after it had been made alkaline with sodium carbonate, the reaction product was extracted first with ether and then with chloroform. The ethereal fraction yielded the initial neoline and the chloroform fraction yielded amorphous N-norneoline.

SUMMARY

The presence of a $C_6(OCH_3)$–$C_7(OH)$–$C_8(OH)$ chain in the molecule of a C_{19} diterpene base leads a high intensity of the peak of $(M - 15)^+$ ion at the expense of the $C_6(OCH_3)$ group and considerably suppresses the competing processes of the formation of the $[M - OH(OCH_3)]^+$ ions in the case of the alkaloids and of the $(M-56)^+$ ions in the case of the anydroxy bases. Where either of these two elements of this chain is absent, the $(M - 15)^+$ ions are formed mainly by the detachment of CH_3 grom the N-ethyl group. A scheme of the origin of the $(M - 56)^+$ ions in the case of the 1-α-hydroxy bases has been substantiated.

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ALKALOIDS OF Nitraria schoberi. STRUCTURE OF NITRARAINE

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The dehydration of nitraraine leads to the formation of 1-(2',6'-dimethylbenzyl)-β-carboline, together with other products. Several isomeric 1-(dimethylbenzyl)-β-carbolines have been synthesized for comparison. The products of acylation, hydrogenation, and oxidation of the alkaloid nitraraine have been studied. The results obtained have shown its structure as (±)-16-hydroxymethylyohimb-16-ene.

Continuing a study of the alkaloids of the epigeal part of Nitraria schoberi L., growing in the Kyzyl-Kum, from the combined mother liquors of the fractions with pH 6.5-3 [1] we have isolated a white crystalline base with the composition $C_{20}H_{24}N_2O$ (M^+ 308.18886), mp 208-281°C $[\alpha]_D \pm 0°$ (Py, *c* 1) , which we have called nitraraine (I). The UV spectrum of the alkaloid showed absorption maxima at 227, 284, and 292 nm (log ε 4.56, 3.87, 3.79), which are characteristic for the chromophoric group of compounds of the β-carboline series.

The IR spectrum of (I) contained absorption bands due to the vibrations of the following bonds: ano-disubstituted benzene ring (740 cm^{-1}), C–O in primary alcohols (1020 cm^{-1}), a substituted indole nucleus (1450, 1470, 1570, 1630 cm^{-1}), saturated C–H (2850, 2920 cm^{-1}),

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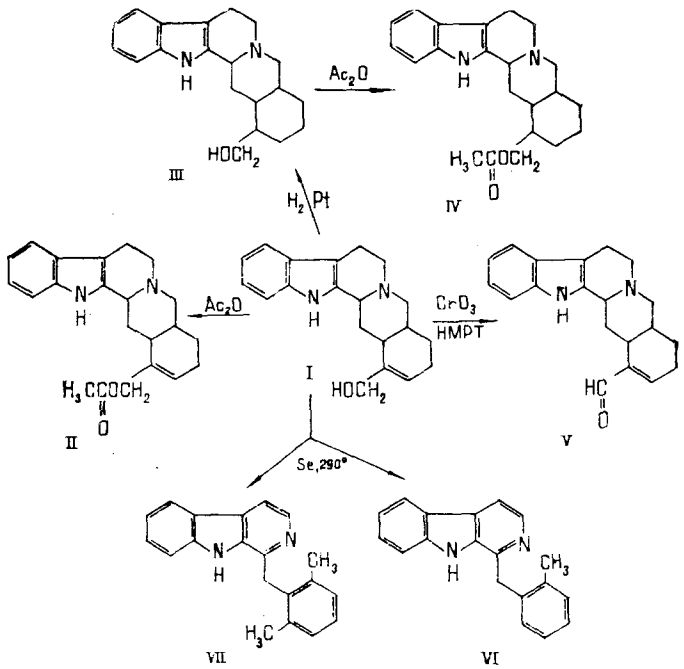
associated active hydrogen (O–H, N–H; 3260 cm^{-1}), and others.

