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Flavonoids of *Limoniastrum feei*

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Abstract: Phytochemistry investigation of the water-acetone extract of twig part of *Limoniastrum feei* led to isolation of four flavonoids. The structures of these compounds were identified as 6,3',4'-Tri-methoxy 3,5,5'-trihydroxy flavonol (1), 3-(6"-malonyl 2"-ramnosyl glucosil) 6,3',4'-tri-methoxy 5,5'-dihydroxy flavonol (2), Tetraacetate 7-dihydroxy-4'-Methoxy 8-O-β-glucopyranoside isoflavone (3) and Tetraacetate 7,4'-diMethoxy 8-O-β-glucopyranoside isoflavone (4) using spectroscopic analysis.

Key words: *Limoniastrum feei*, Plumbagenaceae, flavonol, flavonol glycoside, isoflavone

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 (Ozenda, 1983; Maire, 1953; Cheriti *et al*., 2004).

The other uses of *Limoniastrum feei* are as an antibacterial, for treatment bronchitis, stomach infection (Cheriti, 2000). A previous investigations revealed that methanol extract from *Limoniastrum feei* leaves contained potential antifungal agent against *C. albican* and antibacterial agent against *E. coli* (Belboukhari *et al*., 2005).

In this study, we describe the isolation of four flavonouds from *Limoniastrum feei* as wel as the elucidation of their structures using spectroscopic analysis.

MATERIALS AND METHODS

General Experimental Procedure

UV spectra were obtained in MeOH solvent with UNICAM UV300 spectrophotometer. IR spectra were obtained with a AVATAR 320 FT-IR spectrophotometer. The NMR spectra were taken on a Bruker GP 250 (^{1}H, 250 MHZ; ^{13}C, 125 MHZ) Spectrometer. EIMS spectra were obtained on a VG Trio-2 spectrometer. TLC was carried out on silica gel 60 F_{254} 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 2000 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 (Belboukhari *et al*., 2005). The leave, stem and twig were separated and dried, the twig part of plants were grounded into powder from using the grinder.

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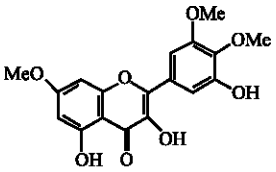
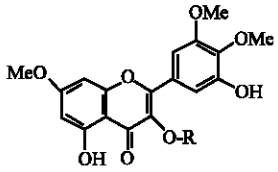
Extraction and Isolation

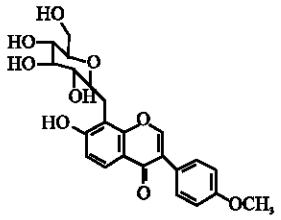
The dried twig part of plants (100 g) of *Limoniastrum feei* were extracted with acetone-water (70:30) using soxhlet apparatus, reflux for 3 h was performed. The residue was evaporated in vacuo apparatus until two third, the third of aquous residue was partitioned sequentially with n-hexan, ethyl ether, EtOAc and n-BuOH (Hostettman *et al*., 1998; Hamburger and Cordell, 1987). To purify and to identify the constituents of the fraction butanol (1.4 g) one 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) (Belboukhari and Cheriti, 2006), the compound 1 correspond to the fraction 4 (8 mg) and the compound 2 with (56 mg) appears in the Fractions (32-55), the compound 3 (17 mg) in two fractions (56-57) and the compound 4 (87 mg) in fractions (70-97).



(1)



(2) R = glucoside-6"-malonyl,2"-ramnosyl



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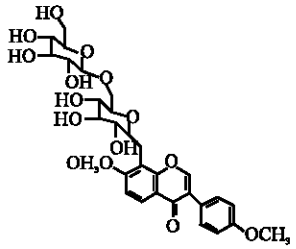

(4)

RESULTS AND DISCUSSION

Phytochemical investigation of twig part of *Limoniastrum feei* led to isolation of four flavonoids from the butanol fraction using column chromatography.

According to the results of IR analysis of all compounds, the absorption bands observed toward (3348-3448 cm^{-1}) correspond to the vibration of elongation Ô-H (valence vibration), the aliphatic links C-H is presented in the IR specter by fine and intense bands toward the 2951 cm^{-1} (asymmetric valance vibration of the CH_3). The frequency of vibrations situated between (2918-2934 cm^{-1}) corresponds to it: asymmetric valance vibration of the CH_2, the bands of absorption to 2852 cm^{-1} associate has vibrations of symmetrical valence of the CH_2 (Cheriti, 2005). The frequency of vibration (989.98 cm^{-1}) corresponds to the distortion vibration out of the plan of the unsaturated hydrocarbons. The valence vibration of the cyclic ketones to six linkages or more, or aliphatic ketones (C = O) to be located toward 1716 cm^{-1}, one specified little that has 1738 cm^{-1}, the vibration are associate has some feature carbonyl for a saturated ester. The vibrations have 1765 and 1771 cm^{-1} corresponds to the ester of alcohol vinyl that possess the fragment of structure following:

-CO-Ô-C = C

this grouping entails an increase important of the frequency of vibration carbonyl (vinyl acetate absorb to 1776 cm^{-1} and the phenyl acetate absorb to 1770 cm^{-1}). The vibration of distortion outside of the plan of aromatic C-H depends maiuly of the position of the various substituting to fix on the benzene and not of their nature (Harborne *et al*., 1986).

