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SECONDARY METABOLITES FROM *Genista ferox*

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The genus *Genista* is known to contain a variety of secondary metabolites of various types, especially isoflavonoids and flavonoids, which have been shown to be biologically active [1, 2].

In continuation of our previous studies of the *Genista* species (Fabaceae), occurring in Algeria, we have examined *Genista ferox* Poirret [3], which is endemic to North Africa. This medicinal herb has been used for traditional healing by many people in the east region of Algeria. Only one study concerning the alkaloid content of this species was published in 1966 [4]. Our aim is to study the flavonoid content in this species.

The present paper describes the phytochemical study of the chloroform and ethyl acetate-soluble parts of the aqueous ethanol extract of the aerial parts of the Algerian species.

Genista ferox was collected during the flowering phase in May 2000, in the East of Algeria, and was authenticated by Dr. D. Sarri (Biology department, University of M′Sila, Algeria). A voucher specimen has been deposited in the Herbarium of the Department of Nature and Life Sciences, Mentouri University, Constantine (GFL10/05/00).

Aerial parts of *Genista ferox* were dried (1800 g) and macerated three times with EtOH for 24 hours. After removal of chlorophyll with petroleum ether (5 g), the remaining aqueous solution was extracted successively with $CHCl_3$, EtOAc, and *n*-BuOH. We obtained 27 g of the chloroform extract, 11 g of the ethyl acetate extract, and 43 g of the *n*-BuOH extract.

The chloroform extract of *G. ferox* was chromatographed on a 230–400 mesh silica gel column eluted with a gradient of naphtha–EtOAc. This yielded 22 fractions, from which the most important compounds **1** and **2** were isolated and purified by preparative TLC on silica gel using naphtha–CH_2Cl_2 (2:8) as the elution system for compound **1** and naphtha–EtOAc (1:1) for compound **2**.

The ethyl acetate extract of *G. ferox* was chromatographed on a 230–400 mesh silica gel column eluted with a gradient of petroleum ether–EtOAc–acetone. This yielded 31 fractions, from which one compound was isolated and purified by preparative TLC on silica gel using chloroform–acetone (9:1) as the elution system, and three compounds were isolated and purified by preparative TLC on polyamide using toluene–EtOH–methyl ethyl ketone (4:3:3) as solvent. Purification of each compound for spectral analysis was carried out using MeOH over Sephadex LH-20 column.

The structures were elucidated using modern methods of analysis, in particular, UV spectrophotometry, NMR and its various experiments, as well as mass spectrometry (EI-HR-MS). All these data were in good agreement with the respective literature data [5–7].

Compound 1. $C_{20}H_{40}O$, mp 108°C. Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 296 $[M]^+$ (4.69), 278 $[M - 18]^+$ (8.72), 218 (47.65).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT 90; 135): 140.1 (C-3), 123.0 (C-2), 59.4 (C-1), 39.8 (C-4), 39.4 (C-14), 37.4 (C-10), 37.3 (C-8), 37.3 (C-12), 36.6 (C-6), 32.8 (C-7), 32.7 (C-11), 27.9 (C-15), 25.1 (C-5), 24.8 (C-13), 24.4 (C-9), 22.7 (C-17), 22.6 (C-16), 19.7 (C-19), 19.7 (C-18), 16.3 (C-20).

The compound was identified as phytol.

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Compound 2. $C_{29}H_{50}O$, mp 133°C. Mass spectrum (HR-MS, 70 eV), *m/z* (I_{rel}, %): 414 $[M]^{+\cdot}$ (100), 399 $[M - 15]^+$ (26.99), 396 $[M - 18]^+$ (63.89), 381 $[M - 18 - 15]^+$ (21.22), 273 $[M - C_{10}H_{21}]^+$ (17.96), 255.

This compound was characterized as β-sitosterol.

Compound 3. $C_{15}H_{10}O_5$, mp 292°C. UV (MeOH, λ_{max}, nm): 261, 331 sh; + NaOH: 274, 323; + $AlCl_3$: 273, 310, 374; + $AlCl_3$/HCl: 273, 310, 374; + NaOAc: 269 sh; + NaOAc/H_3BO_3: 261 sh.

This compound was characterized as genistein.

Compound 4. $C_{15}H_{10}O_5$, mp 349°C. UV (MeOH, λ_{max}, nm): 268, 335; + NaOH: 276, 325, 392; + $AlCl_3$: 274, 303, 350, 382; + $AlCl_3$/HCl: 278, 303, 318, 380; + NaOAc: 276, 308, 380; + NaOAc/H_3BO_3: 269, 343. Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 270 $[M]^+$ (100), 153 $[A_1 + H]^+$ (52.08), 118 $[B_1]^+$ (32.65).

This compound was characterized as apigenin.

Compound 5. $C_{21}H_{20}O_{10}$, mp 226°C. UV (MeOH, λ_{max}, nm): 268, 334; + NaOH: 275, 392; + $AlCl_3$: 273, 299, 340, 381; + $AlCl_3$/HCl: 272, 299, 341, 379; + NaOAc: 269, 373; + NaOAc/H_3BO_3: 269, 340.

This compound was characterized as apigenin 7-*O*-glucoside.

Compound 6. $C_{15}H_{10}O_6$, mp 330°C. UV (MeOH, λ_{max}, nm): 255, 264, 291, 350; + NaOH: 267, 329, 402; + $AlCl_3$: 273, 303, 422; + $AlCl_3$/HCl: 274, 297, 358, 385; + NaOAc: 254, 269, 352; + NaOAc/H_3BO_3: 269, 401.

Mass spectrum (EI, 70 eV), *m/z* (I_{rel}, %): 286 $[M]^+$ (100), 258 $[M - CO]^+$ (14.96), 153 $[A_1 + H]^+$ (25.19), 134 $[B_1]^+$ (10.23).

This compound was characterized as luteolin.

All these structures are reported for the first time from *G. ferox* Poirret.

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REFERENCES

1. G. Block, B. Patterson, and A. Subar, *Nutr. Cancer*, **18**, 1 (1992).
2. L. P. Van de Vijer, A. F. Kardinaal, D. E. Grobbee, H. M. Princen, and Van den Poppel, *Prostaglandins, Leukotrienes, Essential Fatty Acids*, **57**, 479 (1997),
3. P. Quezel and S. Santa, *Nouvelle Flore de l'Algerie et des Regions Desertiques et Meridionales*, Tome **II**, Edition CNRS, Paris, 1963,
4. G. Faugeras and R. Rene, *Klasse Chem., Geol. Biol.*, **3**, 235 (1966).
5. T. J. Mabry, K. R. Markham and M. B. Thomas, *The Systematic Identification of Flavonoids*, Springer, New York, 1970.
6. K. R. Markham, *Techniques of Flavonoid Identification*, Academic Press, London, 1982.
7. K. R. Markham and H. Geiger, *Advance in Research Since 1986*, J. B. Harborne (ed.), Chapman and Hall, London, 1993.