Bull. Pharm. Sci., Assiut University, Vol. 26, Part 1, June 2003, pp. 1-3.

A NEW SECOIRIDOID GLUCOSIDE FROM *JASMINUM AZORICUM* L.

A. A. Attia and A. M. A. Abd El-Mawla

Department of Pharmacognosy, Faculty of Pharmacy, Assiut University, Assiut, Egypt

في هذا البحث تم فصل مركب جديد من نوع الاريدويدجلوكوزيد من نبات الياسمين ازوريكم وهو مركب أ وقد تم التعرف على هذا المركب بواسطة التحاليل الطبيعية والكيميائية والاشعة دون الحمراء وفوق البنفسجية والرنين المغناطيسى البروتونى والكربونى بانواعها المختلفه.

A new secoiridoid glucoside has been isolated from the methanolic fraction of the leaves of Jasminum azoricum L. The structure of the isolated compound have been identified by spectral analysis.

INTRODUCTION

Plants of the genus *Jasminum* are ornamental trees or shrubs, commonly cultivated for their fragrant flowers which yield an essential oil used in perfumery.

Several plants of the genus *Jasminum* have been reported to contain iridoid and secoiridoid glucosides.[1-6] *Jasminum* species are used in the folk medicine as anthelmintic, lactagogue and for treatment of skin diseases.[7] In addition to the above mentioned uses, other useful application in facial paralysis, common cold, headache, uterine haemorrhage, arthritis, ulcers abdominal pain, conjunctivitis and dermatitis have been reported.[8-10] Furthermore, they were reported to relieve bronchial spasms and for dysmenorrhea to promote labor.[11]

In a previous paper[12] we reported the structure of a new and known secoiridoid glucosides which were isolated from the leaves of *Jasminum azoricum* L. In the course of further studies on the secoiridoids of the same plant we isolated and identified a new secoiridoid glucoside from the methanoilc extract of leaves.

EXPERIMENTAL

Melting point was determined on Koffler,s heating stage microscope. ^{1}H-NMR and ^{13}C-NMR spectra were taken on GNM-1 at 400 and 100 MHz and Bruker AM-400 and 100. Spectra were determined in DMSO-d_6 using TMS as internal standard. FAB-MS was taken in JEOL. JMS 600. IR (KBr) an a Unicam SP 200 spectrophotometer and UV spectra were recorded in CH_3OH using a Unicam SP 800 spectrophotometer. The optical rotation ($[\alpha]_D$) was measured on Perkin Elmer Polarimeter 341. Silica gel GF 254 was used for TLC and spots were visualized under UV light (254 nm) and also by spraying with anisaldehyde-H_2SO_4 reagent followed by heating for 10 minutes. Silica gel (Merck) was used for column chromatography.

Plant material

Jasminum azoricum L. leaves were collected in March 2001 from plants growing at the experimental station of Faculty of Agriculture, Assiut University, Assiut, Egypt. The plants were identified by Prof. Dr. Abd El-Aziz Fayed Prof. of Taxonomy, Faculty of Science, Assiut University, Assiut.

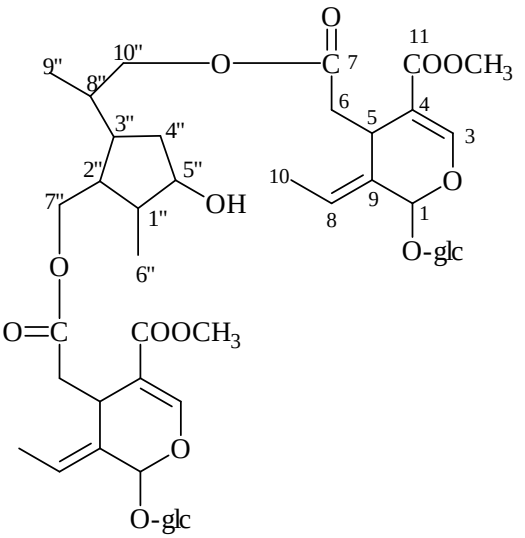
Extraction and isolation

1 Kg of the dried leaves of *J. azoricum* L. were extracted with hot methanol. After removal of the solvent in vacuo, the residue (120 g) was suspended in water and then successively extracted with petrol, $CHCl_3$ and n-butanol. The n-butanol layer was concentrated in vacuo to give a viscous residue (20 g), of which 10 g was chromatographed on a silica gel column, eluting with $CHCl_3$-CH_3OH-H_2O (40:10:1-10:10:1) to give 5 fractions (1-5), fraction 3 (2 g) was

Received in 6/8/2002 & Accepted in 23/9/2002

chromatographed on silica gel column eluting with $CHCl_3$-CH_3OH (9:1-7:3) to afford compound **A** (80 mg).

Compound A: A yellowish amorphous powder (CH_3OH), m.p 135-138°, $[\alpha]_D^{20}$ – 178.3° (c 1.0, CH_3OH), FAB-MS m/z: 959 $[M-H]^-$. It showed a UV maximum at 235 nm (CH_3OH) and IR bands at 3450, 1695, 1620 cm^{-1}. ^{1}H-NMR (DMSO-d_6) : δ 1.08 (3H, d, J= 7.0 Hz, H-6``), 1.12 (3H, d, J= 6.8 Hz, H-9``), 1.7 (3H, br d, J= 6.6 Hz, H-10 X 2), 3.65 (6 H, s, OCH_3 x 2), 4.66 (2H, d, J= 7.6 Hz, H-1` x 2), 5.86 (2H, br s, H-1 x 2), 6.0 (2H, m, H-8 x 2), 7.52 (2H, s, H-3 x 2). ^{13}C-NMR data see Table 1.