Compound 1 and 2 was obtained as yellow amorphous powders. The compound 1 is a flavonol aglycone and represent the skeleton of basis of the compound 2, UV spectra of 1 and 2 in methanol showed λ_{max} 286, 312 for compound 1 and 281, 296, 334 for compound 2. the shift in the λ_{max} on the addition of diagnostic reagents confirmed the presence of free hydroxyl groups, suggesting that compound 1 are hydroxyl group in position 3 and 2 are each glycosylated at the 3-position of the aglycone. the results of ^1H NMR indicate the presence of three methoxyl groups in 7, 3',4' position. The ^{13}C NMR spectra of 1 and 2 were very similar, except for the signal corresponding to the glycosyl group. The characteristic carbonyl carbon signals of a malonyl group were observed at δ 168.23 and 169.96 for compound 2 (Gohar, 2002; Mabry *et al*., 1970; Bacon and Mabry, 1976). Compound 3 was a viscous gum and showed phenol characteristics in positive reaction with $FeCl_3$ reagents, it has the quasi molecular formula $C_{30}H_{31}O_{14}$, calculated by EIMS and ^{13}C NMR data, consistent with its $[M+H]^+$ at m/z 615. The UV spectrum with absorption bands at 211, 254, 306 um suggested an isoflavone skeleton. The ^1H NMR spectrum displayed a characteristic singlet at δ_H 7.85 for H-2 of an isoflavone, two doublets with ortho coupling constant 9.0HZ at δ_H 8.05 and 7.05 for H-5 and H-6, respectively and a pair of doublets of a p-disubstituted phenyl at δ_H 7.47 and 6.98. The methoxy group at δ_H 3.84 was assigned to C-4' in phenyl as irradiation of the aromatic protons (H-3', H-5') at δ_H 6.98. In addition, the proton signals ascribable to the glucose unit were observed together with the methyl protons of four acetyl groups (δ_H 2.20, 2.12, 2.07 and 2.06), indicating the presence of glucose as tetra-acetate derivative. The results of displacement proton at δ_H 4.99 and corresponding carbon at 131.1 indicated that the glucose unit was attached to the 8-hydroxyl of the isoflavone moiety.

There for, 3 was characterized as 7,8-dihydroxy-4'-Methoxy 8-O-β-glucopyranosyl isoflavone. And was confirmed by comparison to previously reported data (Rukachaisirikul *et al*., 2002). The molecular formula of compound 4 was determined to be $C_{41}H_{47}O_{20}$ based on the ^{13}C NMR spectral data and EIMS [m/z 858, M^+]. A positive reaction with in $FeCl_3$ reagent also displayed the phenol characteristics of this compound. ^1H and ^{13}C NMR spectrums were similar to those of compound 3, except absence of hydroxyl group at the 7-position and presence a second unit in substituting glucosyl. The ^1H NMR suggested the presence of two methoxyl groups at δ_H 3.84 and 3.99, respectively in C-4' and C-7 positions. Comparison of its ^1H NMR spectrum of compound 3 indicated that compound 4 also contained β-glucopyranosyl and α-ramnopyranosyl residues with anomeric protons at δ_H 5.22 (6.8Hz) and 4.56(1.6Hz) which were attributed to H-1'' of the glucose unit and H-1''' of the rhamnose unit, respectively. The presence of an α-ramnosyl residue was confirmed by a methyl doublet at δ_H 1.11 (J = 6.3 HZ). Therefore the compound 4 has been identified to: 8-hydroxy 4',7-dimethoxyisoflavone 8-O[α-ramnopyranosyl-(1-6)]-β-glucopyranoside (Markham and Geiger, 1994).

6,3',4'-Tri-methoxy 3,5,5'-trihydroxy flavonol (1)

R_f = 0.8, UV (MeOH): maxima a 286 and 312 nm, IR(KBr): 3410, 2934, 2847, 1689, 1558, 1430, 1377, 1115, 1033, 771 cm^{-1}. ^1H NMR: 6.70(H-6), 6.84(H-8), 7.35(H-2'), 6.93(H-6'), 3.12, 3.05, 3.23 ($O-CH_3$).

