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CONVOLINE — A NEW ALKALOID FROM *Convolvulus krauseanus*

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A new alkaloid has been isolated from the epigeal part of *Convolvulus krauseanus* Regel. et Schmalh., and its structure has been established as (±)-3-veratroyl-N-hydroxynortropane.

Five alkaloids (convolvine, convolamine, convolidine, phyllalbine, and convolicine) have previously been isolated from the epigeal part of *Convolvulus krauseanus* Regel. et Schmalh. collected in the environs of the village of Bakhmal (Turkestan range) [1]. Continuing the separation of the mother liquors of the combined alkaloids, by chromatography on a column of silica gel the ethereal eluates have yielded a crystalline base with mp 184-185°C, R_f 0.85 [system I: chloroform–methanol–ammonia (8:2:0.1)], which differed from the tropane alkaloids that have been described. We have called it convoline (I).

The IR spectrum of the alkaloid contains the absorption bands of active hydrogen (3245 cm^{-1}), of a conjugated ester carbonyl (1705 cm^{-1}), and of a 1,2,4-trisubstituted benzene ring (830, 885, 1600, 1515 cm^{-1}). The 1,2,4-substitution in the aromatic ring was confirmed by the presence in the PMR spectrum of (I) of the signals from H_a and H_b protons in the 7.70-7.50 ppm region (2 H, m) and from H_c at 6.92 ppm (1 H, d). The spectrum also showed the signals from two aromatic methoxy groups (6 H, s; 3.89 ppm), of a diagnostic proton at CH_3 (1 H, t; 5.06 ppm), of methylene protons at 1.8-2.35 ppm, and of C_1 and C_5 methine protons at 3.55 ppm (2 H, m).

The mass spectrum showed the peaks of the molecular ion (M^+ 307). Ions with m/z 290 $(M - 17)^+$ 182, 165, 142, and 125, which are characteristic for alkaloids of the propane series, were also present. In the mass spectrum of the deuteration product of (I), the M^+ peak and also the peaks of the amino alcohol moiety were displaced by 1 m/z. With acetic anhydride, convoline gave a monoacetyl derivative with mp 130-131°C (M^+ 349), in the IR spectrum of which the band of active hydrogen had disappeared and an additional band of an ester carbonyl group had appeared at 1760 cm^{-1}, which shows the presence of a hydroxy group in the alkaloid. The PMR spectrum of convoline acetate showed at 1.99 ppm a three-proton singlet from the protons of an acetoxy group, and the signals from the C_1 and C_5 protons had undergone a paramagnetic shift by 0.17 ppm.

The facts given above show that convoline is an ester of a substituted tropine and an aromatic acid. The structure of the acid moiety of the molecule was determined by the hydrolysis of the base. From the acid part of the hydrolysate an acid was isolated which was identified by its R_f value and a mixed melting point as veratric acid. The amino alcohol moiety resinified. From the resulting resin by purification was isolated a very small amount of an amorphous substance (II) for which only the spectral characteristics are given.

A characteristic feature of the PMR spectrum of (II) is the upfield shift of the signals of the protons at C_1 and C_5, and also of the C_3-αH [by 3.43 ppm (2 H, m) and 3.82 (1 H, t),

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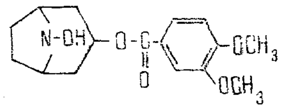
respectively]. The mass spectrum showed the M^+ peak with m/z 143 and the peaks of ions with m/z 126 $(M - OH)^+$ 115, 98, 82, and 78. A comparison of the mass spectra of (II) and tropine showed that they differed by 2 m/z. Since (I) did not contain a $N{-}CH_3$ group, we assumed that in convoline there was probably a N—OH group in place of the $N{-}CH_3$ group. To confirm this, we measured the accurate masses of the ions M^+ and the fragmentary ions of (I):

m/z	Accurate mass	Composition
307	307.1408	$C_{16}H_{21}O_5N$
291	291.1463	$C_{16}H_{21}O_4N$
290	290.1379	$C_{16}H_{20}O_4N$
142	142.0876	$C_7H_{12}O_2N$
125	125.0851	$C_7H_{11}ON$

The presence of a hydroxylamine group was also confirmed by the positive reaction of convoline with Fehling's reagent [2].

For a definitive determination of the structure of the alkaloid, we effected the passage from convoline to convolvine [3] and back. Thus, when (I) was reduced with zinc in acid, a product identical with convolvine was obtained, and the oxidation of convolvine with hydrogen peroxide gave convoline.

On the basis of the chemical reactions performed and the results obtained we propose for convoline the structure of (±)-3α-veratroyl-N-hydroxynortropane



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EXPERIMENTAL

Alkaline Hydrolysis of Convoline. A solution of 100 mg of the base in 5 ml of 10% ethanolic KOH solution was boiled for 5 h. After the end of the reaction (monitoring by TLC), the methanol was driven off in vacuum. The dry residue was treated with ether at the boil (4 × 100 ml). The combined ethereal extracts were concentrated. The oily residue was purified by treatment with petroleum ether. M^+ 143.