The mass-spectrometric fragmentation of (I) was close to that of the yohimbine alkaloids, m/z: 308 (M^+, 80%), 307 (M – 1; 50), 291 (M – 17; 6), 277 (M – 31; 3), 223 (6), 197 (12), 184 (9), 171 (27), 170 (100), 169 (42), 156 (10), 144 (10). The alkaloid was sparingly soluble in organic solvents and its PMR spectrum was therefore obtained in trifluroacetic acid. It showed the presence of a trisubstituted double bond in the molecule (m, 1 H, 5.22 ppm).

The acetylation (I) with acetic anhydride in pyridine led to the formation of a mono-O-acetyl derivative (II, M^+ 350), the IR spectrum of which showed an intense absorption band of an ester carbonyl group (1740 cm^{-1}). The PMR spectrum of (II) ($CDCl_3$) contained the signals of a >N—H indole proton at 7.9 ppm (br. s, 1 H), of the aromatic protons of an indole nucleus (6.85-7.45) (see, for example, [2]), and a one proton broadened singlet from an olefinic proton at 5.32 ppm. The protons of an acetoxymethyl group resonated in the 4.39 ppm region (br.s, 2 H).

The Adams hydrogenation of (I) in ethanol (scheme 1) led to the absorption of one molecule of hydrogen and the formation ofa mixture of two isomers, one of which crystallized from ethanol with mp 285-287°C (III). In the mass spectrum of (III) the maximum peaks were those of the molecular ion (M^+ 310) and the M – 1 ion, the remainder of the fragmentation being similar to that of (I) (Table 1). The PMR spectrum of (III) lacked signlas in the region of olefinic protons, and in the IR spectrum the absorption at 800-850 cm^{-1} that was present in the spectrum of (I) had disappeared.

The mass spectrum of the product of the acetylation of dihydronitraraine (IV) contained the M^+ and M – 1 peaks as those of the maximum intensity, and the fragmentation in the region of medium mass numbers (223-144) was typical for the yohimbine alkaloids [3] (Table 1). The signal of the acetoxymethyl group in the PMR spectrum of (IV) appeared in the form of an unresolved doublet with J = 8 Hz at 4.08 ppm ($CDCl_3$).



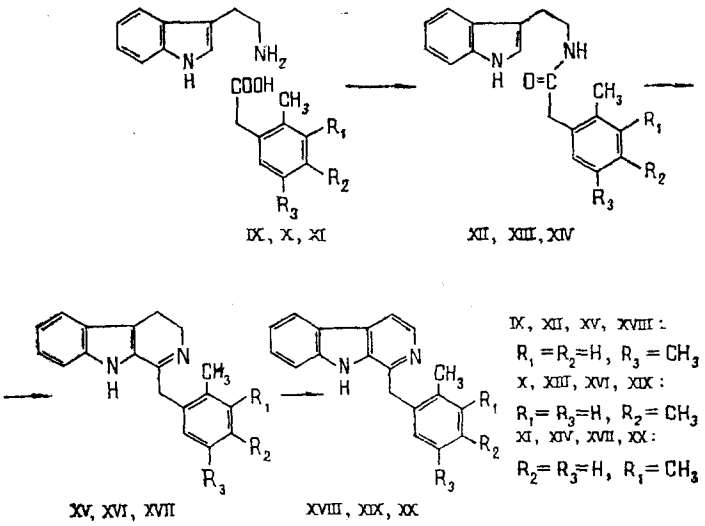
Scheme 1. Transformations of Nitraraine.

The oxidation of (I) with chromium trioxide (scheme 1) in hexamethylphosphorotriamide [4] led to the aldehyde (V) (M^+ 306) the IR spectrum of which showed a strong absorption band of an α,β-unsaturated aldehyde at 1680-1690 cm^{-1}. This information was supported by the PMR spectrum, in which the signal of an aldehyde proton appeared in the 9.32 ppm region in the form of a singlet, and the signal of an olefinic proton resonated, because of conjugation, at 6.34 ppm (br. s, 1 H).

