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(±)-CORYSOLIDINE, A SPIROBENZYLISOQUINOLINE ALKALOID FROM *CORYDALIS SOLIDA*

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Key Word Index—*Corydalis solida*; Fumariaceae; alkaloids; spirobenzylisoquinoline; (−)-corpaine; (±)-corysolidine; ledeborine.

Abstract—The whole plant of *Corydalis solida*, of Turkish origin, furnished (−)-corpaine as well as the new spirobenzylisoquinoline (±)-corysolidine.

INTRODUCTION

The genus *Corydalis* is known for its elaboration of spirobenzylisoquinoline alkaloids possessing two oxygenated functions in ring C [1]. While investigating the contents of the small bulbous plant *Corydalis solida* (L.) Swartz. of Turkish origin, we were able first to reisolate the known spirobenzylisoquinoline corpaine (**1**), initially found in *C. paczoskii*, and for which no specific rotation had been recorded [2]. Our corpaine, $C_{20}H_{19}O_6N$, mp 190–192° (benzene), lit. mp 204° (EtOH) [2], had an NMR spectrum (360 MHz, $CDCl_3$) corresponding to that reported in the literature, and possessed $[\alpha]_D^5$ −105° (*c* 0.07; MeOH).

RESULTS AND DISCUSSION

Accompanying (−)-corpaine (**1**) was the new isomeric spirobenzylisoquinoline (±)-corysolidine (**2**), which exhibited a flat CD curve in methanol. Structure **2** had originally been proposed for the spirobenzylisoquinoline ledeborine of undetermined specific rotation [3]. That assignment for ledeborine, however, was modified at a later date [4] when the positions of the phenolic function and the methoxyl group in the molecule were reversed to fit the NMR spectral data which included a three-proton singlet upfield at δ3.40, typical of a C-2 methoxyl in a spirobenzylisoquinoline system.

The 360 MHz ($CDCl_3$) NMR spectrum for corysolidine has been summarized adjacent to structure **2**. Significantly, the methoxyl signal appears downfield at δ3.86, indicating that this group is at C-3 rather than at C-2 [1]. A telling feature of the NMR spectra of corpaine (**1**) and corysolidine (**2**) is that H-8 appears relatively upfield at δ5.09 in (−)-corpaine (**1**), but falls further downfield at δ5.64 in the case of (±)-corysolidine (**2**). These chemical shifts are consonant with an anti relationship between H-8 and the nitrogen atom in **1**, and with the alternate syn relationship in **2** [1]. Corpaine (**1**) shows an IR carbonyl band at 1710 cm^{-1}, and the corresponding absorption in corysolidine (**2**) is at 1712 cm^{-1}. Additionally, the UV spectra for the two compounds are almost identical (Experimental).

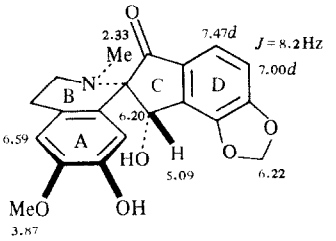
It became relevant at this stage to determine whether corysolidine (**2**) was a true natural product or an artifact of isolation. If it were an artifact, corysolidine would have been formed from (−)-corpaine during chromatography through a retrograde aldol condensation, with cleavage of the C-8 to C-14 bond. Aldol recyclization would then lead to a racemate. A necessary corollary requirement would then be that the recyclization step would lead solely to corysolidine (**2**) and not to corpaine (**1**) since no racemic corpaine could be detected in out plant extracts.

That (±)-corysolidine (**2**) is very probably an alkaloid and not an artifact was indicated by the fact that the spirobenzylisoquinoline diol raddeanine (**4**), obtained from *C. ledebouriana*, is known in the racemic form [5]. Such a racemate could be formed from *in vivo* reduction of the C-2 O-methylated analog of (±)-corysolidine (**2**), which would correspond to the known alkaloid (±)-raddeanone (**3**) found in *C. ochotensis* [6]. It is unlikely that reduction of a ketonic function to an alcohol would have occurred on a chromatographic column.

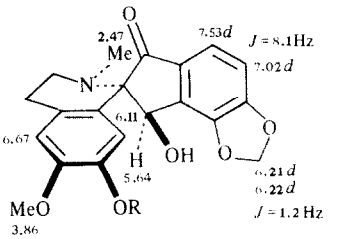
EXPERIMENTAL

Plant collection and extraction. Corydalis solida (whole plant) was collected in Bağsaray village, in the province of Burdur, in southwestern Anatolia, on April 5, 1982. A voucher specimen, No. 609, was deposited in the herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Ege University. The dried plant was powdered (2.4 kg) and extracted with cold EtOH. The EtOH soln was filtered and the solvent evaporated under red. pres. to yield a thick dark brown residue (428 g). This material was treated with 5% HCl. The resulting aq. soln was basified with NH_4OH and extracted with $CHCl_3$. Evaporation of the organic solvent provided a crude alkaloidal extract (14 g), which was placed on a silica gel column (70–230 mesh). The initial solvent was $CHCl_3$. Elution was with $CHCl_3$, and then with $CHCl_3$ containing increasing percentages of MeOH.

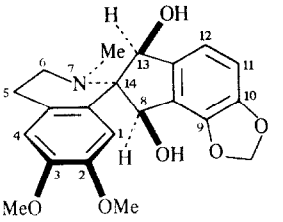
(−)-*Corpaine* (**1**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 3544: UV λ_{max}^{MeOH} nm



1



2 R = H (with NMR)
3 R = Me



4

(log ε): 236 (4.41), 291 (4.05), 313 (3.97): CD Δε nm: −2.2 (288), 0 (260), negative tail below 248 nm: crystalline material (24 mg).

(+)-*Corysolidine* (**2**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1712, 3544: UV λ_{max}^{MeOH} nm (log ε): 236 (4.32), 290 (3.90), 310 (3.84): $C_{20}H_{19}O_6N$: amorphous (6 mg).

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