8. Men'shikov, G. P. and Denisova, S. I. (1953) *Sb. Statei Obshch. Khim.* **2**, 1458; (1955) *Chem. Abstr.* **49**, 5496f.
9. Furuya, T. and Araki, T. (1968) *Chem. Pharm. Bull.* **16**, 2512.
10. Ulubelen, A. and Doganca, S. (1970) *Tetrahedron Letters* **30**, 2583.
11. Ulubelen, A. and Doganca, S. (1971) *Phytochemistry* **10**, 441.
12. Culvenor, C. C. J., Edgar, J. A., Frahn, J. L., Smith, L. W., Ulubelen, A. and Doganca, S. (1975) *Australian J. Chem.* **28**, 173.
13. Fell, K. R. and Peck, J. M. (1968) *Planta Med.* **16**, 411.
14. Jacops, W. A. and Hoffmann, J. (1926) *J. Biol. Chem.* **67**, 609.
15. Karrer, W. (1958) *Konstitution und Vorkommen der Organischen Pflanzenstoffe* p. 262. Birkhauser Verlag, Basel.

Phytochemistry, 1977, Vol. 16, p. 500. Pergamon Press, Printed in England.

ALKALOIDS OF *CALTHA LEPTOSEPALA* AND *CALTHA BIFLORA*

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Key Word Index—*Caltha leptosepala*; *Caltha biflora*; senecionine; magnoflorine; *N,N*-dimethyl lindcarpine.

The genus *Caltha* has world-wide distribution in the northern hemisphere and has been the subject of early European reports of toxicity in cattle and horses [1]. In our present investigation of *Caltha leptosepala* and *C. biflora*, we isolated the pyrrolizidine alkaloid senecionine. One of the symptoms on ingestion of this alkaloid (severe gastrointestinal irritation [2]) corresponds to the reported symptom of *Caltha* poisoning [3]. The second alkaloid isolated has PMR, UV, and R_f's (cf ref. 4) identical to those of the quaternary aporphine alkaloid *N,N*-dimethyl lindcarpine. It has now come to our attention that the spectral and physical properties of *N,N*-dimethyl lindcarpine and its isomer, magnoflorine, are being reinvestigated [5]. Since the properties of these two aporphine alkaloids are very similar [6], the aporphine alkaloid could be either of these alkaloids or a mixture of the two. This is the first report to our knowledge of a pyrrolizidine alkaloid occurring in Ranunculaceae and the first report of the co-occurrence of pyrrolizidine and aporphine alkaloids.

EXPERIMENTAL

Extraction and isolation. Air-dried root and aerial parts of *Caltha leptosepala* DC were collected in Larimer County, Cameron Pass, Roosevelt National Forest, Colorado, U.S.A. Air-dried aerial parts of *C. biflora* DC were collected at Hood River Meadows, Mt. Hood National Forest, Oregon, U.S.A. (Specimens deposited in Colorado State herbarium.) *C. leptosepala* dried aerial parts (1 kg) and roots (1 kg), resp, were extracted with C_6H_6–BuOH (1:1) soln (6 l.) and 10% $NaHCO_3$ (1.5 l.) for 24 hr. The filtrate was extracted with M H_2SO_4 and this aq. soln was then extracted sequentially with $CHCl_3$ at pH 1 and 8.5. The latter $CHCl_3$ extract was chromatographed on Sephadex LH-20 $CHCl_3$–MeOH (1:1). The eluate yielded senecionine as shown by identical UV, IR, PMR, MS and $[\alpha]_D^{25}$ to lit [7–9] data, aerial parts (0.005%) and roots (0.002%). Several minor alkaloids were also detected but not identified. *C. leptosepala* aerial parts were then re-extracted with MeOH and this soln was filtered and evaporated. Residue was treated with 1% H_2SO_4 which was then made basic with NaOH and extracted with H_2O satd *n*-BuOH. The *n*-BuOH extract was chromatographed on a low pressure liquid system using a cellulose column and elution with 0.1 M HCl at 7 kg/sq cm, 15 ml/min. The eluate yielded a quaternary aporphine alkaloid which by lit. values [4] is identical to *N,N*-dimethyl lindcarpine. (0.01%): PMR (DMSO-d_6) 2.93 (s, 3H, N—Me), 3.40 (s, 3H, N—Me), 3.82 and 3.85 (*d*, 6H, —Me), 6.98 (s, 3H, Ar H's); UV λ_{max}^{MeOH} 225 nm, 277 and 320, $\lambda_{max}^{0.01\ N\ HCl\ in\ MeOH}$ 223 nm, 267 and 303. TLC of the extracted roots showed that they also contain this alkaloid. A standard sample was unavailable, and we have been informed that conclusions regarding the identity of any isolated alkaloids as *N,N*-dimethyl lindcarpine or magnoflorine cannot be established at this time [5]. *C. biflora* (1 kg) was treated in a similar manner as *C. leptosepala* but yielded only senecionine (0.001%).

REFERENCES

1. Long, H. C. (1917) *Plants Poisonous to Livestock*. Cambridge Univ. Press, Cambridge.
2. Kingsbury, J. M. (1964) *Poisonous Plants of the United States and Canada* p. 142. Prentice-Hall, Englewood Cliffs, N.J.
3. Harris, P. N., Anderson, R. C. and Chen, K. K. (1943) *J. Pharmacol. Exptl. Therap.* **78**, 372.
4. Doskotch, R. A. and Knapp, J. E. (1971) *Lloydia* **34**, 292.
5. Beal, J. L. and Doskotch, R. W., private communication. Drs. Doskotch and Beal have informed us that many literature references where magnoflorine has supposedly been identified may be error because of the similarity in properties between it and *N,N*-dimethyl lindcarpine.
6. Guinaudeau, H., Leboeuf, M. and Cave, A. (1975) *Lloydia* **38**, 275.
7. Atal, C. K. and Kapur, K. K. (1966) *Tetrahedron Letters* **6**, 537.
8. Culvenor, C. C. J. and DalBon, R. (1964) *Australian J. Chem.* **17**, 1296.
9. Bull, L. B., Culvenor, C. C. J. and Dick, A. T. (1968) *The Pyrrolizidine Alkaloid* (ed. Neuberger and Tatum) Vol. IV, pp. 37 and 280, No. IX. Holland, Amsterdam.