

(–)–Corydalmine from *Corydalis Chaerophylla* Growing in Nepal

R. N. Jha*

Department of chemistry, Trichandra Campus, Tribhuvan University, Kathmandu, Nepal
e-mail: jha_ramnarayan07@yahoo.com

Abstract

(–)–Corydalmine was isolated from the roots of *Corydalis chaerophylla* and identified by spectral analysis.

Keywords: (–)–corydalmine, *corydalis chaerophylla*

Introduction

Corydalis chaerophylla DC. Prodr. (Fumariaceae), is a glabrous herb and is distributed in Himalayas, Naga Hills and in Nepal East, Central and West. It grows in damp and shady places at 2130-2770 m altitude. A number of medicinal value has been reported in Indian and Chinese system of medicine for *Corydalis* species¹⁻⁴ but no medicinal use of this plant has been reported in literature. Previous studies on *Corydalis* genus have led to the isolation of many alkaloids^{5,6}. Owing to its unusual geographical location, it was decided to analyze the plant in terms of its alkaloidal content. In this paper, the structural elucidation of compound isolated from the roots of *Corydalis chaerophylla* is studied.

Experimental Methods

The melting point was determined on a Toshniwal apparatus and was uncorrected. UV spectrum was recorded with Perkin-Elmer Lambda Spectrophotometer using spectral methanol. An IR spectrum was recorded in KBr pellets. Optical rotation was determined with Perkin-Elmer 141 photoelectric Polarimeter at temperature range 20-25°C. ¹H NMR and ¹³C NMR spectra were recorded in 500 MHz in CDCl₃ and CD₃OD using tetramethyl silane (TMS) as internal reference. A mass spectrum was performed on Kratos M-50 mass spectrometer operating at 70 eV. The purity of substance was checked on TLC plates.

* Corresponding author

The roots of *Corydalis chaerophylla* was collected from Kathmandu Valley, Nepal and identified by comparison with the authentic herbarium specimen at the National Herbarium Laboratory, Kathmandu, Nepal.

Air-dried roots of *Corydalis chaerophylla* (435 g) was extracted with methanol for seven days using soxhlet extractor. After removal of methanol under reduced pressure, the residue (55 g) was treated with 7 % citric acid and separated to alkaloidal fraction according to the procedure of G. Rucker et al.⁷.

The fraction obtained using above procedure was analyzed on TLC for alkaloids by spraying with Dragendorffs reagent. The chloroform extract (21 g) was chromatographed over silica-gel column using solvents of increasing polarity. The eluates from C₆H₆:CHCl₃ (15:58) on crystallization from methanol yield 30 mg of (-) - Corydalmine.

(-)-**Corydalmine**: M. P. 172-173°C, (α)_D²⁰ - 300°C(c, 1.40, MeOH), uv λ_{\max} (MeOH, nm), 206, 230 sh, 284, IRV_{max} (KBr, cm⁻¹) 3000 - 3500°, ¹H NMR (in Table 1); ¹³C NMR (in Figure 1), ms (m/z, relative intensity, %) 341(10), 307 (9), 279 (15), 190 (31), 167 (40), 149 (100), 71 (30), 57 (45).

Table 1: 500 MHz ¹H NMR spectral data of Corydalmine in CDCl₃+ CD₃OD

Chemical shift	Proton count	Splitting pattern	Probable assignments
2.40-3.42	8H	<u>m</u>	C - 5, CH ₂ , C- 6-CH ₂ , C-13-CH ₂ , C-8-H and C-14-H
3.72	3H	<u>S</u>	1 Ar-ome
3.73	3H	<u>S</u>	1 Ar-ome
3.74	3H	<u>S</u>	1 Ar-ome
4.10	1H	<u>d</u> (J = 16Hz)	C-8-H
6.48	1H	<u>S</u>	C-4-H
6.66	1H	<u>S</u>	C-1-H
6.69	1H	<u>d</u> (J = 8Hz)	C-11-H
6.77	1H	<u>d</u> (J = 8Hz)	C-12-H

Results and Discussion

(-)-Corydalmine was isolated from the chloroform extract using the procedure of Rucker et al.⁷. The molecular formula of compound based on the high resolution mass spectrum was formed to be C₂₀H₂₃NO₄; ms; m/z 341 (M⁺), 190, 149 (base peak). A fragmentation pattern indicative of tetrahydroprotoberberine could be easily rationalized (scheme I) from these data^{8, 9}. The ultraviolet spectrum in MeOH showed absorption maxima at 206, 230 sh, and 284 nm like that of tetrahydroprotoberberine alkaloids¹⁰. The IR spectrum contained an absorbance at 3500 cm⁻¹ (OH stretch) indicating the presence of hydroxyl group. The ¹H NMR spectrum also confirmed the tetrahydroprotoberberine nature of the structure. In order to assign unambiguously the ¹H- and ¹³C-NMR spectra and

determine the exact position of the substituents on rings A and D, a detailed ^1H – and ^{13}C – NMR study was undertaken.

