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CONPROPINE, A NEW ALKALOID FROM THE AERIAL PART OF *Convolvulus subhirsutus* FROM UZBEKISTAN

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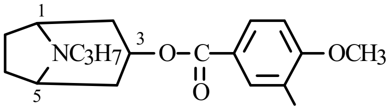
The known alkaloid convolvidine and a new base conpropine, for which the structure N-*propylconvolvine was proposed, were isolated from total alkaloids from the aerial part of* Convolvulus subhirsutus.

Key words: *Convolvulus subhirsutus*, alkaloids, convolvidine, conpropine, *N*-propylconvolvine.

We previously reported the isolation from the aerial part and roots of *Convolvulus subhirsutus* indigenous to Uzbekistan of six alkaloids (convolvine, convolamine, convolidine, phyllalbine, phyllalbine *N*-oxide, nortropine) [1].

In continuation of the study of the aerial part of *C. subhirsutus* collected in Tashkent Oblast′ [1], an alkaloid with mp 189-190°C that was identified from the R_f value and mixed melting point with an authentic sample of convolvidine was isolated from the total alkaloids of the nonphenolic part after removal of convolvine and convolamine [2]. Chromatography over a column of aluminum oxide of the mother liquors of the nonphenolic part of the total bases from hydrocarbon:$CHCl_3$ fractions isolated a new amorphous base that differed in physicochemical properties and chromatographic mobility from tropane bases that have been described in the literature. We called it conpropine (**1**).



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The IR spectrum of **1** exhibited absorption bands for an ester carbonyl (1708 cm^{-1}), a 3,4-disubstituted aromatic ring (1610, 1580, 870, 810), and stretching and bending CH_3-, CH_2-, and CH-groups (2980, 2920, 1425, 1280). The PMR spectrum of the base contained resonances for protons of two aromatic methoxyls as two 3H singlets at 3.92 and 3.90 ppm. A 3H triplet from resonances of a primary methyl appeared at strong field and was centered at 0.90 (J = 6.8 Hz). A 2H multiplet of the CH_2 bonded to the N atom was observed at 2.65-2.20. The range 3.50-3.25 had a 2H resonance from the two methine protons on C-1 and C-5 of the tropane moiety. The four CH_2 groups of the tropane ring in the C-2, C-4, C-6, and C-7 positions gave a 10H multiplet in the range 2.20-1.35, probably because the resonance from the protons of the CH_2 group bonded to the primary methyl appeared here also. A 1H triplet from Hα-3 occurred at 5.25 and is diagnostic for tropane alkaloids esterified at the C-3 hydroxyl. Resonances of the three protons of the aromatic ring with characteristic *ortho*- and *para*-substitution were found at 7.70-6.75. The isolated α-proton appeared as a doublet with J = 2.0 Hz at 7.51. The other α-proton of the aromatic ring gave a doublet of doublets (*meta*-constant J ≈ 2.0 Hz and *ortho*-constant J ≈ 8.5 Hz) at 7.60. Finally, the β-proton resonated at 6.86 as a doublet (J ≈ 8.5 Hz).

The mass spectrum of **1** exhibited a peak for the molecular ion with *m/z* 333 (20%) and fragment ions with *m/z* 304 (25), 182, 168, 165, 148, 124, 111, 97, 96, 95, and 77 that were characteristic of tropane alkaloids isolated from *C. subhirsutus* and *C. pseudocanthabrica* [3]. The appearance in the spectrum of peaks for ions with *m/z* 182, 181, 165, and 154 indicated that the isolated alkaloid was a tropane base esterified at the C-3 hydroxyl of the tropane ring and was the ester of the saturated aminoalcohol nortropine and 3,4-dimethoxybenzoic (veratric) acid. This was also confirmed by the PMR spectrum of the alkaloid that was described above.

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Considering the IR (absence of an absorption band for active H), PMR, and mass spectra in addition to the molecular weights of the alkaloid ($[M]^+$ 333), the acyl group (182 amu), and the unsubstituted tropane core, it can be assumed that **1** contains a substituted N atom, the substituent of which was the C_3H_7 radical. It could have been either isopropyl or propyl. The mass spectrum argued in favor of the latter. Thus, a peak for an ion with *m/z* 304 was one of the strongest in the spectrum and corresponded to loss of an ethyl group $[M - 29]^+$. If the substituent on the N atom had been isopropyl, the mass spectrum would have been expected to have an ion with *m/z* 318 corresponding to loss of a methyl from the isopropyl group. This was not observed. Cleavage of a propyl radical from the molecular ion was not observed (although this pathway is also possible). However, it was lost from the aminoalcohol ion with *m/z* 152 after preliminary loss from $[M]^+$ of the veratroyl ion (181 amu).

The ion with *m/z* 152 in the mass spectrum of conpropine was weak and corresponded to cleavage of the C-3–O^- bond with charge on the tropane core. Loss from this ion of C_3H_6, C_3H_7, and C_3H_8 fragments gave stronger peaks for ions with *m/z* 108, 109, 110, and 111. The peak intensities for veratric acid with *m/z* 181 and 165 were rather strong due to the lack of a steric effect from the propyl group and the reduced probability of localizing positive charge on the tertiary N atom.

Thus, spectral data and comparison with tropane alkaloids suggested the structure (±)-*N*-propyl-3α-veratroylnortropane for conpropine.

EXPERIMENTAL

IR spectra in KBr disks were recorded on a Perkin—Elmer Model 2000 IR spectrometer. NMR spectra were recorded on a Tesla BS-567A instrument (100 MHz, $CDCl_3$ solvent, HMDS internal standard, -scale). Mass spectra were obtained in a Kratos mass spectrometer.

Isolation and separation of the total alkaloids has been reported [1].

Isolation of Convolvidine. The nonphenolic part of the total alkaloids (2.0 g) was extracted with hydrocarbons by heating on a water bath (50 mL × 3). The precipitate (0.9 g, convolvine, convolamine) that formed from the combined hydrocarbon extracts and the crystals (0.3 g, convolvine) that formed after condensing the mother liquors were removed. The remaining hydrocarbon solution was evaporated. The solid was recrystallized from acetone to afford crystals (0.09 g), mp 189-190°C (convolvidine).

Isolation of Conpropine. The total alkaloids of the nonphenolic part (0.7 g) that were insoluble in hydrocarbons were placed on a column of aluminum oxide (1:20 ratio, 14.0 g) and eluted with hydrocarbons, hydrocarbons:$CHCl_3$, and $CHCl_3$. The hydrocarbons:$CHCl_3$ fractions (1:3) afforded the amorphous base conpropine (20 mg).

PMR spectrum (, ppm, J/Hz): 0.90 (3H, t, J = 6.8, CH_3), 2.20-1.35 (10H, 5-CH_2), 2.65-2.20 (2H, CH_2), 3.50-3.25 (2H, m, H-1,5), 3.92 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 5.25 (1H, t, H-3α), 7.70-6.75 (3H, m, H-Ar).

Mass spectrum (*m/z*, %): 333 (20) $[M]^+$, 304 (25), 182, 165, 154, 148, 124, 111, 97, 96, 95, 77.

REFERENCES

1. A. M. Gapparov, N. A. Razzakov, and S. F. Aripova, *Khim. Prir. Soedin.*, 242 (2007).
2. S. F. Aripova and S. Yu. Yunusov, *Khim. Prir. Soedin.*, 657 (1986).
3. S. F. Aripova, Author's Abstract of a Doctoral Dissertation in Chemical Sciences, Tashkent (1991).