroform (**B**) and n-butanol (**C**) in succession. Each fraction was dried over anhydrous sodium sulphate and concentrated to syrupy residue.

Received in 19/10/1996 & Accepted in 13/1/1997

Column chromatographic fractionation of chloroform fraction

The chloroform fraction **B** (6 g) was slurried with 12 g silica gel (E.Merck) and transferred to the top of a column (120 x 4.5 cm) of activated silica gel, previously packed by the wet method in hexane-ethyl acetate (9:1). Gradient elution with hexane-EtOAc was performed and the effluent was collected in fractions (250 ml). Each fraction was concentrated under reduced pressure and screened for its contents by TLC using solvent system hexane-ethyl acetate (3:2). Fractions were then grouped according to similar contents as **B**-1 (hexane-EtOAc, 9:1), **B**-2 (hexane-EtOAc, 7:3), **B**-3 (hexane-EtOAc, 3:2) and **B**-4 (EtOAc).

Fine separation of components of sub-fraction B-4

Separation of sub-fraction **B**-4 components (2.5 g) was achieved by using firstly ODS column eluted with acetonitrile-water (3:7) to remove fatty alcohols, followed by flash silica gel column eluted with acetone-chloroform (3:2) which resulted in isolation of two compounds **G-1** and **G-2**.

Dictamnoside A (G-1): White powder, m.p. 183-186°; $[\alpha]_D$ -19.99 (MeOH, c= 0.18); UV (MeOH) nm: 275 and 225; IR spectrum (KBr) cm^{-1}: 3450, 1626, 1600, 1504, 990, 914, 862, 847 and 754; Negative FAB MS m/z : 379 $[M+Na]^+$ (95), Molecular formula $C_{17}H_{24}O_8$, 195 $[M\text{-glucose} + 2H]^+$, 131 $[M\text{-glucose} - 2OMe]^+$; ^{1}HNMR spectrum (400 MHz), CD_3OD) and ^{13}CNMR spectrum (100 MHz, CD_3OD) Table 1.

Citrusin C (G-2): White powder, m.p. 129-131° (lit. 129-130, 130-131°);[8,10] $[\alpha]_D$ -54 (EtOH, c= 1.03) (lit. -54.85),[9] UV (MeOH) nm: 275 and 225; IR spectrum (Kbr) cm^{-1}: 3450, 1510, 1260, 1220, 1070 and 1020; Mass spectrum FAB MS m/z: 349 $[M+Na]^+$, Molecular formula $C_{16}H_{22}O_7$, 164 $[M\text{-glucose}]^+$; ^{1}HNMR spectrum (400 MHz, CD_3OD) and ^{13}CNMR spectrum (100 MHz, CD_3OD) Table 1.

RESULTS AND DISCUSSION

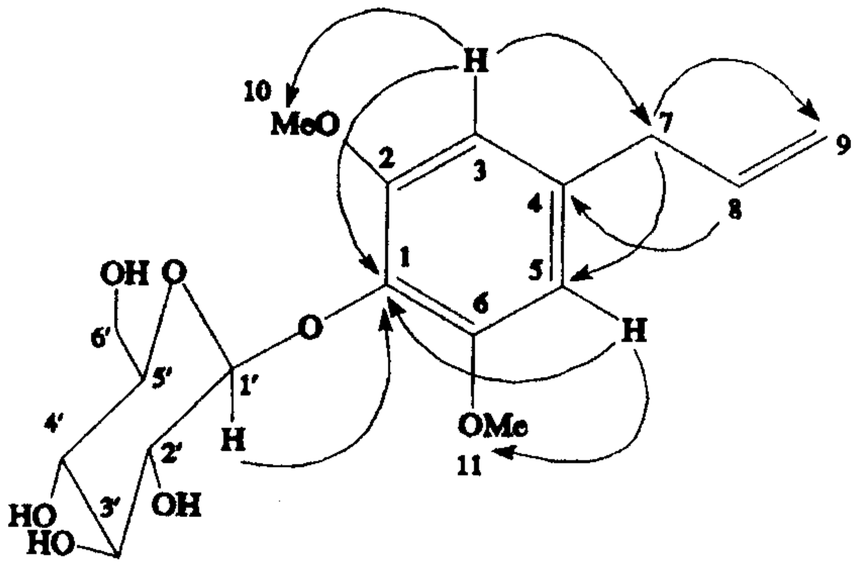
Partition of methanol extract of *Glinus lotoides* herb with hexane, chloroform and n-butanol, led to the isolation of two compounds (**G-1** and **G-2**) from the chloroform-soluble fraction.