The reaction mixture remaining after the treatment with ether was dissolved in 10 ml of 20% hydrochloric acid solution and extracted with ether (5 × 50 ml). The combined ethereal extracts were dried with calcined calcium chloride and concentrated. This gave 40 mg of a crystalline substance with mp 180-181°C. A mixed melting point with an authentic sample of veratric acid gave no depression of the melting point.

Convoline Acetate. A solution of 50 mg of the base in 1 ml of acetic anhydride was kept at room temperature for 24 h. The excess of acetic anhydride was driven off in vacuum, the residue was dissolved in water, and the solution was made alkaline with ammonia and extracted with ether. The ethereal solution was dried with sodium sulfate. After the solvent had been driven off, the residue was treated with petroleum ether, to give 20 mg of a pulverulent product. M^+ 349. IR spectrum: 1760 cm^{-1}. PMR spectrum: δ 1.99 ppm (3 H, s).

Reduction of Convoline. Over 2 h with continuous stirring, 1 g of zinc dust was added in portions to a solution of 20 mg of convoline in 3 ml of 10% hydrochloric acid solution. After the end of the reaction (monitored by TLC) the mixture was made alkaline with concentrated ammonia solution and was treated with ether (2 × 50 ml). The ethereal extracts were dried with potassium carbonate and concentrated. This gave crystals with mp 114-115°C showing no depression of the melting point with a sample of convolvine.

Oxidation of Convolvine. A mixture of 20 mg of convolvine and 2 ml of perhydrol was left at room temperature in a dark place for a day. After the end of the reaction (TLC), the solution was made alkaline with concentrated ammonia solution and was treated with ether (2 × 40 ml). The ethereal extract was dried with potassium carbonate and concentrated. This gave crystals with mp 183-184°C showing no depression of the melting point with convoline.

SUMMARY

The new base convoline has been isolated from the epigeal part of *Convolvulus krauseanus* Regel. et Schmalh., and its structure has been established from spectral characteristics and some chemical transformations.

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ALKALOIDS OF *Glaucium corniculatum*

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The alkaloids from the epigeal part of the wild blackspot horn poppy have been studied. Twelve alkaloids have been isolated of which one — norbracteoline — proved to be new. Its structure has been established. Dehydrocorydine, predicentrine, glaufidine, thalicmidine, reticuline, and stylopine α-methohydroxide have been isolated from this plant for the first time.

From the cultivated plant *Glaucium corniculatum* (L.) J. Rudolf have been isolated 13 alkaloids belonging to four groups of isoquinoline bases [1]. Three alkaloids have been found in the wild blackspot horn poppy: protopine, allocryptopine, and corydine [2]. We have studied the epigeal part of *G. corniculatum* collected in the Georgievsk region of Stavropol'krai at the end of flowering-beginning of fruit-bearing.

Ethanolic extraction yielded 1.36% of combined alkaloids. The nonphenolic fraction of this combined material contained sanguinarine, dehydrocorydine, predicentrine, isocorydine, corydine, protopine, and allocryptopine. From the combined phenolic alkaloids we isolated predicentine, isocorydine, corydine, glaufidine, thalicmidine, reticulin, and new base (I), from chloroform — dehydrocorydine, isocorydine, corydine, thalicmidine, protopine, and allocryptopine. From the quaternary fraction we isolated stylopine α-methohydroxide in the form of the iodide. The known alkaloids were identified by direct comparison with authentic samples [3-5, 9]. The UV spectrum of the amorphous optically active base (I) is characteristic for 1,2,9,10-tetrasubstituted aporphine alkaloids (λ_{max} 220, 280, 310 nm) [6]. The IR spectrum of (I) shows absorption bands at (cm^{-1}) 3285 (NH), 3400 (OH), and 1520 (aromatic rings). The mass spectrum contains the peak of the molecular ion with m/z 313, a strong peak of the $(M-1)^+$ ion, and also the peaks of ions with m/z 298 $(M-15)^+$, 296 $(M-17)^+$, 284 $(M-29)^+$, 282 $(M-31)^+$, and 156.5 (M^{++}). This pattern of the spectrum confirms that the base belongs to a 1,2,9,10-tetrasubstituted aporphine alkaloid [7].

The PMR spectrum of (I) showed signals in the form of singlets from two methoxy groups at 3.83 ppm and from three aromatic protons at 6.43, 6.66, and 7.97 ppm, and also multiplets in the 2.5-4.0 ppm region from seven protons. The absence of the signal of a N-methyl group from the NMR spectrum and also the presence of the peak of the $(M-29)^+$ ion in the mass spectrum showed the secondary nature of the nitrogen atom.

The spectral characteristics permit the base (I) to be assigned to noraporphine alkaloids of the type of glaucine with two methoxy groups and two hydroxy groups.

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