Thus, an analysis of the spectral characteristics of nitraraine and also of its derivatives – dihydronitraraine, acetyldihydronitraraine, and nitrarine aldehyde (scheme 1) –

permitted the conclusion that the molecule of (I) was based on the yohimban skelton in ring E of which there was a double bond directly connected with a hydroxymethyl group. Yohimbine alkaloids with substitution in any of the four possible positions of ring E have been described. To establish the position of the substituent and to confirm the presence of the yohimbane skeleton we therefore dehydrogenated (I) with selenium at 290°C. Three products were isolated from the reaction mixture – (VI), (VII) (scheme 1), and (VIII). According to the melting point and UV spectrum published for the product of the dehydrogenation of yohimbine and yohimbyl alcohol – yobirine – (VI) was identical with the latter [5-7]. In all these properties, compound (VII), was extremely close to (VI): the same coloration of the spots on TLC, similar R_f values, the existence of fluorescence in acid solutions of both compounds, similar UV spectra. However, the molecular weight of (VII) (M^+ 286) was 14 mass units greater than that of yobirine, and its fragmentation included the successive ejection of two methyl groups (M – 15, M – 30). Product (VIII) had mp 110-115°C, and its UV spectrum was similar to those of alstyrine and tetrabirine [8]. Its molecular weight (M^+ 292) and mass-spectrometric fragmentation permitted the assumption that (VIII) was possibly a methylalstyrine

Thus, the results of the dehydrogenation of (I) confirmed the yohimbine skeleton of the alkaloid. With the somewhat uncertain assumption that dehydration took place without the migration of the substituents, the establishement of the position of the second methyl group in (VII) permitted the determination of the position of the hydroxymethyl group in (I). With this aim, we synthesized the isomeric 1-(2',5'-..., 1-(2',4'-..., and 1-(2',3'-dimethylbenzyl)-β-carbolines (scheme 2).



Scheme 2. Synthesis of 1-(dimethylbenzyl)-B-carbolines.

In turn, the p-, m-, and o-xylenes were chloromethylated with formalin in hydrochloric acid [9]. The compounds obtained were converted by the Grignard reaction into the corresponding acids (IX, X, XI), which, after condensation with tryptamine and cyclization of the resulting amides by the Bischler-Napieralski reaction, followed by dehydrogenation led to the corresponding 1-(dimethylbenzyl)-β-carbolines (XVIII, XIX, XX).

All the compounds obtained and the product of the dehydrogenation of nitraraine (VII) were similar to one another in their properties and spectral charecteristics. However, when they were deposited together on a TLC plate not one of the three substances synthesized proved to be identical with compound (VII). Consequently, only the last of the four possible structural variants remained for it, namely: 1-(2',6'-dimethylbenzyl)-β-carboline. A compound with this structure was isolated by Karrer et al. from the products of the dehydrogenation of yohimbyl alcohol. In its melting point and UV spectrum [5] it was identical with the compound (VII) that we had obtained.

Thus, an investigation of the reactivity of nitraraine and an analysis of the spectral characteristics of the alkaloid and its derivaties permit the conclusion that it has the structure of 16-hydroxymethylyohimb-16-ene. An optically active form of apoyohimbyl alcohol has been obtained synthetically by reducing apoyohimbine with lithium tetrahydroaluminate [10].

EXPERIMENTAL

Mass spectra were obtained on MKh-1303 and MKh-1310 instruments with a system for direct introduction into the ion source; IR spectra were obtained on a UR-20 spectrophotometer (KBr); UV spectra on a Hitachi instrument in ethanol; and PMR spectra on a JNM-4H 100/100 MHz spectrometer in $CDCl_3$, unless otherwise stated, with HMDS as internal standard (δ scale). For column chromatography we used commerical alumina (activity grade II) and silica gel L 100/160. TLC was carried out with type L 5/40 silica gel and on silufol plates. The solvents and solvent systems were: 1) benzene; 2) benzene–methanol (8:3, 4:1, 9:1, 14:1); 3) chloroform–ethanol (2:1); 4) chloroform–acetone–ethanol (6:2:1); 5) chloroform–acetone–methanol–conc. ammonia (5:3:1:0.1; 5:4:1:0 [sic]); 6) hexane–ethyl acetate (7:3); 7) chloroform–acetone–ethyl acetate–formamide (5:3:1:1); 8) benzene–ethyl acetate–diethylamide (7:2:1);and others.

