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STRUCTURE AND ABSOLUTE CONFIGURATION OF COLLUTINE

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Continuing an investigation of the mixture of bases from the epigeal parts of Colchicum luteum Baker, we have isolated, in addition to substances known previously [1, 2], a new compound which we have called collutine. Collutine has the composition $C_{21}H_{25}O_5N$, mp 192-194°C, $[\alpha]_D$ −182° (c 1.7; chloroform), mol. wt. 371 (mass spectrometry). From the nature of its UV spectrum, with an adsorption maximum at 238 nm (log ε 4.3) and an inflection at 275 nm (log ε 2.81), this base resembles compounds of the homoproaporphine and homomorphinandienone series, which are biogenetically related to the tropolone alkaloids [3, 4]. The IR spectrum of the base (Fig. 1) shows the presence of an α, β-unsaturated carbonyl group and of an aromatic nucleus (1660, 1630, 1600, and 1560 cm^{-1}) and of hydroxy (3450 cm^{-1}) and methylene (2940, 1455 cm^{-1}) groups. In its mass spectrum, collutine differs sharply from the homoproaporphine alkaloids and is close to the homomorphinandienone compounds. Its mass spectrum has the main peaks of ions with m/e 371 (M^+, 100%), 356 (16%), 340 (10%), 328 (10%), and 210 (22%). From the specific color reaction with concentrated sulfuric acid [5], this base can also be assigned to the group of compounds of the type of androcymbine.

The NMR spectrum of collutine (Fig. 2) shows the signals of three methoxy groups (3.98, 3.80, and 3.59 ppm), a N-methyl group (2.35 ppm), and three aromatic protons (one-proton singlet at 6.77 ppm and two-proton singlet at 6.22 ppm).

On methylation with diazomethane, collutine formed a methyl ether which was chromatographically identical with O-methylandrocymbine [6]. This shows that the oxygen substituents in the homomorphinandienone skeleton of collutine are present in the same positions as in androcymbine.

On the basis of the results of a comparison of the spectral characteristics of collutine and known homomorphinandienone alkaloids, a structure with a hydroxy group at C_2, C_3, C_4, or C_6 may be proposed for this base. Structures with the hydroxy group at C_2 or C_3 are excluded for collutine, since they correspond to the alkaloid CC-10 [7] and to androcymbine [8]; the structure with the hydroxy group at C_6 can also be excluded, since the three-proton singlet at 3.59 ppm corresponds to an olefinic methoxy group in ring D [9]. Thus, the most probable structure for collutine is that with the hydroxy group in position C_4, i.e., the structure of 4-hydroxy-2,3,6-trimethoxyhomomorphinandienone: (See scheme on next page.)

On the basis of literature information [10], the one-proton singlet at 6.77 ppm in the NMR spectrum of collutine can be assigned to the C_5 position and the two-proton singlet at 6.22 ppm to C_1 and C_8.

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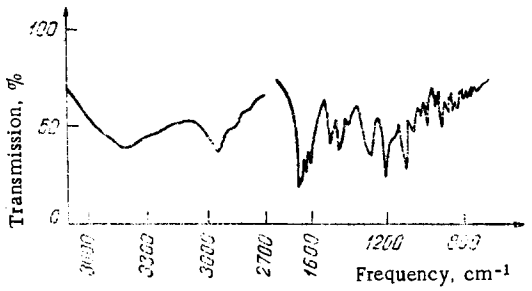


Fig. 1. IR spectrum of collutine (in KBr).

