Short Communication

Pak. j. sci. ind. res., vol. 35, no. 3, March 1992

Chemical Constituents of *Solidago Petradoria*

M.A. METWALLY AND M. ABDEL-MOGIB
Department of Chemistry, Faculty of Science, University of Mansoura, Mansoura, Egypt

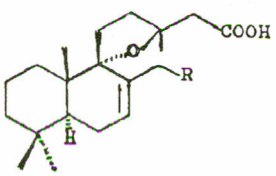
(Received December 16, 1991; revised April 8, 1992)

Solidago species (family Compositae, tribe Astereae, subtribe Solidaginae) have been used for centuries in European folk medicine for the treatment of chronic nephritis, kidney and bladder stones, rheumatism and ulcerations, as well as used as diuretics and for the treatment of cystitis [1]. Although limited information is available on the constituents of *Astereae* plants, typical constituents are clerodane [2-9] and labdane [9-14] diterpenoids. Triterpenoids [15,16], sesquiterpenoids [9,17] and acetylenic compounds [18,19] have also been isolated. In this paper, we report the chemical constituents of *Solidago petradoria* which has not been investigated previously.

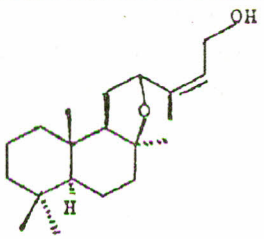
The air-dried plant material (aerial parts, collected from Colorado, USA., 320 gm) was extracted with light petroleum/ether/methanol (1:3:1). The extract was defatted with cold methanol and separated by CC (SiO_2) to 3 fractions. Fraction I (eluted with light petroleum/ether 3:1) afforded 1 (11 mg). Fraction II (eluted with light petroleum/ether 1:1) was further purified by TLC (silica gel, light petroleum/ether 2:3) to give 2 (5 mg). Fraction III (eluted with ether/methanol 9:1) was purified by TLC (silica gel, ether) affording 3 (5 mg).

The roots (300 gm) were processed in the same manner. The fraction eluted with light petroleum/ether 9:1 afforded 3- angeloxygermacrene D (5 mg). The fraction obtained with light petroleum/ether 1:1 gave 1 (5 mg). The fraction eluted with ether afforded 3 (10 mg) after TLC purification (silica gel, ether). The polar fraction obtained with ether gave β-farnesene (6 mg).

An extract of the aerial parts of *S.petradoria* Blake afforded three labdane derivatives *1*, [20], *2* [20] and *3* [21], while an extract of the roots gave β-farnesene and 3-angeloxygermacrene D as well as the labdane derivatives 1 and 3.



1, R = H
2, R = OAc



3

When compound 1 was treated with diazomethane in ether the corresponding methyl ester was produced (singlet at δ 3.65 in the ^{1}H-NMR). The ^{1}H-NMR spectrum of 1 showed a diterpenoid acid with a methyl carbinol singlet (δ1.39), three tertiary methyl singlets (δ 0.90, δ 0.86 and δ 0.82), an olefinic methyl signal (δ 1.77 br s) coupled with an olefinic proton multiplet at δ 5.62, and two doublets with geminal coupling of 15 Hz arising from a methyl group adjacent to the carboxylic function (δ 2.56 and δ 2.69). Comparison with authentic spectra showed its identity as grindelic acid [20].

The ^{1}H-NMR spectrum of 2 showed nearly the same signals as that of 1 in addition to an acetate group singlet at δ 2.06 and two signals in the downfield region [δ 4.51 d(13) and δ 4.65 d(13)]. The signal of H-17 at δ 1.77 was no longer present, indicating the position of the acetate group. Comparison with authentic spectra confirmed its identity [20].

The ^{1}H-NMR spectrum of 3 showed again a diterpenoid pattern with 5 methyl signals, 3 of which were assigned to tertiary methyl groups (δ 0.81s, δ0.82s and δ 0.86s), one was a methyl carbinol (δ1.12s) and the fifth was an olefinic methyl group (1.65 br s). In the downfield region of the spectrum there was an olefinic proton signal at δ5.78 br t (7 Hz), coupled with a hydroxymethylene group signal at δ 4.19 br d (7 Hz), and a broad triplet at δ 4.30 (8.5 Hz) due to a proton attached to an oxygen atom. These data were in agreement with those of labdane alcohol 3 [21].

Acknowledgement. The authors are indepted to Prof. Dr. F. Bohlmamm, Institute of Org. Chem., TU-Berlin, for the plant material and the spectral measurement.

Key words: *Solidago petradoria*, Compositae, Labdane derivatives.

References

1. A. Goswein, R.N. Baruah, R.P. Sharma, J.N. Baruah, P. Kulanthivel and W. Herz, Phytochem., **23,** 837 (1984).
2. M.S. Henderson, R.Mc Crindle and D. Mc Masters, Can. J. Chem., **51,** 1346 (1973).
3. M.S. Henderson, R.D.H. Murray, R.Mc Crindle and D.Mc Masters, Can. J. Chem., **51,** 1322 (1973).
4. A.B. Anderson, R.Mc Crindle and E. Nakamura, Chem. Commun., 453 (1974).
5. T. Anthonson and G. Bergland, Acta. Chem., Scand., **25,** 1924 (1971).
6. R.Mc Crindle and E. Nakamura, Can. J. Chem., **52,** 2029 (1974).

7. G. Ferguson, W.C. Marsh, R.Mc Crindle and E. Nakamura, Chem. Commun., 299 (1975).
8. H. Tsuji, Y. Tani and H. Uedo, Nippon Nogei Kagaku Kaishi, 609 (1977).
9. F. Bohlmann, U. Fritz, R.M. King and H. Robinson, Phytochem., **19,** 2655 (1980).
10. H. Gerland, Pharmazie, **20,** 523 (1965).
11. T. Anthonson, Tetrahedron, **26,** 3091 (1970).
12. C. Anthonson, P.H. Mc Cabe, R.Mc Crindle and R.D.H. Murray, Tetrahedron, **25,** 2233 (1969).
13. T. Anthonson and G. Bergland, Acta Chem. Scand., **27,** 1073 (1973).
14. X. A. Dominguez, D. Butruille, I. Sandler and G. Vazquez, Rev. Latinoam. Quim., **6,** 159 (1975).
15. K. Hiller, S. Genzel, M. Murach and P. Franke, Pharmazie, **30,** 188 (1975).
16. H. Tsuji, Y. Tani and H. Ueda, Nippon Nogei Kagaku Kaishi, **49,** (1978).
17. J. Krepinsky and V. Herout, Collect. Czech. Chem., Commun., **27,** 2459 (1962).
18. F. Bohlmann, T. Burkhardt and C. Zdero, *Naturally Occuring Acetylenes* (Academic Press, London and New York, 1973).
19. K. Ichihara, T. Kawai, M. Kaji and M. Noda, Agric. Biol. Chem., **40,** 353 (1976).
20. B.N. Timmermann, D.J. Luzbetak, J.J. Hoffmann, S.D. Jolad, K.H. Schram, R.B. Bates and R.E. Klenck, Phytochem., **22,** 523 (1983).
21. F. Bohlmann, C. Zdero, R.M. King and H. Robinson, Phytochem., **18,** 621 (1979).