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Isoflavone and flavone derivatives from aerial part of *Limoniastrum feei*

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ABSTRACT

*Seven new flavonoids, named : 7-O- (α - ramnopyranosyl- (1-6) - β-glycopyranosyl) - 3 (3'', 4'' dimethyl-3'' penténYl) 4', 5-dihydroxy flavones (**1**) , the second compound 4' - methoxyisoflavone 7-O-β-glycopyranoside (**2**), 6-C-β- (2'' - O β – gluco-pyranosyl-glucopyranosyl) - 5,7,4' - trihydroxy flavones (**3**) , the fourth compound 5-hydroxy 3', 4' – methoxyisoflavone (**4**) , 5,4' - diméthoxy-3,6-dihydroxy flavonol(**5**), 3-hydroxy-5,6,7,4' – tetra-Methoxyflavone (**6**) , 7,8- (2''', 2''' – di-Methylchromeno) -6-prenyl-3,5,4'-trihydroxy-flavone (**7**) were isolated from aerial parts of Limoniastrum feei, The structures were determined on basis of spectroscopic methods..*

Keywords: *Limoniastrum feei*, plumbagenacea, flavonoid, tannin, Medicinal plant.

INTRODUCTION

One of the medicinal plants used to treat gastric infections is *Limoniastrum feei* (Plumbagenaceae). The plant is native to southeast of Algeria (Saoura, region of Bechar) northern Africa [1-3] .

The other uses of *Limoniastrum feei* are as an antibacterial, for treatment bronchitis, stomach infection [4]. A previous investigations revealed that methanol extract from *Limoniastrum feei* leaves contained potential antifungal agent against C. albican and antibacterial agent against E. coli [5].

In this study, we describe the isolation of seven flavonoids from aerial part of *Limoniastrum feei* as wel as the elucidation of their structures using spectroscopic analysis.

MATERIALS AND METHODS

General Experimental Procedure

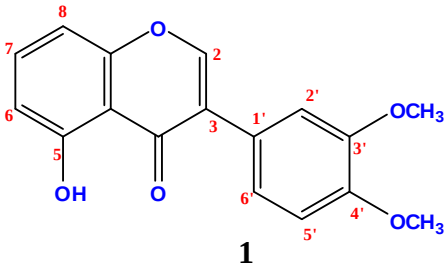
IR spectra were obtained with a AVATAR 320 FT-IR spectrophotometer. The NMR spectra were taken on a Bruker GP 250 (^{1}H, 300 MHZ; ^{13}C, 125 MHZ) Spectrometer. TLC was carried out on silica gel 60 F254 plates (Merck, Germany). Column chromatography was performed over silica gel 60 (Merck, particle size 230-400 mesh).

Plant Materials

The whole plants of *Limoniastrum feei* were collected in March 2005 from kenadsa: (region of Bechar) Algeria. The botanical identification and a voucher specimen is conserved at the Phytochemical Herbarium of Phytochemistry and Organic Synthesis Laboratory of University Center of Bechar under to accession number CA99/14 [5]. The leave, stem and twig were separated and dried, the twig part of plants were grounded into powder from using the grinder.

Extraction and Isolation

The dried twig and stem part of plants (100 g) of *Limoniastrum feei* were extracted with acetone-water (70:30) using soxhlet apparatus, reflux for 3 h was performed. The residue was evaporated in vacuo apparatus until two third, the third of aquous residue was partitioned sequentially with HCl , ethyl ether, EtOAc and dichloromethane [6,7]. To purify and to identify the constituents of the fraction dichloromethane, EtOAc and ethyl ether achieved some separations by liquid chromatography on column, one using a column in glass of type,: 20/300 mm (29/39) full with a stationary phase of silica gel (0.20 mm) and the mobile phase chosen for this separation is: Acetone/Toluene/Formic Acid. (60:80:10) [8] , the compound 1 , compound 2 and compound 3 correspond to the fraction 1 and the compound 4 appears in the Fractions 2, the compound 5 in fractions 3 , the compound 6 and compound 7 in fractions 4 and the compound 8 appears in the Fractions 5 .