Isolation of Nitraraine (I). The material (20 g) from the combined chloroform extracts of the fractions with pH 6.5 and 4 from the polybuffer separation of the total chloroform-extracted material and also 30 g of the fractions with pH 6.5-3 from the analogous separation of the combined ether-extracted material [1] were chromatographed separately on columns of alumina with elution by ether. The first eluates yielded the known alkaloid tetramethylene-tetrahydro-β-carboline [11], mp 147-148°C (petroleum ether). Treatment of the following fractions with methanol gave 1.3 g of technical (I) (0.0006% on the weight of the dry raw material). After crystallization from ethanol, mp 280-281°C.

O-Acetylnitraraine (II). A mixture of 70 mg of (I), 1 ml of freshly purified pyridine, and 0.8 ml of freshly distilled acetic anhydride was left at room temperature for 20 h. The solvent was evaporated off in vacuum, and the residue was treated with 1.5 ml of water, the mixture then being neutralized to pH 7 with concentrated ammonia solution. The precipitate that deposited was filtered off and was washed with water and then with methanol and was dried. This gave 41 mg (50%) of (II) with mp 89-91°C (methanol). Mass spectrum, m/z: 350 (M^+, 44%), 349 (M − 1.26%), 307 (M − 43; 4), 291 (M − CH_3COO; 35), 277 (M − 73; 4), etc.

Dihydronitraraine (III). With heating, 290 mg of (I) was dissolved in 120 ml of ethanol and the solution was added to 190 mg of platinum oxide in a round-bottomed flask. The reaction mixture was saturated with hydrogen with continuous shaking. After 6 h (chromatographic monitoring), the reaction had ceased, and the catalyst was filtered off. TLC in system 3 showed the formation of two products (R_f 0.8 and 0.4). The solvent was evaporated to 1/3 of its initial volume. On standing, 80 mg (28%) of (III) deposited in the form of white crystals with mp 285-287°C (R_f 0.8).

O-Acetyldihydronitraraine (IV). A mixture of 40 mg of (III), 0.8 ml of pyridine, and 0.7 ml of freshly distillied acetic anhydride was left at room temperature for 22 h. The isolation and purification of the product were performed as described for (II). This gave 19.5 mg (44%) of (IV) in the form of colorless plates with mp 93-95°C (methanol). Mass spectrum, m/z: 352 (M^+, 97%), 351 (100), 309 (3), 293 (9), 279 (3), and other peaks.

Nitraraine Aldehyde (V). To 0.25 ml of hexamethylphosphorotriamide (HMPT) freshly distilled over calcium oxide 70 mg of CrO_3 was added in portions. The mixture was stirred with a magnetic stirrer in a conical flask fitted with a calicum chloride tube for 15 min. It was then allowed to stand at room temperature for 1 h and then a solution of 60 mg of (I) in 1.5 ml of HMPT was added and the mixture was stirred again (with chromatographic monitoring). After 3.5 h the reaction solution was poured into a vessel containing ice water, the mixture was made alkaline with 5% caustic soda, and the product was extracted first with ether and then with chloroform.

Both extracts were washed with 5% caustic soda solution and with water and were then dried over anhydrous sodium sulfate. The two extracts were purified in parallel by the usual method for bases: they were extracted with 5% sulfuric acid, the extract was washed with chloroform, and the acid solution was then made alkaline with 5% caustic soda and the products were extracted with ether. The solvent was distilled off and the residue was transferred to a volumn of silica gel and was eluted first with chloroform and then with chloroform–methanol (4:1). The first chloroform–methanol extracts yielded the aldehyde in the form of an amorphous powder. The amount of (V) obtained from the two extracts was 32 mg (50%). Mass spectrum m/z: 306 (M^+, 100%), 305 (90), 278 (35), 277 (30), 197 (20), etc. IR spectrum, ν_{max}, cm^{-1}: 3400-3150 (>NH), 2930-2810 (C–H sat.), 1685 (H–C(=O)–conj.), 750, etc.

