

## 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

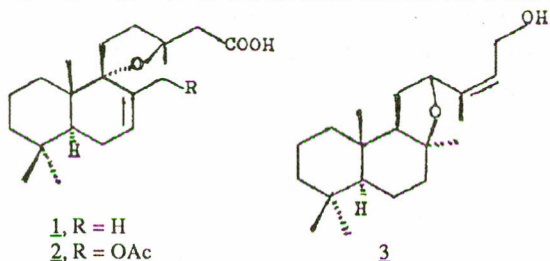
(Received December 16, 1991; revised April 8, 1992)

*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<sub>2</sub>) 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  $\beta$ -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  $\beta$ -farnesene and 3-angeloxygermacrene D as well as the labdane derivatives 1 and 3.



When compound 1 was treated with diazomethane in ether the corresponding methyl ester was produced (singlet at  $\delta$  3.65 in the <sup>1</sup>H-NMR). The <sup>1</sup>H-NMR spectrum of 1 showed a diterpenoid acid with a methyl carbinol singlet ( $\delta$  1.39), three tertiary methyl singlets ( $\delta$  0.90,  $\delta$  0.86 and  $\delta$  0.82), an olefinic methyl signal ( $\delta$  1.77 br s) coupled with an olefinic proton multiplet at  $\delta$  5.62, and two doublets with geminal coupling of 15 Hz arising from a methyl group adjacent to the carboxylic function ( $\delta$  2.56 and  $\delta$  2.69). Comparison with authentic spectra showed its identity as grindelic acid [20].

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

The <sup>1</sup>H-NMR spectrum of 3 showed again a diterpenoid pattern with 5 methyl signals, 3 of which were assigned to tertiary methyl groups ( $\delta$  0.81s,  $\delta$  0.82s and  $\delta$  0.86s), one was a methyl carbinol ( $\delta$  1.12s) 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  $\delta$  5.78 br t (7 Hz), coupled with a hydroxymethylene group signal at  $\delta$  4.19 br d (7 Hz), and a broad triplet at  $\delta$  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 indebted to Prof. Dr. F. Bohlmann, 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 Occurring 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).

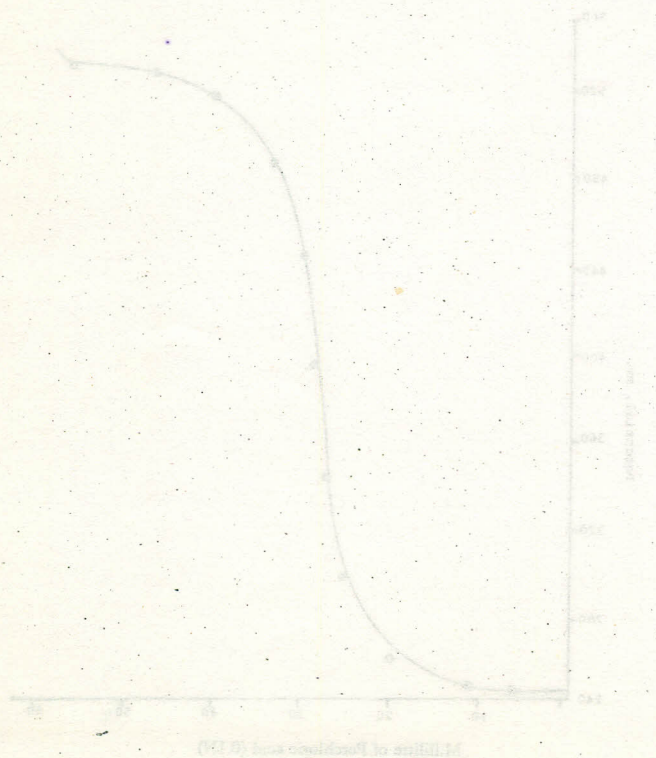
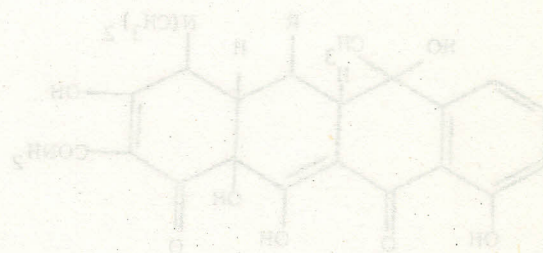


Fig. 1. Measurement of potential (mV) as a function of ml of titrant using oxystyrylic hydrocholoride.

Microbiological assay is sensitive but requires a long period of incubation and lacks precision and specificity. Spectrophotometric methods are either insensitive due to interferences from other materials [14]. Other methods involve elaborate instrumentation or have low sampling frequency. This paper describes a non-aqueous titrimetric method for the determination of oxystyrylic hydrocholoride based on the liberation of the drug as the base followed by its extraction in chloroform and treating the base with perchloric acid in dioxane or acetic acid.

Four oxystyrylic hydrocholoride or the solid dosage form of the drug was weighed as such or by emptying the capsule to contain 150 mg or suitable quantity of the oxystyrylic hydrocholoride. To this was then added 10 ml of distilled water transferred to a separating liquid completely with the addition of a few milliliters of water and was saturated with about 2 gm of sodium chloride. One ml of 30% potassium hydroxide solution was added to render the system basic completely. The base was extracted with three times 10 ml of chloroform. The combined chloroform extracts were washed with 10 ml water and the aqueous washings were re-extracted with further 10 ml of chloroform. The extract was combined with the original extract. The chloroform extract was made free