Compound A

Table 1: ^{13}C-NMR spectral data of compound A (in DMSO-d_6).

C		DEPT	C		DEPT
Iridoidal part			**Tetraol part**		
1	93.0	CH	1``	45.8	CH
3	153.3	CH	2``	47.9	CH
4	107.6	C	3``	38.0	CH
5	30.1	CH	4``	36.7	CH_2
6	39.8	CH_2	5``	79.2	CH
7	170.6	C	6``	18.1	CH_3
8	123.0	CH	7``	65.0	CH_2
9	129.3	C	8``	42.5	CH
10	13.0	CH_3	9``	15.0	CH_3
11	166.0	C	10``	61.8	CH_2
OCH_3	51.1	CH_3			
Glucose					
1`	99.0	CH			
2`	73.1	CH			
3`	78.5	CH			
4`	69.8	CH			
5`	77.2	CH			
6`	61.0	CH_2			

RESULT AND DISCUSSION

A new secoiridoid glucoside named compound A was obtained from the methanolic extract of the leaves of *Jasminum azoricum* L. Compound A was assigned the molecular formula $C_{44}H_{64}O_{23}$ (negative ion FAB-MS: $[M-H]^-$ = m/z 959). It showed UV absorption (CH_3OH) at 235 nm and IR bands at 3450, 1695, and 1620 cm^{-1}. The ^{1}H-NMR spectrum exhibited a singlet characteristic of the C-3 proton of oleoside[13] type secoiridoid glucoside at δ 7.52 (2H, s), signals for a vinyl methyl group at 1.70 (6H, s), an 11-carbomethoxy group at 3.65 (6H, s), an anomeric protons at 4.66 (2H, d, J= 7.6 Hz), an allylic acetal protons at 5.86 (2, br. s) and an olefinic protons at 6.0 (2H, m). Comparison of ^{13}C-NMR spectra of compound A with that of molihuaside D previously isolated from *Jasminum sambac*[14] revealed that compound A containing 1 mole of oleoside at C-10`` and lacked 1 mole of oleoside at the C-5`` since the signals of C-1`` and C-4`` of the tetraol part to shift downfield and the signal of C-5`` of the tetraol part to shift upfield in comparison with similar secoiridoid glucoside containing 1 mole of oleoside at the C-5``. The only difference between compound A and the previously isolated glucoside molihuaside D is the presence of CH_3 group at C-9``; appears at δ 1.12 in $^1$H-NMR (3H, d, J= 6.8 Hz) and at δ 15.0 in $^{13}$C- and DEPT-NMR spectra. This $CH_3$ group is absent in molihuaside D indicating the presence of C-9`` as methyl group in compound A. From the above mentioned data and comparison with those of molihuaside D revealed that compound A was similar to molihuaside in that, both of them having two iridoidal glucoside units were linked to the C-10`` and the C-7`` positions of the tetraol part. The only difference between them was that compound A has C-9`` methyl group instead of hydroxymethyl group in molihuaside D. This suggestion supported by the upfield shift of C-8`` in compound A and downfield shift in molihuaside D. This compound A is new iridoidal glucoside that has not been reported before.

Acknowledgements

The authors are indebted to the members of Central Lab. of Assiut University for performing the mass and NMR measurements.

REFERENCES

1- K. Inoue, T. Tanahashi, H. Inouye, F. Murai and M. Tagawa, Phytochemistry, 21, 359-361 (1982).
2- S. A. Ross and M. A. Abdel-Hafiz, Journal of Natural Products, 47, 736-737 (1984).
3- T. Tanahashi, N. Nagakura, K. Inoue, H. Inouye and T. Shingu, Chem. Pharm. Bull., 35, 5032-5035 (1987).
4- T. Tanahashi and N. Nagakura, Tetrahedron Letters, 29, 1793-1796 (1988).
5- T. Tanahashi, Y. Takenaka and N. Nagakura, Phytochemistry, 41, 1341-1345 (1996).
6- Y. Shen, S. Lin and C. Chein. Jaspolyside, Phytochemistry, 42, 1629-1631 (1996).
7- M. Sharaf, "An English-Arabic Dictionary of Medicine, Biology, Allied Sciences", 2nd Ed., 42 (1982).
8- R. N. Chopra, "Indigenous drugs of India". U. N. Dhur and Sons, Private Ltd., Calcutta, 2nd , Ed., 64 (1949).
9- Kunming Institute of Botany, Flora Yunnanica Tomus, Academica Sinica, 4, 668 (1986).
10- Jiangsu New Medical College, The Dictionary of Traditional Chinese Medicines, Shanghai People Press, Shanghai, 197 (1977).
11- L. Ac. Dan Kenner and M. D. Yves Requena, "Botanical Medicine", An European Professional Prespective, 245 (1996).
12- A. A. Attia, Bull. Pharm. Sci., Assiut University, 23, 73-78 (2000).
13- H. Inouye, T. Yoshida, S. Tobita, K. Tanaka and T. Nishioka, Tetrahedron, 30, 201 (1974).
14- Y. Zahang, Y. Liu, X. Pu and C. Yang, Phytochemistry 38, 899-903 (1995).