Dehydrogenation of Nitraraine with Selenium. A carefully ground mixture of 430 mg of (I) and 600 mg of powered seleniun in two test-tubes was placed in a sand bath heated to 280°C. The temperature was raised to 290°C after 12 min and then the reaction was continued at this temperature for an other 3 min. After cooling, the test-tubes with the sintered mass were ground in a morter, mixed with alumina, and, after the mixture had been placed in a thimble, the products were extracted with ether in a Soxhlet apparatus for 10 h, and the solvent was distilled off. This gave 350 mg of a mixture of substances which, on TLC in system 2, showed six spots. separation was carried out by preparative chromatography in a layer of silica gel/gypsum in the benzene–methanol (4:1) system. Three main fractions were isolated from which the following substances were obtained:

compound (VI) (16 mg), mp 215-217°C (repurification from ether). UV spectrum, $\lambda_{max}^{ethanol}$: 236, 289, 338, 352 nm; $\lambda_{max}^{ethanol+H^+}$: 251, 305, 372 nm;

compound (VII) (34 mg), mp 206-210°C. Mass spectrum, m/z: 286 (M^+, 82%), 285 (M − 1.29%), 271 (M − 15; 100), 256 (M − 30; 12), 167 (6). UV spectrum, $\lambda_{max}^{ethanol}$: 236, 289, 338, 352 nm (log ε: 4.45, 4.11, 3.65, 3.63); $\lambda_{max}^{ethanol+H^+}$: 252, 304, 374 nm; and

compound (VIII) (20 mg), mp 110-115°C (colorless flakes from ethanol). Mass spectrum m/z: 292 (M^+, 74%), 277 (M − 15; 100), 262 (M − 30; 7), etc. UV spectrum: λ_{max}: 325-335 nm; λmin: 275 nm.

Indole-3-carbaldehyde. A three-necked flask fitted with a thermometer, stirrer, and condenser with calcium chloride tube was charged with 0.6 mole (46 ml) of dimethylformamide and was cooled to −5°C; then, with sitrring, 0.1 mole (9.2 ml of phosphorus oxychloride was added, the temperature being kept below 10°C. To this mixture 0.05 mole of commerical indole was added in portions at room temperature, after which the reaction mixture was stirred at 25°C for 30 min, and then 20 g of finely ground calcium carbonate was added and the reaction mixture was heated to 35°C after which the external source of heat was removed. The mixture was stirred at 48-50°C (the temperature being maintained by the heat of the reaction) for 30 min and was then cooled with ice to 10°C and 100 ml of 30% sodium acetate was added. After dilution with water to a volume of 500 ml, the reaction solution obtained was boiled with 0.6 mole of caustic soda for three hours. A copious evolution of dimethylamine took place. The indole that had not reacted was distilled off with steam and the reaction mixture was diluted with water to a volume of 1.7 liters; the solution was then boiled and filtered. Gradual evaporation led to the separation of 5.43 g (75%) of technical indole-3-carbaldehyde with mp 189-191°C. Recrystallization from boiling water gave 4.26 g (59%) of the crystalline aldehyde with mp 195°C [12]

Nitromethane. With stirring, 20 g of sodium bicarbonate was added to a mixture of 0.21 mole of monochloroacetic acid and 50 g of finely crushed ice cooled with ice water. After the evolution of carbon dioxide, a solution of 0.58 mole of soidum nitrite in 40 ml of hot water was added to the reaction flask and the mixture was boiled under reflux until the evolution of carbon dioxide had ceased. Then a descending condenser was attached and the reaction product was distilled off and was separated from water in a seperotory funnel, the aqueous fraction being extracted with ether and the ethereal layer being combined with the initial nitromethane that had separated out; the solution was dried over anhydrous sodium sulfate and the solvent was distilled off. The nitromethane remaining was distilled, the fraction with bp 98-100°C being collected [13].

3-(2-Nitroethenyl)indole. A 100-ml flask was charged with a solution of 0.01 mole of indole-3-carbaldehyde in 40 ml of ethanol, 0.075 g of methylamine hydrochloride, 0.03 g of sodium carbonate, and 0.01 mole of nitromethane. The well-stirred reaction mixture was left at room temperature for 7 days. Then it was evaporated in vacuum to half its initial volume. On cooling, yellowish crystals deposited. After chromatographic purification and crystallization from methanol–petroleum ether (3:1), 1 g (53%) of 3-(2-nitroethenyl)indole was obtained with mp 167-168°C [14].