3-(6"-malonyl 2"-ramnosyl glucosil) 6,3',4'-tri-methoxy 5,5'-dihydroxy flavonol (2)

R_f = 0.6, UV(MeOH): 281, 296, 334, IR (KBr): 3393 (OH), 2951, 2923, 2862 (CH_3,CH_2), 1711 (CH_3COO), 1640 (C = O, C-4), 1601 (C = C) 1514 (arom), 1028, 1121 (C-O), ^1H NMR: 6.70(H-6), 6.84(H-8), 7.20(H-2'), 6.93(H-6'), 3.117, 3.057, 3.229 ($O-CH_3$), 3-glycosil: 5.55(H-1), 3.697(H-2),

3.57(H-3), 3.397(H-4), 3.292(H-5), 3.801(H-Ga),3.397(H-G-b). 2"-ramnosyl: 5.21(H-1), 4.702(H-2), 3.729(H-3)3.397(H-4), 4.1(H-5), 1.03(H-6, CH_3) 1.912, 1.988, 2.086, 2.177, 2.235, 2.027 (CH_3COO), ^{13}C NMR: 162.24(C-2), 129.9(C-3), 174.06(C-4), 151.67(C-5), 129.9 (C-6), 140.1(C-7), 99.79 (C-8), 158.44 (C-9), 105.91(C-10), 122.53 (C-1'), 109.14 (C-2'), 140.1 (C-3'), 145.81 (C-4'), 137.81(C-5'), 109.14(C-6'), 47.77, 48.11, 48.44, 48.78 (CH_3-O), 3-glucosyl: 100.37(C-1), 79.17(C-2), 77.23(C-3), 71.49(C-4), 73.65(C-5), 63.37(C-6) 2"-ramnosyl: 102.62(C-1), 72.68(C-2), 72.35(C-3), 75.07(C-4), 70.43(C-5), 18.3 (C-6), 6"-malonyl: 41.4(CH_2), 28.99, 30.07, 34.9, 38.68, (CH_3COO).

Tetraacetate 7-dihydroxy-4'-Methoxy 8-O-β-glucopyranoside isoflavone (3)

R_f = 0.7, UV(MeOH): 211, 254, 306, IR(KBr): 3448, 2918, 2852, 1727, 1590, 1519, 1170, 1022, 1465, 716 cm^{-1}. ^1H NMR: 7.85(s,H-2), 8.05(d,9.0, H-5), 7.05(d,9.0,H-6), 7.47(d, 9.0, H-2', H-6'), 6.98(d,9.0, H-3',H-5'), 4.99(d,8.1, H-1"), 5.4(dd,9.8, 8.1, H-2"), 5.33 (t,9.8, H-3"), 5.2 (t, 9.8, H-4"), 3.82(ddd, 9.8, 5.6, 2.8, H-5"), 4.3(dd, 12.6, 5.6, H-6"), 3.84(s, 4'-OMe), 2.20, 2.12, 2.07, 2.06 (CH_3CO). ^{13}C NMR: 151.3 (C-2), 125.1 (C-3), 175.6 (C-4), 118.7 (C-10), 124.3 (C-5), 115.3 (C-6), 154.4 (C-7), 131.1 (C-8), 150.2(C-9), 123.5 (C-1'),130.2 (C-2',C-6'), 114.1(C-3',C-5'), 159.9(C-4'), 103.4 (C-1"), 71.0 (C-2"), 72.1 (C-3") 67.9 (C-4"), 72.7 (C-5"), 61.3(C-6"), 55.4 (4'-OMe), 20.6, 20.7 (CH_3CO), 17.6, 170.1, 169.3, 169.2($COCH_3$).

Hexacetate 8-Hydroxy-4',7-dimethoxy iso-flavone8-O-[α-rhamnopyranosyl-(1-6)]-β-gluco pyran-oside, (4)

R_f = 0.4, $C_{41}H_{47}O_{20}$, $[M+H]^+$ a m/z = 859, le spectre UV(MeOH) : 212, 253, 306 nm. IR (KBr): 3404, 3235, 2918, 2841, 1629, 1514, 1377, 1115, 1039 cm^{-1}. ^1H NMR: 8.25(s,H-2), 8.00(d,9.0, H-5), 7.50 (d,8.5,H-2', H-6'), 7.27(d,9.0, H-6), 6.99(d, 8.5, H-3',H-5'), 5.07(d,7.5,H-1"), 4.56(d,1.5, H-1'"), 4.03(s,OMe), 3.82 (s, Ome)3.84-3.37 (m, glucose and rhamnose protons), 1.06(d,6.5,H-6'"). ^{13}C NMR: 152.7(C-2), 124.7(C-3),176.0(C-4), 119.4(C-10), 123.4(C-5), 110.3(C-6), 156.1(C-7), 132.4(C-8), 150.8(C-9), 124.2(C-1'), 130.5(C-2',C-6'), 114.2(C-3',C-5'), 159.9(C-4'), 101.2(C-1"), 72.1(C-2"), 72.9(C-3"), 69.2(C-4"), 74.4(C-5"), 66.5(C-6"), 97.9(C-1'"), 69.6(C-2'"), 69.3(C-3'"), 70.9(C-4'"), 66.9(C-5'"), 17.5(C-6'"), 56.8(7-OMe), 55.6(4'-OMe), 21.0, 20.9, 20.9, 20.8 (CH_3CO). 170.5, 170.3, 170.2, 170.1, 169.9, 169.6 ($COCH_3$).

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