The ^{1}HNMR spectrum of compound **G-1**, showed a doublet at δ 3.34 (2H, d, J= 6.78 Hz) assignable to CH_2 group of a propylene side chain coupled with the neighboring -CH= group; two double doublets at δ 5.04 (1H, dd, J = 1.78 and 10.70 Hz) and at δ 5.10 (1H, dd, J= 1.78 and 17.03 Hz) assignable to two protons of the terminal methylene group which are coupled with each other and with the neighboring proton on C-8 in the propylene residue; a double doublet triplet at δ 5.96 (1H, ddt, J= 6.83, 10.11 and 16.88 Hz) assignable to -CH= group coupled with its surrounding CH_2 and terminal methylene groups of the propylene side chain. A singlet at δ 3.82 (6H, s) for two methoxyl groups at C-2 and C-6; one broad singlet at δ 6.53 integrated for two aromatic protons in addition to sugar moiety signals. Since, there is an anomeric proton signal at δ 4.81 (hidden by H_2O signal and its presence was confirmed by HMQC experiment). It showed its carbon signal at δ 105.56, with coupling value J= 7.83 Hz (which was clear in ^{1}H-^{1}H COSY experiment). The remaining sugar signals were represented by two signals integrated for two protons at δ 3.66 (1H, dd, J = 5.10 and 12.02 Hz, H-6'α) and δ 3.79 (1H, dd, J = 2.43 and 11.87 Hz, H-6'ß) for; one multiplet signal at δ 3.22 for H-5'; one double doublet signal at δ 3.48 (1H, dd, J= 2.46 and 7.52 Hz) for H-2'; and a signal at δ 3.44 (2H, dd, J = 2.75 and 6.74 Hz) integrated for two protons for H-3' and H-4' (overlapping). The ^{1}HNMR and ^{13}CNMR data (Table 1), revealed that the sugar has ß-linkage with the aglycone, due to J value of its anomeric proton. Acid hydrolysis of compound **G-1** with 5% HCl, gave D-glucose. The HMBC experiment showed that, there is a cross peak between the anomeric proton at δ 4.81 and the carbon at δ 134.54, indicating that the sugar linkage to be at C-1. From the above data, we

Table 1: ^{1}HNMR and ^{13}CNMR data (ppm) of compounds **G-1** and **G-2**. (multiplicity and coupling constants in parentheses).

No.	G-1		G-2	
	^{1}HNMR	^{13}CNMR	^{1}HNMR	^{13}CNMR
1	----	134.54(s)	----	146.25(s)
2	----	154.13(s)	----	150.67(s)
3	6.53 (1H, s)	107.52(d)	6.83 (1H, d, J= 2.06 Hz)	114.15(d)
4	----	138.43(s)	----	136.51(s)
5	6.53 (1H, s)	107.52(d)	6.72 (1H, dd, J= 8.25, 2.06 Hz)	122.14(d)
6	----	154.13(s)	7.08 (1H, d, J= 8.25 Hz)	115.91(d)
7	3.34 (2H, d, J= 6.78 Hz)	41.32(t)	3.32 (2H, d, J= 6.79 Hz)	40.70(t)
8	5.96 (1H, ddt, J= 6.83, 10.11, 16.88 Hz)	107.72(d)	5.94 (1H, m)	138.47(d)
9	5.04 (1H, dd, J= 1.78, 10.70 Hz) 5.10 (1H, dd, J= 1.78, 17.03 Hz)	116.20(t)	5.03 (1H, dd, J= 1.78, 10.70 Hz) 5.05 (1H, dd, J= 1.98, 17.04 Hz)	118.19(t)
10,11	3.82 (6H, s)	57.01(q)	3.84 (3H, s)	56.72(q)
1'	4.81 (1H, d, J= 7.83 Hz)	105.56(d)	4.84 (1H, d, J= 7.54 Hz)	103.02(d)
2'	3.48 (1H, dd, J= 2.46, 7.52 Hz)	75.71(d)	3.46 (1H, dd, J= 4.75, 6.89 Hz)	74.89(d)
3'	3.44 (1H, dd, J= 2.75, 6.74 Hz)	75.70(d)	3.46 (1H, dd, J= 4.75, 6.89 Hz)	78.09(d)
4'	3.44 (1H, dd, J= 2.75, 6.74 Hz)	71.29(d)	3.38 (1H, dd, J= 2.02, 4.75 Hz)	71.32(d)
5'	3.22 (1H, m)	78.27(d)	3.30 (1H, m)	77.75(d)
6'	3.66 (1H, dd, J= 5.10, 12.20 Hz) 3.79 (1H, dd, J= 2.43, 11.87 Hz)	62.55(t)	3.69 (1H, dd, J= 5.21, 12.03 Hz) 3.86 (1H, dd, J= 1.50, 12.03 Hz)	62.46(t)