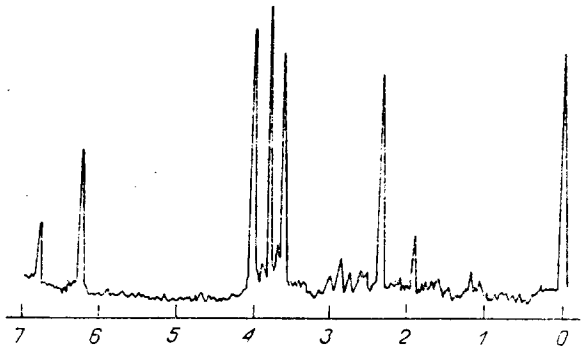
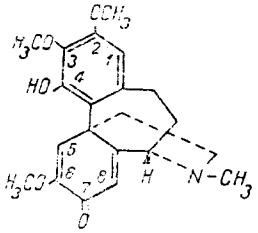


Fig. 2. NMR spectrum of collutine (in $CHCl_3$).



The chemical shifts of the protons and of the methyl groups in the NMR spectrum of collutine agree well with those for homomorphinandienone alkaloids of similar structure [7-10] and correspond to the formula put forward.

From the sign of the specific rotation and by analogy with androcymbine and similar alkaloids, collutine corresponds to the S absolute configuration.

EXPERIMENTAL

The homogeneity of the substances was checked by thin-layer chromatography in KSK silica gel with chloroform–methanol–benzene (20 : 4 : 6) (system 1) and by paper chromatography in n-butanol–5% acetic acid (50 : 50) (system 2).

The UV spectra were taken in a solution of methanol on an SF-4A spectrophotometer, the IR spectra on a UR-10 double-beam spectrometer, the NMR spectra on a XL-100 instrument, and the mass spectra on an MKh-1303 spectrometer.

Isolation of the Bases Fraction. By the methanolic extraction of 8.5 kg of the dried and comminuted epigeal parts of yellow autumn crocus collected in the Bostandykskyi region of the Uzbek SSSR by the usual method [11], we obtained 20.4 g (0.24%) of a strong-base fraction. By crystallization of the mixture of alkaloids from acetone, 10.6 g of luteidine was obtained. The acetone mother liquor contained a mixture of bases with R_f 0.21 (luteinine), 0.33 (luteicine), 0.43 (luteidine) [12], 0.47 (collutine), and 0.54 (unidentified compound) (system 2).

Collutine. The mixture of bases from the acetonic mother liquor from the crystallization of luteidine (5.0 g) was passed through a column containing 500 g of cellulose. The substances were eluted with water-saturated butanol. The first fractions contained a mixture of two substances, with R_f 0.54 and 0.47. The subsequent fractions contained luteidine (R_f 0.43), luteicine (R_f 0.33), and luteinine (R_f 0.21).

The fractions containing the mixture of substances with R_f 0.54 and 0.47 was rechromatographed on a column of alumina. The eluates produced with ether, ether–acetone (9 : 1 and 1 : 1), and acetone contained collutine; subsequent elution with acetone–chloroform (1 : 1) gave the base with R_f 0.54. The collutine was isolated by recrystallization from acetone.

Collutine is readily soluble in chloroform and methanol, less readily in acetone and ether, and sparingly in dilute alkalis. It dissolves in concentrated sulfuric acid with a crimson coloration.

The methiodide was obtained by heating an acetone solution of collutine and methyl iodide; mp 233-234°C (from acetone), R_f 0.12 (system 1; the initial base had R_f 0.47).

O-Methylcollutine. Collutine (10 mg in 2 ml of methanol) was methylated with an excess of diazomethane in n-hexane. The reaction product consisted of a viscous oil with R_f 0.53 (system 1).

O-Methylcollutine methiodide was isolated in the usual way; mp 212-214°C (from acetone), R_f 0.23 (system 1).

SUMMARY

A new base with the composition $C_{21}H_{25}O_5N$, mp 192-194°C, $[\alpha]_D$ −182°C, which has been called collutine, has been isolated from the epigeal parts of Colchicum luteum Baker.

On the basis of UV, IR, NMR, and mass spectra and chemical reactions, the structure of 4-hydroxy-2,3,6-trimethoxyhomomorphinandienone has been proposed for collutine.

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