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SECOIRIDOID GLUCOSIDES FROM *JASMINIUM AZORICUM* L. AND *JASMINIUM GRANDIFLORUM* L.

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في هذا البحث تم فصل مركبين من نوع الاريدويدجلوكوزيد من نبات الياسمين ازوريكم وهما: جاسمينين-١٠-جلوكوزيد وسمباكوزيد-ف وتم فصل أيضا مركبين احدهما من نوع الاريدويد جلوكوزيد وهو اليوروبين والأخر فلافونيد جلوكوزيد وهو الروتين من نبات الياسمين جراندفلورم وقد تم التعرف على هذه المركبات بواسطة التحاليل الطبيعيه والكيميائية والأشعة دون الحمراء وفوق البنفسجية والرنين المغناطيسى البروتونى والكربونى بأنواعها المختلفه.

Jasminin-10``-O-β-D-glucoside and sambacoside F were isolated from the methanolic extract of the leaves of Jasminium azoricum L. Oleuropein and rutin were isolated also from the methanolic extract of the leaves of Jasminium grandiflorum L. The structure of these compounds were established by physical, chemical, chromatographic and spectrosopic methods and this is the first report for their isolation from the titled plants.

INTRODUCTION

Plants of the genus *Jasminium* are ornamental trees or shrubs, commonly cultivated for their fragrant flowers which yield an essential oil used in perfumery. *Jasminium* species are used in folk medicine as anthelminitic, lactagogue and for treatment of skin diseases.[1] Also they were reported to be useful in facial paralysis, common cold, headache, uterine haemorrhage, ulcers, arthrities, weaked eyes, as diuretic, for treatment of diarrhoea, abdominal pain, conjuctivities, dermatities,[2-4] and to relieve bronchial spasms and for dysmenorrhea to promote labor.[5]

In the course of our studies on the iridoid glucosides of *Jasminium* species,[6,7] we elucidated the structure of jasminin-10``-O-β-D-glucoside and 9``-hydroxyjasmesoside-5``-O-Oleoside-11-methyl ester beside the known iridoid glucoside jasmoside. The present work describes the isolation and identification of two iridoid glucosides from the leaves of *Jasminium azoricum* L. together with the iridoid glucoside and flavonoid glycoside from the leaves of *Jasminium grandiflorum* L. This is the first report for the isolation of these compounds from the titled plants.

General procedures

Melting points were uncorr, ^{1}H-NMR and ^{13}C-NMR spectra were taken on GNM-1 at 400 and 100 MHz and Bruker AM-400 and 100. IR (KBr) an a Unicam SP 200 spectrophotometer and UV spectra were recorded in methanol using a Unicam SP 800 spectrophotometer. 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 PF_{254} was used for PLC and bands were detected under UV light. Silica gel (Merck) was used for column chromatography.

Plant materials

The leaves of *Jasminium azoricum* L. and *Jasminium grandiflorum* L. were collected in March 1992 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.

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Extraction and isolation

Dried powdered leaves (2 Kg) of *Jasminium azoricum* L. were extracted with hot methanol. After concentration, the methanolic residue (300 g) was suspended in water and then successively and exhaustively extracted with petrol, chloroform and n-butanol. The n-butanol layer was concentrated in vacuo to give a viscous residue (60 g), of which 20 g were chromatographed on silica gel column with $CHCl_3$-MeOH using gradiant elution method of increasing polarity. Fractions eluted with $CHCl_3$-MeOH (90:10 - 70:30) showed the similar components combined together and concentrated in vacuo to afford a viscous residue (4.5 g) which was chromatographed on another silica gel column eluted with $CHCl_3$-MeOH of an increasing polarity also.

Fractions eluted with $CHCl_3$-MeOH (85-15) were concentrated and crystallized from ethanol to give compound **1** as colourless needles, m.p 152-154°, while the fractions eluted with $CHCl_3$-MeOH (80-20) were combined together and submitted to preparative TLC (using silica gel) and $CHCl_3$-MeOH (70-30) to give compound **2** as white amorphous powder, m.p 146-149°.