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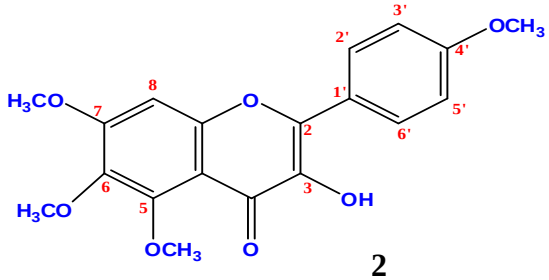

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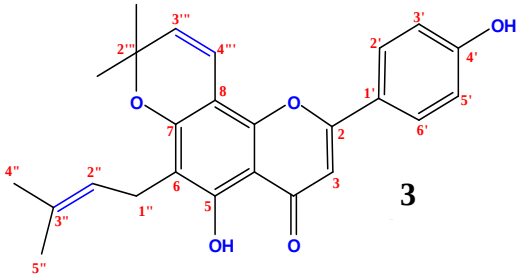

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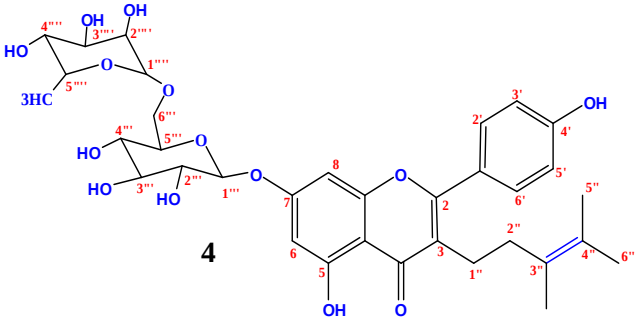

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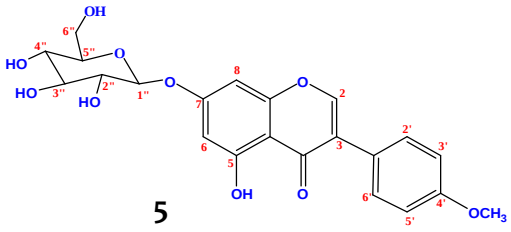

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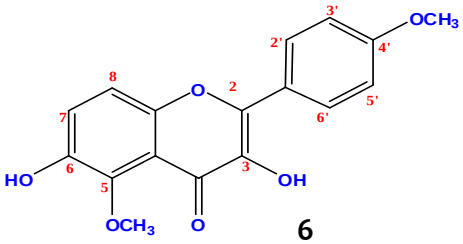

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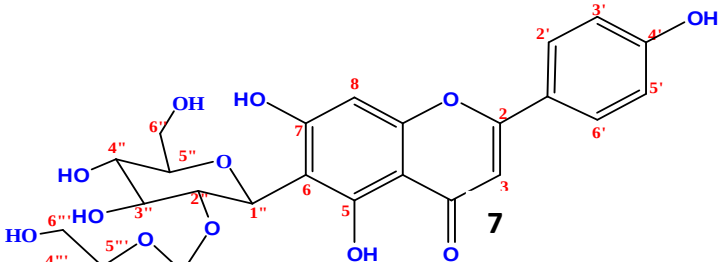

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RESULTS AND DISCUSSION

Phytochemical investigation of twig part of *Limoniastrum feei* led to isolation of seven flavonoids from the dichloromethane and EtOAc and ethyl ether fraction using column chromatography.