Multiplicity was detected by DEPT experiment.
Signals for H-3, H-4, H-10, H-11 and H-3', H-4' in G-1 are overlapping.



HMBC correlations of G-1

assign the structure, eugenol-6-OMe-O-ß-D-glucopyranosyl for the compound **G-1**, which we give the name Dictamnoside A, which is reported here for the first time, while its aglycone eugenol -6-O-methylether was isolated from *Myristica fragrance*.[6,7]

^{1}HNMR, ^{13}CNMR and FAB-MS data for compound **G-2**, revealed that it should be eugenol-1-O-ß-D-glucopyranosyl (citrusin C), that was previously isolated from *Citrus sinensis* OSBECK,[8] *Citrus hassaku* Hort,[8] *Melissa officinalis*[9] and *Perilla frutescens*.[10] From Table 1, it is clear that compound **G-2** is missing one OMe group less than **G-1**, and instead of it, a one proton double doublet appeared at δ 6.72 in the ^{1}HNMR and also the carbon signal (C-6), was shifted upfield to δ 115.91 in the ^{13}CNMR, indicating no substitution on C-6.

Acknowledgements

One of the authors (Dr. A.I. Hamed), is grateful to Tokyo Collegeo f Pharmacy, for the opportunity given to him to complete his practical work. We extend our gratitude to the staff of the analytical laboratory of Tokyo College of Pharmacy for spectral analyses, especially COSY, NOESY, HMBC and HMQC spectra.

REFERENCES

1- L. Boulos, "Flora of Egypt Ckecklist", p.9, Al-Hadara Publishing, Cairo, Egypt (1995).
2- V. Tackholm, "Students Flora of Egypt", Second Edition, p. 228, Cairo University Cooperative Printing Co.; Beirut (1974).
3- I. Springuel, Allaqi Project Working Paper No. 13 (1994).
4- R. N. Chopra, S. I. Nayar and I. C. Chopra, "Glossary of Indian Medicinal Plants", p. 168, CSIR, New Delhi (1956).
5- J. D. Hooker, "Flora of British India", Vol. 5, p. 197, Reeve, London (1885). Through "Medicinal Plants of East & South-east Asia", Lilly M. Perry, p. 6, The MIT Press, Cambridge, London (1980).
6- A. T. Shulgin and H. O. Kerlinger, Naturwissenschaften, 15, 360-361 (1964).
7- A. Rasheed, J. Vlietinck, G. Laekeman, G. Hatfield, J. Janssens, J. Totte and A. G. Herman, Abstract Forschritte in der Arzneimittelforschung, Munchen, 17-20 April, p. 55 (1983).
8- A. Sawabe, Y. Matsubara, H. Kumamoto, Y. Iizuka and K. Okamoto, Nippon Nogeikagaku Kaishi, 60 (8), 593-599 (1986).
9- A. Mulkens and I. Kapetanidis, J. Nat. Prod. 51(3), 496-498 (1988).
10- T. Fujita and M. Nakayama, Phytochemistry, 31(9), 3265-3267 (1982).