Dried powdered leaves (2.5 kg) of *Jasminium grandiflorum* L. were extracted as mentioned above giving a viscous residue (200 g) which was suspended in water and then successively extracted with petrol, chloroform and finally with n-butanol. The n-butnol layer was concentrated in vacuo to give a residue (10 g), which was chromatographed as mentioned above and afforded fractions (1-3).

Fraction 1: which eluted with $CHCl_3$-MeOH (90-10) gave negative results for iridoids.

Fraction 2: eluted with $CHCl_3$-MeOH (85-15) was purified by using preparative TLC ($CHCl_3$-MeOH 80:20) to give compound **3** as white amorphous powder m.p 93-96° with decomposition.

Fraction 3: which eluted with $CHCl_3$-MeOH (70-30) rechromatographed on scilica gel column and eluted with H_2O. Yielded pale yellow crystals of compound **4**, m.p 190-192°.

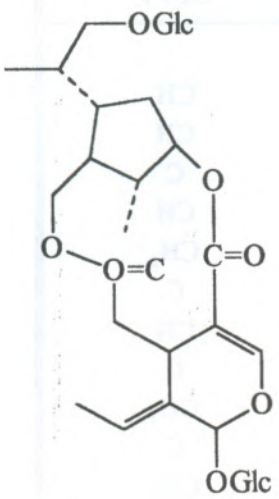
RESULTS AND DISCUSSION

Three iridoid glucosides in addition to rutin were isolated from the methanolic fraction of the leaves of *Jasminium azoricum* L. and *Jasminium grandiflorum* L.

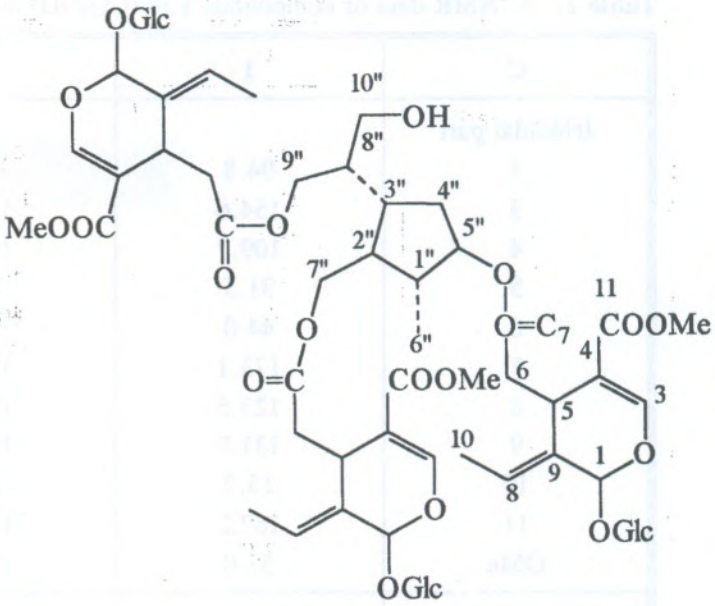
Compound 1 (Fig. 1) was obtained as colourless needles m.p 152-154°. This glucoside exhibited UV absorption at 237 nm and IR bands at 3420, 1735, 1700 and 1630 cm^{-1}. These spectral data suggested the presence of a chromophore O=C-C=CH-O- characterist-ic of iridoid glucosides.[8,9] The ^{1}H-NMR spectrum of compound **1** showed signal for one proton of this chromophore at δ 7.46 (1H, s), signal at δ 1.00 (3H, d, J= 7.6 Hz) for methyl group at C-6``and signals at δ 1.10 (3H, d, J= 6.5 Hz) for methyl group at C-9``,δ 1.80 (3H, dd, J= 7.0 Hz and 1.5 Hz) for 10-H_3, δ 6.1 (1H, br.q. J= 7.0 Hz) for an olefinic proton and signal at δ 4.27 (2H, d, J= 7.6 Hz) due to anomeric protons of the suger. These signals together with ^{13}C-NMR spectrum (Table 1) indicated the presence of oleoside and iridian moieties in the molecule. The ^{13}C-NMR showed 12 signals in the suger region for glucose moieties (Table 1) and signal at 173.1 for the chromophore characteristic for iridoid glucoside.