The study of spectrum RMN-1H of the made up compound 1 watch the presence of :
The singulet with δ=7.74 ppm ascribable to the proton which must be probably aromatic (position H-2),the signal in the form of the doublet with δ=7.53 ppm (d, J=8Hz) is ascribable to proton H-8. The doublet with δ= 7.49 ppm (d,

J=8Hz) corresponding to the proton H-7 ,the signal in the form of a byte of integration (1H) to δ = 7.15 ppm ascribable to proton H-6. The doublet with δ= 7.10 ppm (d, J=4.6Hz), this chemical shift is with the aromatic proton (H-5' position).The doublets of doublets with δ= 7.05 ppm (dd, J =4.6 Hz, J=2 Hz) with an integral 1H corresponding to the proton H-6', the doublet with δ= 7.00 ppm (d, J=2 Hz) allotted to H-2', both singulet with δ=3.81 ppm and δ=3.89 ppm corresponding to the protons of the groupings methoxyl. These data allow the proposal of the structure partial of a flavonoïde for this molecule of the isoflavone type, which is thus the 5-hydroxy -3', 4' – methoxy isoflavone (**1**) . The structure of this molecule is still confirmed by spectrum NMR ^{13}C.

The analysis of spectrum NMR ^{13}C whose results are reveals the presence of seventeen carbon atoms in compound 1, among these carbon atoms one counts one of them announces to δ=193 .15 ppm is ascribable to carbonyl of cycle. One also observes there two signals with δ= 55.32 ppm and δ=55.69 ppm relating to the groupings methoxyl. In addition, the 14 counted carbon atoms made it possible to deduce empirical formula $C_{17}H_{14}O_4$.

The dichloromethane fraction of stem from *Limoniastrum feei* led to isolation of two compounds as: 3-hydroxy-5,6,7,4'-tetramethoxyflavone **(2)** and 2 , 7,8-(2''',2''')-dimethylchromeno)-6-prenyl-3,5,4'-trihydroxyflavone **(3).**

The study of spectrum RMN-1H of compos (4) recorded in $CDCl_3$ shows the presence of: Analysis of the whole of these spectral data , and by comparison with the data of the literature [9] (**SLOAN *et al.*, 2008**) structure of the compound (4) can be established as being the 7-O- (α-- ramnopyranosyl- (1-6) - β-glycopyranosyl) - 3 (3", 4" dimethyl-3" penténYl) 4', 5-dihydroxy flavone . It appears that this compound was indentified for the first time in the *Limoniastrum feei*.

The butanol fraction of stem from *Limoniastrum feei* led to isolation of the isoflavone ,which is thus the 4' - methoxyisoflavone 7-O-β-glycopyranoside **(5)** . This composes was insulated starting from the roots of *Glycyrrhiza glabra* (*Leguminosa*) [10,11] . It appears that this compound was insulated for the first time in the *Limoniastrum feei*.

The HCl fraction of twig from *Limoniastrum feei* led to isolation of the isoflavone . the structure of compound (6) , could be established as follows : 5,4' - diméthoxy-3,6-dihydroxy flavonol .

The ether extract of stem from *Limoniastrum feei* led to isolate of C-glycosyle flavone from butanol fraction can be established as being the 6-C-β-(2''-O- β –gluco pyranosyl glucopyranosyl)-5,7,4'-trihydroxy flavones.

These data allow the proposal of the structure partial of a flavonoïde for this molecule of the type C-glycosylé flavone, which is thus the 6-C-β- (2" - O β - glucopyranosylglucopyranosyl) - 5,7,4' - trihydroxy flavones **(7).**

5-hydroxy -3', 4' - methoxyisoflavone (**1**)
^1H NMR ($CDCl_3$) 7.74 (s,H-2),7.53 (d, 8, H-8), 7.49 (d, 8 ,H-7) , 7.15 (m,H-6), 7.10 (d, 4.6, H-5'), 7.05 (dd, 4.6, 2, H-6') , 7.00 (d, 2 , H-2'), 3.81 and 3.89 (OCH_3).
^{13}C NMR: 161.44 (C-2), 123.36 (C-3), 193.15 (C-4), 132.51 (C-5), 129.73 (C-6), 132.97 (C-7), 120.40 (C-8), 167.21 (C-9), 125.93 (C-10), 131.18 (C-1'), 114.72 (C-2'), 155.23 (C-3'), 154.74 (C-4'), 112.20 (C-5'), 120.82 (C-6'), 55.32 OCH3 -(3'),55.69 OCH3 -(4').