Tryptamine. Method 1. A solution of 1 g (0.0053 mole) of nitroethenylindole in 30 ml of dry tetrahydrofuran was added dropwise with constant stirring to a suspension of 4 g of lithium tetrahydroaluminate in 60 ml of dry diethyl ether. The reaction solution was boiled for 3 h with a reflux condenser fitted with a calcium chloride tube and was then left overnight under normal conditions. The mixture was treated successively with diethyl ether and water and was then made alkaline with dilute caustic soda solution; the ethereal layer was separated off and gaseous hydrogen chloride was passed through it. This gave 0.83 g (80%) of tryptamine hydro-

TABLE 1. Intensities of the Characteristic Peaks of Nitraraine and Its Derivatives (%)

Substance	Ions, m/z							
	M+	M−1	223	184	170	169	156	144
Nitraine	84	48	6	12	100	42	10	10
Acetylnitraaraine	44	26	2	7	100	39	9	11
Nitraraine aldehyde	100	90		22	100	85	21	22
Dihydronitraraine	100	85	7	15	38	51	12	14
Acetyldihydro-(I)	97	100	3	6	26	37	9	14
Yohimbine [3]	80	100	5	15	18	27	15	10

chloride with mp 248-249°C (ethanol—ethyl acetate). Decomposition of the salt gave the base, with mp 114-115°C [14].

Method 2. A mixture of 0.3-0.5 g of d,l-tryptophan and 12-20 g of diphenylmethane was boiled over a burner flame in an atmosphere of nitrogen for 20 min. After cooling, 20-40 ml of a saturated benzene solution of hydrogen chloride was added to be mixture. The precipitate of salts that deposited was separated off and was dissolved in a mixture of ethanol and ethyl acetate. On strong cooling, lustrous colorless crystals deposited with mp 248-249°C. The experiment was repeated several times. Yield 75-90% [15]. 3].

2,5-Dimethylbenzyl Chrloride [9]. A mixture of 124.7 g (1.17 mole) of p-xylene, 100 ml of 40% formalin (1.33 mole of formaldehyde), and 400 ml of concentrated hydrochloric acid was stirred at 60-70°C while being saturated with gaseous hydrogen chloride. The reaction ceased after 6 h. Diethyl ether was added to the reaction mixture, which had separated into layers, and the ethereal layer was spearated off and dried over anhydrous calcium chloride. After the solvent had been distilled off, the only liquids were fractionated in vacuum: a fraction was collected with bp 102°C/13 mm (according to the literature: 103°C/12 mm). This gave 91 g of the desired product, yield 50%.

2,4-Dimethylbenzyl Chloride [9]. A liter flask fitted with a stirrer, reflux condenser and gas feed tube was charged with a mixture of 120.4 g (1.13 mole) of m-xylene, 100 ml of 30% formalin (1 mole of formaldehyde),,and 400 ml of concentrated hydrochloric acid and, simultaneously, with stirring, gaseous hydrogen chloride was passed in. The reaction was performed as described in the preceding experiment. After fractionation, 62 g (36%) of the desired product was obtained with bp 105-110°C/20 mm (according to the literature, 100-105°C/14 mm).

2,3-Dimethylbenzyl Chloride [9]. o-Xylene (1.1 mole) was subjected to the chloromethylation reaction with formalin (1 mole of formaldehyde) and hydrogen chloride under similar conditions. The reaction products were separated by distillation in the vaccum of a water pump. A fraction with bp 105-106°C/11 mm was collected. This gave 60 g (35%) of a mixture of 2,3- and 3,4-dimethylbenzyl chlorides.