The above data U.V., IR, ^{1}H-NMR and ^{13}C-NMR reveald that compound **1** is Jasminin-10``-O-ß-D-glucoside that was previously isolated from *Jasminium mesnyi* Hance.[6,16]

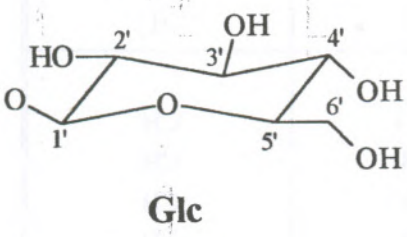
Compound 2 (Fig 1): A white amorphous powder m.p 146-149°. It showed a UV maximum at 237 nm (MeOH) and IR (KBr) bands at 3440, 1710, 1630 cm^{-1}. These spectral data suggested the presence of a chromophore O=C-C=CH-O- characteristic of iridoid glucosides. The ^{1}H-NMR spectrum of compound **2** exhibited triplicate signals for protons of the above mentioned chromophore at δ 7.56 (3H, s, 3 x H-3), one methyl group at δ 1.07 (3H, d, J= 7.0 Hz), three vinyl methyl groups at δ 1.73 (9H, d, J= 7.0 Hz), three carbomethoxy groups at δ 3.65 (9H, s) three olefinic protons at δ 6.18 (3H, br. q., J= 7.0 Hz, 3 x H-8) and anomeric



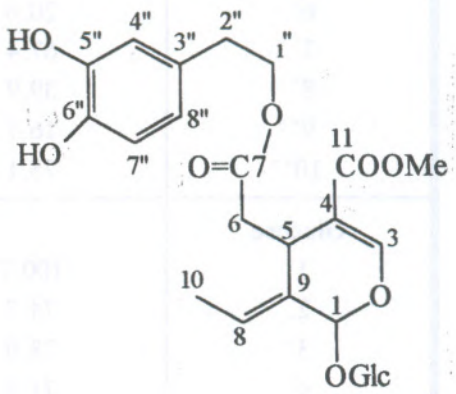
Compound 1



Compound 2



Glc



Compound 3

(Fig. 1)

Table 1: ^{13}C NMR data of compounds **1** in (CD_3OD) and **2** in (C_5D_5N).

C	1	2	DEPT
Iridoidal part			
1	94.8	94.5	CH
3	154.6	154.1	CH
4	109.7	108.6	C
5	31.5	30.9	CH
6	44.0	40.6	CH_2
7	173.1	171.5	C
8	123.5	123.9	CH
9	131.2	130.6	C
10	13.2	13.4	CH_3
11	167.2	166.9	C
OMe	52.0	51.3	CH_3
Tetraol			
1``	44.7	43.7	CH
2``	52.0	48.1	CH
3``	42.3	39.2	CH
4``	35.9	34.8	CH_2
5``	82.6	82.2	CH
6``	20.6	18.8	CH_3
7``	67.4	68.3	CH_2
8``	39.9	44.0	CH
9``	16.1	65.8	CH_3^1, CH_2^2
10``	75.1	61.5	CH_2^2
Glucose			
1`	100.7	101.3	CH
2.	74.7	74.8	CH
3`	78.0	78.3	CH
4`	71.4	71.4	CH
5`	78.4	78.8	CH
6`	62.8	62.8	CH_2

* Glucoside **1** shows additional signals due to C-1´´´-C-6´´´ of the glucosyl moiety at 104.2, 75.1, 77.8, 71.6, 78.4 and 62.6 respectively.

Table 2: ^{13}C NMR data of compounds **3** in (C_5D_5N).

