Chemistry of Natural Compounds, Vol. 48, No. 3, July, 2012 [Russian original No. 3, May–June, 2012]

SESQUITERPENE LACTONES AND FLAVONOIDS FROM *Centaurea foucauldiana*

C. Bensouici,[1] A. Kabouche,[1] Z. Kabouche,[1]*
R. Touzani,[2] and C. Bruneau[3]

UDC 547.473+547.972

The *Centaurea* genus contains more than 700 species [1] from which about 50 grow in Algeria [2]. *Centaurea* species, rich in flavonoids and sesquiterpene lactones [3–9], are used to treat inflammations, cardiovascular problems, ulcers, and hepatic desorders [10–14].

We report here, for the first time, the flavonoids and sesquiterpene lactones of the endemic species *C. foucauldiana* Maire [2].

Aerial parts of *C. foucauldiana* Maire were collected on May 2008 at the Aures region. A voucher specimen was deposited at the herbarium of the faculty of sciences, LOST, University Mentouri-Constantine (LOST Cf.05.08).

The air-dried powdered aerial parts of *Centaurea foucauldiana* (1 kg) were extracted in a Soxhlet apparatus with chloroform. The residue (8 g) was column chromatographed on silica gel (70–200 mesh) eluted with cyclohexane and dichloromethane, then with dichloromethane–ethyl acetate, and finally with ethyl acetate–methanol with increasing polarity. Repeated CC over silica gel using CH_2Cl_2–EtOAc and CH_2Cl_2–MeOH mixtures and TLC over silica gel using the preceding mixtures led to compounds **1–7**, which were identified by ^{1}H NMR and ^{13}C NMR, DEPT, and high technique experiments, COSY, HMQC, HMBC, and NOESY, and, in addition, with UV, IR, and HR-ECI-MS, and all these data were in good agreement with the respective literature data [15–22].

Compound 1. $C_{17}H_{14}O_7$. Characterized as 5,7,4′-trihydroxy-6,3′-dimethoxyflavone (jaceosidin).

Compound 2. $C_{19}H_{18}O_7$. Characterized as 5-hydroxy-6,7,3′,4′-tetramethoxyflavone (3′-*O*-methyleupatorin).

Compound 3. $C_{18}H_{16}O_7$. Characterized as 5,4′-dihydroxy-3′,6,7-trimethoxyflavone (cirsilineol).

Compound 4. $C_{16}H_{12}O_7$. Characterized as 5,7,3′,4′-tetrahydroxy-6-methoxyflavone (nepetin).

Compound 5. $C_{20}H_{26}O_7$. Characterized as 8α-*O*-(3,4-dihydroxy-2-methylenebutanoyloxy)dehydromelitensine.

Compound 6. $C_{20}H_{26}O_7$. Characterized as 8α-*O*-(3,4-dihydroxymethylenebutanoyloxy)salonitenolide (cnicin).

Compound 7. $C_{22}H_{28}O_8$. IR (KBr, ν_{max}, cm^{-1}): 3395, 2930, 2870, 1770, 1710, 1705, 1630, 1566, 1460, 1165, 1070, 965. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.90 (3H, s, H-14), 2.02 (1H, m, H-2b), 2.12 (1H, m H-3b), 2.17 (3H, s, H-2′′), 2.36 (1H, dd, J = 11.7 and 11.5, H-9b), 2.49 (1H, m, H-2a), 2.55 (1H, m, H-3a), 2.61 (1H, dd, J = 3.5 and 11.5, H-9a), 3.10 (1H, dd, J = 1.5 and 10.7, H-7), 3.46 (1H, m, H-4′b), 3.75 (1H, dd, J = 3.5 and 11.0, H-4′a), 4.50 (1H, dd, J = 3.5 and 7.0, H-3′), 4.56 (2H, s, H-15), 4.80 (1H, br.d, J = 10.4, H-6), 5.09 (1H, ddd, J = 3.5, 10.5 and 11.5, H-8), 5.35 (1H, t, J = 7.7, H-1), 5.80 (1H, d, J = 1.5, H-13b), 6.02 (1H, s, H-5′b), 6.26 (1H, d, J = 10.5, H-5), 6.33 (1H, s, H-5′a), 6.37 (1H, d, J = 1.5, H-13a). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 16.8 (C-14), 21.1 (C-2′′), 24.6 (C-2), 27.0 (C-3), 46.5 (C-9), 50.4 (C-7), 65.7 (C-4′), 66.8 (C-15), 70.1 (C-8), 70.7 (C-3′), 77.1 (C-6), 126.5 (C-5′), 128.1 (C-13), 125.1 (C-5), 128.6 (C-1), 131.6 (C-10), 133.9 (C-11), 137.1 (C-4), 139.9 (C-2′), 164.9 (C-1′), 169.3 (C-12), 170.4 (C-1′′). HR-MS *m/z* 421.4529 $[M + H]^+$. Compound **7** was characterized as (6*R*,7*R*,8*S*,3′*R*)-8α-*O*-(3′,4′-dihydroxymethylene-2′-butanoyloxy)-15-acetoxyhelianga-1(10),4(5),11(13)-trien-6,12-olide.