2,5-Dimethylphenylacetic Acid (IX). A 250-ml three-necked flask fitted with a stirrrer, dropping funnel, and reflux condenser with calcium chloride tube was charged with 2.4 g (0.1 g-atom) of magnesium turnings, and 30 ml of absolute ether was added. Then 3 ml of a solution of 15.8 g (0.1 mole) of 2,5-dimethylbenzyl chloride in 50 ml of absolute ether was run in from the dropping funnel. A small crystal of iodine was added to initiate the reaction, and the flask was immersed in a bath of hot water. Then, when the ether became turbid and began to boil, the water bath was removed; the reaminder of the solution of 2,5-dimethylbenzyl chloride was added dropwise at such a rate that the ether boiled gently and uniformly. When the addition of the reagent was complete (1.5 h), the reaction mixture was heated on the water bath for another 1.5 h, after which the magnesium had dissolved completely. Then solid carbon dioxide was added until the mixture solidified and the exterior of the flask had become coated with snow. With stirring, 40 ml of 12% hydrochloric acid was added dropwise and the ethereal layer that separated was taken off; the aqueous fraction was extracted three times with ether. Compound (IX) was extracted from the combined ethereal solutions with 5% caustic soda solution, and the alkaline extract was separated off and acidified with hydrochloric acid. The 2,5-dimethylphenylacetic acid that separated off was filtered off, washed with cold water, and dried. The yield of (IX) was 9.8 g (60%), mp 128-130°C (hot water); according to the literature [16]: mp 128-129°C. PMR spectrum, ppm: 2.21 (s, 6H, CH_3—Ar—CH_3);

3.5 (2H, s, Ar—CH_2—COOH); 6.92 (s, 3H, (Ar − H); 11.82 (s, 1 H, —COOH).

2,4-dimethylphenylacetic Acid (X). The reaction of 0.1 mole of 2,4-dimethylbenzyl chloride with 0.1 g-atom of magnesium was performed as described in the preceding experiment. When the alkaline solution was acidified, compound (X) did not precipitate and it was therefore extracted with ether, and the solvent was distilled off. This gave 4.66 g (28%) of (X) with mp 102-103°C (water); according to the literature [17]: mp 101°C, 104°C. PMR spectrum, ppm: 2.19 (s, 6H, CH_3—Ar—CH_3); 3.49 (s, 2H, Ar—CH_2—COOH); 6.91 (br. s, 3H, Ar—H); 12.25 (br.s, 1H, —COOH).

2,3-Dimethylphenylacetic Acid (XI). The reaction of 0.1 mole of the mixture of 2,3- and 3,4-dimethylbenzyl chlorides with 0.1 g-atom of magnesium turnings followed by the addition of solid carbon dioxide was carried out in the manner described for 2,5-isomer. White crystals were obtained which (according to TLC) consisted of a mixture of 2,3-dimethylphenylacetic and 3,4-dimethylphenylacetic acids.

3-[β-(2',5'-Dimethylphenylacetamido)ethyl]indole (XII). A carefully ground mixture of 3.2 g (0.02 mole) of tryptamine and 3.3 g (0.02 mole) of (IX) was heated in a round-bottomed flask at 190-215°C for 20 min. The cooled reaction product was crystallized from ethyl acetate, giving a 3 g (49%) of the amide (XII) in the form of colorless silky needles with mp 112-113°C.

3-[β-(2',4'-Dimethylphenylacetamido)ethyl]indole (XIII). A carefully ground mixture of 0.01 mole of tryptamine and 0.01 mole of (X) was subjected to a condensation reaction. The product was isolated by the method described above, giving 2.01 g (65%) of the amide (XIII) with mp 131-134°C.

3-[β-(2',3'-Dimethylphenylacetamido)ethyl]indole (XIV). A ground mixture of 0.005 mole of tryptamine and 0.005 mole of the mixture of 2,3- and 3,4-dimethylphenylacetic acids was heated at 197°C for 30 min. The product was worked up as in the preceding experiment, giving colorless crystals consiting of a mixture of the 2',3'- and 3',4'- isomers. Yield 60%.

3,4-Dihydro-1-(2',5'-dimethylbenzyl)-β-carboline (XV). A mixture of 1 g (0.0033 mole) of the amide (XII) and 2 ml of $POCl_3$ in 40 ml of asbolute benzene was boiled for 1 h. Benzene was distilled off in vacuum and the residue was boiled with dilute acetic acid; the acid solution was filtered in the hot state and, after cooling, concentrated ammonia solution was added. The light yellow precipitate that deposited was separated off and dried in a desiccator. This gave 0.85 g (90%) of (XV) which, without further treatment, was used in the following stage of the synthesis.