C	3	DEPT
Iridoidal part		
1	94.5	CH
3	153.9	CH
4	108.3	C
5	30.6	CH
6	40.3	CH_2
7	171.3	C
8	123.7	CH
9	129.9	C
10	13.2	CH_3
11	166.8	C
OME	51.1	CH_3
Tetraol		
1``	65.8	CH_2
2``	34.4	CH_2
3``	129.3	C
4``	116.9	CH
5``	146.6	C
6``	145.2	C
7``	116.2	CH
8``	120.2	CH
Glucose		
1`	100.79	CH
2.	74.3	CH
3`	78.2	CH
4`	71.01	CH
5`	77.7	CH
6`	62.16	CH_2

protons at δ 4.49 (3H, d, J= 8.0 Hz, 3 x H-1`), suggesting the presence of three oleoside methyl ester in the molecule. The ^{13}C-NMR signals (Table 1) showed that compound **2** containing an iridoidal glycoside unit (Oleoside methyl ester unit) at the C-9`` causing the downfield shift of the C-9`` of the tetraol part to 65.8,[11] also compound **2** have another iridoidal glycoside unit at C-5`` causing the signals of C-1`` and C-4`` of the tetraol part to shift upfield and the signal of the C-5`` to shift downfield,[11] also compound **2** have a third iridoidal glycoside unit at C-7`` causing the downfield shift of the C-7`` to 68.3 and upfield shift of C-2`` to 48.1,[11] these findings can only be explained by the esterification of the 7``-hydroxy group of the triol with the carboxy group of the oleoside methyl ester. On comparison of the ^{13}C-NMR spectrum of compound **2** with that of a known compound, sambacoside F,[9] and its three iridoidal glycoside units which are linked to C-5``,C-7`` and C-9`` positions of the tetraol part, revealed that they were identical. From the above evidence compound **2** is sambacoside F

that was previously isolated from *Jasminium sambac* L.[9] and for the first time from *Jasminium azoricum* L.

Compound 3 (Fig. 1) was isolated from the n-butanol fraction of *Jasminium grandiflorum* L. as a yellowish amorphous powder, m.p 93-96° with decomposition it showed UV absorption (MeOH) at 230 and 283 and IR (KBr) at 3450, 1711, 1630, 1520 and 1436 cm^{-1}. These spectral data suggested the presence of an aromatic portion together with a chromophore O=C-C=CH-O- characteristic of iridoid glucosides and also related to the irioid glucoside Oleuropein. The ^{1}H-NMR spectroscopy of compound **3** exhibited a singlet at δ 7.64 (1H, s) due to a proton of the carboxyenolic chromophore, multiplet at δ 6.74-7.18 (3H, m) assigned to three aromatic protons, singlet of a methoxycarbonyl group at δ 3.69 (3H, s) an olefinic proton at 6.15 (1H, br. q) an allylic acetal proton at δ 5.42 (1H, s), signal for a vinyl methyl group at δ 1.76 (3H, d, J= 7.0 Hz) and an anomeric proton at δ 4.45 (1H, d, J= 7.0 Hz), a signal due to Ar-C$\underline{H}_2$CH_2O- at δ 3.3 (2H, t, J= 7.0 Hz) and at δ 4.25 (2H, br. t, J= 7.0 Hz) due to Ar-CH_2C$\underline{H}_2$O-. The UV, IR and ^{1}H-NMR data revealed that the compound **3** is very similar to Oleuropein glucoside. This assumption was further supported by the near coincidence of the ^{13}C-NMR spectrum (Table 2) of compound **3** with that of Oleuropein.[12] From the above evidence compound **3** is Oleuropein glucoside which was previously isolated from *Jasminium polyanthum* Franch.[13,14]

Compound 4: From the comparative study of UV and ^{1}H-NMR data of compound **4** with those reported from rutin,[15,16] also m.p, m.m.p and co-chromatography, compound **4** was found to be rutin.

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