All the compounds are reported for the first time from the species. Sesquiterpene lactones **5–6** are very commonly found in *Centaurea* species, while compound **7** is reported for third time [21, 22].

1) Universite Mentouri-Constantine, Laboratoire d′Obtention de Substances Therapeutiques (L.O.S.T), Campus Chaabat Ersas, 25000, Constantine, Algeria, e-mail: zkabouche@yahoo.com; 2) Universite Mohamed Premier, LCAE-URAC 18, COSTE, Faculte des Sciences, Oujda & Faculte Pluridisciplinaire Nador, Morocco; 3) UMR 6226-CNRS-Universite de Rennes1, Sciences Chimiques de Rennes, Campus de Beaulieu, Avenue du General Leclerc, 35000, Rennes cedex, France.
Published in *Khimiya Prirodnykh Soedinenii*, No. 3, May–June, 2012, pp. 457–458. Original article submitted April 2, 2011.

0009-3130/12/4803-0510

ACKNOWLEDGMENT

The authors are grateful to ANDRS and to the DG-RSDT at the MESRS (Ministery of Scientific Research, Algeria) for financial support.

REFERENCES

1. D. J. Mabberley, *The Plant Book*, Cambridge University Press, 1987.
2. P. Quezel and S. Santa, *Nouvelle Flore de l'Algerie et des Regions Desertiques et Meridionales*, C.N.R.S., Paris, 1963.
3. A. Rustaiyan, A. Niknejad, and Y. Aynehchi, *Planta Med.*, **44**, 185 (1982).
4. H. Skaltsa, D. Lazari, C. Panagouleas, E. Georgiadou, B. Garcia, and M. Sokovic, *Phytochemistry*, **55**, 903 (2000).
5. G. Massiot, A. M. Morfaux, L. Le Men-Olivier, J. Bouquant, A. Madaci, A. Mahamoud, M. Chopova, and P. Aclinou, *Phytochemistry*, **25**, 258 (1986).
6. A. Nacer, J. Boustie, A. Bernard, R. Touzani, and Z. Kabouche, *Chem. Nat. Comp.,* **42**, 230 (2006).
7. A. Kabouche, Z. Kabouche, R. Touzani, and C. Bruneau, *Chem. Nat. Comp.*, **46**, 966 (2010).
8. Garcia-Moreno and D. G. Gravalos, *Fitoterapia*, **68**, 281 (1997).
9. A. Karioti, H. Skaltsa, D. Lazari, M. Sokovic, B. Garcia, and C. Harvala, *Z. Naturforsch.*, **57C**, 75 (2002).
10. A. F. Barrero, J. E. Oltra, M. Alvarez, D. S. Raslan, D. Saude, and M. Akssira, *Fitoterapia*, **71**, 60 (2000).
11. A. F. Barrero, M. Herrador, M. Arteaga, P. Cabrera, E. Rodriguez-Garcia, I. M. Garcia-Moreno, and D. G. Gravalos, *Fitoterapia*, **68**, 281 (1997).
12. V. Saroglou, A. Karioti, C. Demetzos, K. Dimas, and H. Skaltsa, *J. Nat. Prod.*, **68**, 1404 (2005).
13. E. Yesilada, I. Gurbuz, E. Bedir, I. A. Tatli, and I. A. Khan, *J. Ethnopharmacol.*, **95**, 213 (2004).
14. E. Koukoulitsa, H. Skaltsa, A. Karioti, C. Demetzos, and K. Dimas, *Planta Med.*, **68**, 649 (2002).
15. K. R. Markham, *Techniques of Flavonoids Identification*, Academic Press, London, 1982.
16. Z. F. Ahmed, H. Rimpler, F. M. Hammouda, A. M. Rizk, and S. L. Ismail, *Phytochemistry*, **9**, 1595 (1970).
17. N. A. El-Emary, *Fitoterapia*, **54**, 133 (1983).
18. S. M. Adekenov, G. M. Kadirberlina, V. I. Sadykova, T. I. Kupriyanova, and A. D. Kagarlitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 65 (1986).
19. E. Wollenweber, K. M. Valant-Vetschera, and S. Ivancheva, *Phytochemistry*, **26**, 181 (1987).
20. P. Janackovic, V. Tesevic, S. Milosavljevic, V. Vajs, and P. D. Marin, *Biochem. Syst. Ecol*., **32**, 355 (2004).
21. M. L. Cardona, B. Garcia, F. I. Navarro, and J. R. Pedro, *Nat. Prod. Lett*., **5**, 47 (1994).
22. H. Lakhal, T. Boudiar, A. Khalfallah, A. Kabouche, R. Touzani, C. Bruneau, and Z. Kabouche, *Nat. Prod. Commun.,* **5**, 849 (2010).