3,4-Dihydro-1-(2',4-dimethylbenzyl)-β-carboline (XVI). A mixture of 0.001 mole of the amide (XIII) and a 1 ml of $POCl_3$ was boiled in 25 ml of absolute benzene. After 30 min the reaction had gone to completion (chromatographic monitoring). The product was isolated as described in the preceding experiment. Yield 0.274 g (94%) of technical product.

3,4-Dihydro-1-(2',3'-dimethylbenzyl)-β-carboline (XVII). A mixture of 0.003 mole of (XIV), containing the 3,4- isomer as an impurity, and 2 ml of phosphorus oxychloride in 40 ml of absolute benzene was boiled for 1 h. The benzene was evaporated off in vacuum and the residue was treated with dilute acetic acid; the mixture was heated in a steam bath, filtered, and cooled. Compound (XVII) was precipitated by the addition of ammonium solution. The yield of technical product was 90%.

1,(2',5'-Dimethylbenzyl)-β-carboline (XVIII). A mixture of 290 mg (0.001 mole) of (XV) and 100 ml of palladium black was carefully ground in a round-bottomed flask and was heated (in the vacuum of water pump) at 180-200°C for 0.5 h. After cooling, the sintered mass was boiled in methanol, and the catalyst was filtered off. The methanolic solution of the dehydrogenation product was boiled with activated carbon and filtered, and the solvent was distilled off. The successive treatment of the residue with aqueous methanol and then with toluene gave 181 mg (63%) of (XVIII) in the form of white silky needles with mp 226-227°C. Mass spectrum, m/z: 286 (M^+, 70%), 285 (M − 1; 20), 271 (M− 15; 100), 256 (M − 30; 23), 181 (3), 168 (1), 167 (2). IR spectrum,* ν_{max}: 3490 (s), 3130 (s), 3050 (br.s), 2955 (br.s), 2860 (bs.s), 2765 bs.s), 1880 (bs.s), 1715 (s), 1630 (s), 1610 (s), 1570 (d), 1510 (d), 1485 (s), 1460 (s), 1435 (s), 1380 (s), 1330 (s), 1290 (s), 1260 (s), 1240 (s), 1225 (s), 1190 (s),

*s − singlet; br.s − broadened singlet; d − doublet; t − triplet; intense signals are underlined.

1155 (s), 1130 (s), 1080 (d), 1040 (s), 1015 (s), 890 (s), 815 (t), 770 (s), 750 (d).

1-(2',4'-Dimethylbenzyl)-β-carboline (XIX). A carefully ground mixture of 200 mg (0.0007 mole) of (XVI) and 80 mg of palladium black was heated at 180-200°C in vacuum for 0.5 h. The product was isolated as described for (XVIII); mp 219-220°C (treatment with toluene). Mass spectrum, m/z: 286 (M^+, 69%), 285 (M − 1; 22), 271 (M − 15; 100), 256 (M − 30; 22), 181 (3), 168 (5), 167 (2). IR spectrum, ν_{max}: 3420, 3125, 3055 (d), 2965 (t), 2865 (bs.s), 2770 (d), 1900 (d), 1630 (s), 1610 (s), 1570 (s), 1510 (d), 1485 (s), 1460 (s), 1440 (s), 1330 (s), 1380 (s), 1310 (s), 1290 (s), 1270 (s), 1260 (s), 1235 (s), 1190 (s), 1160 (s), 1130 (s), 1110 (s), 1080 (d), 1040 (s), 1020 (s), 885 (d), 855 (s), 830 (s), 810 (d), 770 (t), 750 (d).

1-(2',3'-Dimethylbenzyl)-β-carboline (XX). Compound (XVII) (0.001 mole) was dehydrogenated in the presence of 80 mg of palladium black. The conditions for the reaction and for the isolation of the products were similar to those described in the preparation of (XVIII) and (XIX).

SUMMARY

On the basis of the results of ananalysis of the spectral characteristics of the alkaloid nitraraine and also of the product of its chemical transformations, its structure has been established as (±)-16-hydroxymethylyohimb-16-ene. In order to prove the structure of the dehydrogenation products, a number of isomeric 1-(dimethylbenzyl)-β-carbolines have been synthesized. The reactivity of the nitraraine molecule has been studied.

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