3-hydroxy-5,6,7,4'-tetramethoxyflavone (2)
^1H NMR ($CDCl_3$) δ 7.19 (s,H-8) , 7.64 (m,H-2'), 7.64 (m, 3'), 3.76(s,H-4') ,7.11 (m, H-5'), 7.64 (m ,H-6')

7,8-(2''',2''')-dimethylchromeno)-6-prenyl-3,5,4'-trihydroxyflavone(**3**) :
^1H NMR ($CDCl_3$) δ 7.15(s,H-3), 7.42 (m, H-2'), 7.05(s, H-3'), 7.05(s, H-5'), 7.42 (m ,H-6'), 3.79 (s,H-1"), 5.30 (s ,H-2"), 1.95 (s, 4"-CH_3), 1.95 (s,5"-CH_3), 1.57 (s,2"' -CH_3), 6.33 (d ,2, H-3"'), 7.01 (s, H-4"')

7-O-(α-ramnopyranosyl-(1-6)-β-glycopyranosyl)-3-(3'',4''diméthyl-3'' penténYl) 4',5-dihydroxy flavones (**4**)
IR (KBr, cm^{-1}) 3404.5, 2923,2847, 1716, 1612, 1459, 1383, 1219, 1091, 985,694, 745.
^1H NMR ($CDCl_3$) δ 6,93(s, H-6) , 7,34 (d, 2.0,H-8), 7.41 (m, H-5' and H-3'), 7.49(dd, 8.5, 2.2, H2', H-6') 4.16 (d, J=7,4 ,H-1'") ,4.02, (s, H-1""). 3.82-3.58 (m, protons gly), 3.12(s, H-6"' a), 3.05 (d, 8.7, H-6"'b) , 2.76(m, H -1") 2.65 (m , H -2"), 2.42 (s,H-3"),1.24 (s, methyl H-5"and H-6'')

4' - methoxyisoflavone 7-O-β-glycopyranoside (5)
^1H NMR ($CDCl_3$) δ 8,28(s, H-2), 7,98(s, H-5), 7.46(d, 3,H-6), 7.76(d, 5, H-2' et H-6',2H), 7.34 (s,H-8), 7.11 (m, H-3' et H-5'), 4.55(s, H-1'''), 3.34-3.49(m, protons Glc).

5,4'-diméthoxy-3,6-dihydroxy flavonol (6)
IR (KBr, cm^{-1}) 3251 ,2945 ,2798,1743.85 ,1640,1448 ,1650 ,1399 ,705 ,1066
^{1}H NMR ($CDCl_3$) δ 7.71 (d,8.3 ,H-2' et H-6'), 7.58(d,2, H-8), 7.37(d,2, H-7), 6.96(d,8.3, H-3' et H-5'), 3.96(s,4-OCH_3), 3.96(s,5-OCH_3).

6-C-β-(2''-O- β -glucopyranosylglucopyranosyl)-5,7,4'-trihydroxy flavone (7)
^{1}H NMR ($CDCl_3$) δ 7.47 (d, 2, H-2' et H-6'), 6.83(2.0, H-3', H-5 '),6.75(s, H-3), 5.22 (d, 2.2, H -1''), 4.15(d,2, H-1'''), 4.13(d, 2.0, H-2''), 3.89-3.87(m, H-2'''and H-6''), 3.80-3.79(m, H -3'', H-4'' et H-5''),3.66-3.57(m, H -3''' , H-4''' et H-5'''), 3.47 (d ,7, H-6''a and H-6'' b).

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