CONVOLACINE – A NEW ALKALOID FROM Convolvulus subhirsutus

S. F. Aripova and O. Abdilalimov

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Plants of the genus Convolvulus were first studied by Orekhov and Konovalova [1] and then by Yunusov et al. They isolated two alkaloids from Convolvulus pseudocanthabrica and C. subhirsus – convolvine and convolamine [1, 2].

Continuing the study of the alkaloids of C. subhirsutus, we have obtained another nine bases in addition to those mentioned above: confoline, convoline, convolidine, convolicine, convosine, subhirsine, convolvidine, convolamine N-oxide, and a new base, which we have called convolacine [3-11].

Convolacine (I) is an optically inactive minor base isolated from the mother liquors of the total alkaloids of the roots of C. subhirsutus; it has not been detected in other species of bindweed.

In the IR spectrum of (I) there were two bands of ester carbonyls, at 1730 and 1700 cm^{-1}, and also absorption bands of a 1,2,4-trisubstituted benzene ring (820 and 885 cm^{-1}). The PMR spectrum of the alkaloid exhibited signals at (δ, ppm): 2.03 (3H, s) from the protons of the methyl group of an acetoxy residue; 2.23 – a singlet with an intensity of three proton units, which we ascribed to a $N-CH_3$ group; and 3.89 – a sharp six-proton singlet from the protons of two aromatic methoxy groups. At 3.25 there were the signals (1H each) from H-1 and H-5, and at 5.00 (1H, m) that of the 3α-H atom of a tropane nucleus. Aromatic protons resonated in the regions of 6.87 (1H, d, H_c, J = 7 Hz), 7.55 (1H, d, H_a, J = 7 Hz, J = 2 Hz), and 7.67 (1H, d, H_b, J = 2 Hz).

The mass spectrum showed the peaks of the molecular ion (M^+ 363) and of fragmentary ions with m/z 348 $(M - 15)^+$, 304 $(M - 59)^+$, 290, 182, 165, 140, and 124, which are characteristic for alkaloids of the tropane series [12]. The spectral characteristics of the alkaloid showed that it was a new one, not described in the literature, and consisted of a diester of the substituted aminoalcohol tropine in which one of the esterifying acids was an aromatic acid – 3,4-dimethoxybenzoic (veratric). The presence of a veratroyl group as an acid moiety in the alkaloid molecule was clearly shown by its mass spectrum: the presence of the diagnostic ions with m/z 182, 165, and 151 was a confirmation of this fact.

A characteristic feature was the ejection by the molecular ion of a fragment with m/z 59, corresponding to the splitting out of an acetoxy group. The mutual positions of the above-mentioned esterifying groups were deduced from the following considerations. In the PMR spectrum of (I) a one-proton multiplet at 5.00 ppm, which is diagnostic for 3α-substituted tropane alkaloids, showed that the position of esterification by one of the acids, namely the veratric acid, was C-3. In favor of this conclusion was the fact that all alkaloids isolated from the Convolvulus genus possess substitution at C-3 in the form of a veratric or vanillic acid residue.

In the mass spectra of the tropane alkaloids and of some pyrrolidine alkaloids the main direction of fragmentation is the α-cleavage of the ring with the subsequent elimination of an ethylene molecule [12]. Such a pattern was observed in the mass spectrum of (I). The most acceptable position for the acetoxy group is at C-6(7) of the tropane nucleus. In this case, on mass-spectrometric fragmentation, as the result of the α-cleavage of the C-1–C-7 and C-5–C-6 bonds that is characteristic for the tropane alkaloids [12] and the ejection of a fragment with m/z 86 ($CH_3COOCH=CH_2$) one should expect the appearance of the peak of an ion with m/z 277 $(M - 86)^+$ in the spectrum, but this was not in fact observed. In all probability, what takes place here is the elimination of the fragment with m/z 86 not from the molecular ion but from an ion with m/z 182 formed as the result of the splitting out of a veratric acid residue from the molecular ion $(M - 181)^+$. The peak of the ion so arising, with m/z 96 $(182 - 86)^+$ had a considerable intensity. The formation of the ion with m/z 96 by the

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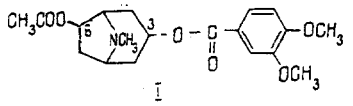
elimination of an acetoxyethylene fragment showed that the acetoxy group in convolacine is located at C-6(7). The C-2(4) position for the acetoxy group was excluded for biogenetic reasons.

In the PMR spectrum of (I) there were two one-proton triplets at 5.00 and 4.77 ppm, due to the H-3 and H-6 protons of the tropane nucleus, respectively, which were analogous to those of the acetyl derivative of the alkaloid physochlaine – (±)-3α-(p-methoxyphenylacetoxy)-tropan-6β-ol [13].

A triplet at 5.00 ppm was due to the H-3β proton of (I). This signal is typical for esters of tropan-3β-ol and differs substantially from the H-3 signal of tropan-3α-ol, which is observed in the form of a quintet – at, for example, 5.27 ppm in tropacocaine. Consequently, the veratroyl group at C-3 in convolacine, as in all the new Convolvulus tropane alkaloids, has the same orientation as in tropine, i.e., the α-orientation.

A one-proton quartet at 4.77 ppm in the PMR spectrum of the base was assigned to the signal of the proton at C-6. The nature of the splitting and the chemical shift of this proton were similar to those for the proton at C-6 in (+)-3α-acetoxy-6β-hydroxytropane [14]. This showed that the acetoxy group in convolacine has the β-configuration.

Thus, convolacine is (±)-6β-acetoxy-3α-veratroyltropane, and its structure is expressed by the following formula:



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