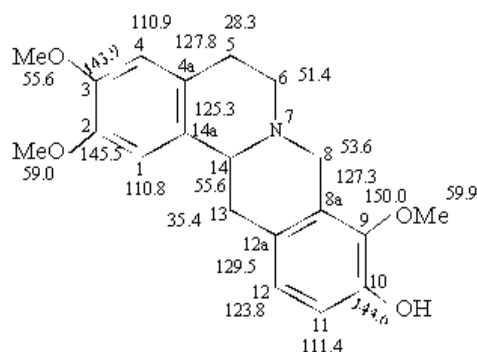
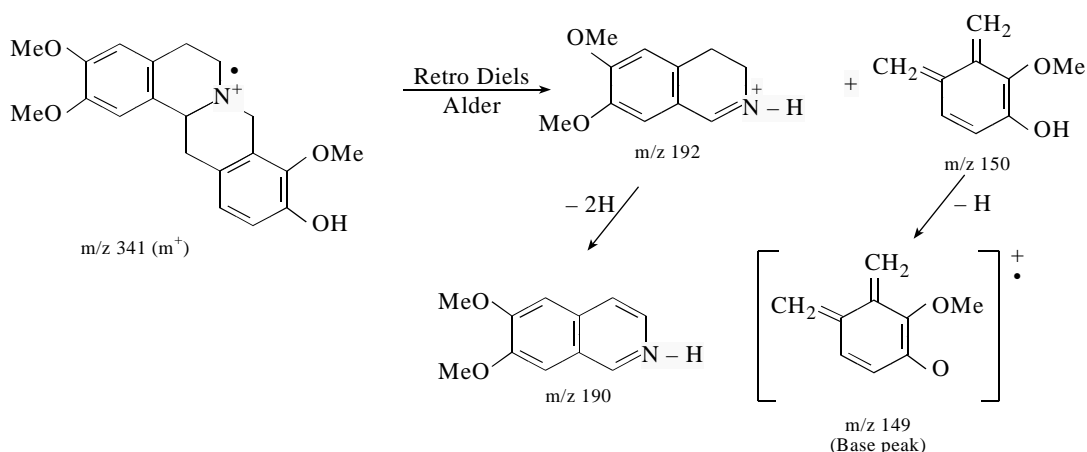


Figure 1: ^{13}C -NMR chemical shifts of (-)-corydalmine in ppm.

Examination of the ^1H NMR spectra of this alkaloid (Table 1) shows clearly that the protons at C-8 appears as a doublet ($J = 16$ Hz) at about 4.10 ppm, due to presence of C-9 oxygen substitute. Placement of the OH-group in ring D at C-10 was elucidated by mass fragmentation pattern (Scheme 1). Thus, it is concluded from this study that one methoxy group and one hydroxyl group in the ring D of this compound are located at C-9 and C-10, respectively. Both ^1H NMR and ^{13}C NMR were employed to determine the substitution pattern in ring A of the compound. ^1H NMR spectrum showed singlets for the two aromatic protons in ring A, which suggested that they were para to each other (i.e. at the 1- and 4-positions) and thus the two methoxyl groups were at C-2 and C-3.

Comparison of the ^{13}C NMR of this compound with that of (-)-Corydalmine¹¹, a known tetrahydropyridopyridine with methoxy group at 2,3,9 and hydroxyl group at 10 positions, established that the compound was the same.

Scheme 1: Mass spectral fragmentation schemes for (-) Corydalmine (I)



Conclusion

The structure of (–)-Corydalmine was elucidated by physical, chemical and spectroscopic methods as well as comparison of its spectral data with those in the literature^{9,11}. This is the first report of the occurrence of (–)-Corydalmine in *Corydalis chaerophylla* growing in Nepal.

Acknowledgements

The authors are grateful to Prof. Dr. H. C. Jha, University of Bonn, Germany for spectral analysis. Author is also thankful to Prof. Dr. V. B. Pandey, Department of medicinal chemistry, Banaras Hindu University, Varanasi, India for his support to complete this work.

References

1. *Flora of Kathmandu Valley*, Bulletin of the Department of Medicinal plants, Thapathali, Kathmandu, Nepal. 1986, **11**, 150.
2. *The Wealth of India*, Raw materials, CSIR, New Delhi, India, 1950. II, 358.
3. M. Liden, *Rheedeia*, 1995, **5**, 2.
4. W. Tang and G. Eisenbrand, *Chinese Drugs of Plant Origin*, Springer Verlag, New York, 1992, 377.
5. R. H. Raffauf, *A Handbook of Alkaloids and Alkaloid containing Plants*, Wiley Interscience, New York, 1970.
6. G. A. Cordell, *Introduction to alkaloid. A Biogenetic Approach*, Wiley Interscience, New York, 1981, 472.
7. G. Rücker, E. Breitmair, G -L. Zhang and R. Mayre, *Phyto.Chem.*, 1994, **36(2)**, 519.
8. C. Y. Chen and D. B. MacLean, *Can. J. Chem.*, 1968, **46**, 2501.
9. C. K. Yu, D. B. MacLean, R. G. A. Rodrigo and H. H. F. MaNske, *Can. J. Chem.*, 1970, **40**, 3673.
10. M. Shama, *The Isoquinoline Alkaloids*, Academic Press, New York, 1972, 308.
11. E. B. Hanssen and H. C. Chiang, *J. Org. Chem.* 1977, **35**, 88.