SYNTHETIC ANALOGS OF *Peganum* ALKALOIDS.

I. SYNTHESIS OF METHOXY- AND HYDROXY-SUBSTITUTED DEOXYVASICINONES AND DEOXYPEGANINES

A. Karimov, M. V. Telezhenetskaya,
and S. Yu. Yunusov

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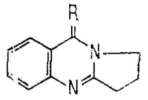
6-Methoxy-, 7-methoxy-, and 8-methoxydeoxyvasicinones have been synthesized by the reaction of substituted (3-methoxy-, 4-methoxy-, and 5-methoxy-) anthranilic acids with α-pyrrolidone. The demethylation of these compounds has given the corresponding hydroxy-substituted analogs of deoxyvasicinone, and the reduction of the products obtained with zinc in hydrochloric acid has given the hydroxy- and methoxy- analogs of deoxypeganine. 8-Hydrooxydeoxypeganine dimethyl-, ethyl-, and butylcarbamates have been obtained by the carbamoylation of 8-hydroxydeoxypeganine.

In view of the high biological activity of deoxypeganine [1], the synthesis of analogs of alkaloids of the peganine series is of definite interest.

The direct introduction of functional groups into various positions of ring A of deoxyvasicinone (I) and deoxypeganine (II) is extremely difficult: Only the nitration and sulfochlorination of (I) in position 6 under severe conditions are known [10]. Consequently it is necessary first to introduce the substituent into the initial compounds.



I. R = O
II. R = H_2

We have synthesized methoxy- and hydroxypeganines substituted in all the positions of ring A [2, 3] starting from substituted o-nitrotoluenes, by the stepwise growth of the side chain and construction of ring C and then the closure of ring B. A more convenient method of synthesizing the peganines and deoxypeganines (DOPs) is the reduction of the corresponding vasicinones and deoxyvasicinones (DOVs). The latter are synthesized by the condensation of anthranilic acid (AA) with lactim ethers [4-6], immino ketenes with lactams [7], and anthranilic acid and its esters with lactams [8, 9]. In this case the starting materials already have rings A and C and on condensation ring B is closed.

We shall give the results of the synthesis of the 6-methoxy-, 7-methoxy-, and 8-methoxyderivatives and the corresponding hydroxy-substituted analogs of deoxypeganine and deoxyvasicinone. We first synthesized the corresponding methoxy-substituted analogs of anthranilic acid. Alkoxy-substituted anthranilic acids can be obtained by two most rational routes: by the oxidation of substituted isatins [11] and via substituted o-nitrobenzoic acids [12, 13].

5-Methoxy- and 3-methoxyanthranilic acids (IX and X) were synthesized by the oxidation of the corresponding isatins (VII and VIII) [11]. To obtain the (VII) and (VIII) we used o- and p-anisidines (III and IV), from which by the Sandmeyer reaction [16] we synthesized the p- and o-methoxyisonitrosoacetanilides (V and VI). Cyclization of the latter to the isatins took place under the action of sulfuric acid with heating. The yield of product depends greatly on the concentration of sulfuric acid and the temperature.

There is contradictory information in the literature on the synthesis of (VII) and (VIII). Some workers consider that p-methoxyisonitrosoacetanilide (V) does not cyclize to

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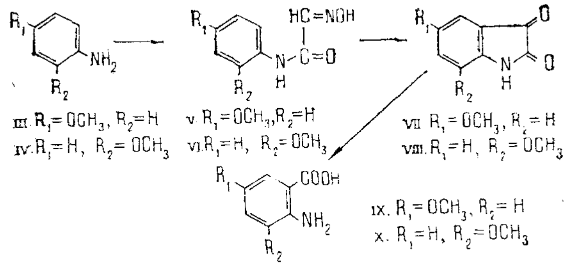
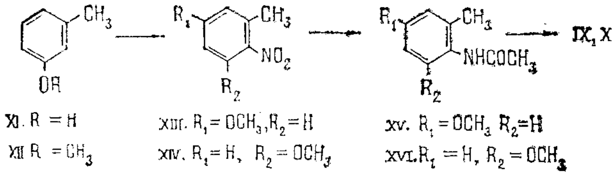
(VII) [18], while others have obtained compound (VII) [11, 14]. We did not succeed in obtaining (VII) in satisfactory yield by a method for its synthesis given in the literature [11, 14]. By varying the parameters of the reaction we selected the optimum conditions and obtained (VII) in good yield.



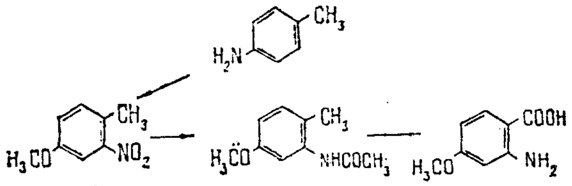
Sandmeyer considered that the cyclization of (VI) into (VIII) does not take place [16] although other authors [15, 17] subsequently succeeded in obtaining (VIII) by his method, but, unfortunately, they do not give the experimental details or the yields of product. The o-methoxyisonitrosoacetanilide that we obtained cyclized to (VIII) with difficulty, and we were unable to increase the yield of the latter by varying the reaction conditions.

We also synthesized compounds (IX) and (X), starting from m-cresol by the scheme given below:



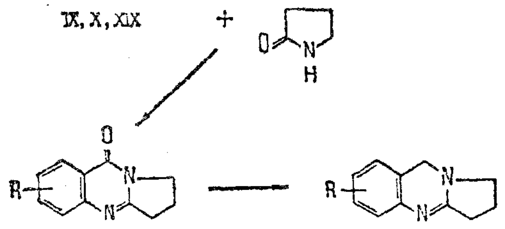
On comparing the two methods with respect to the ease of obtaining the intermediate compounds and the yield of final products, we came to the conclusion that (IX) should be obtained via (VII) and (X) via 3-methoxy o-nitrotoluene.

To obtain 4-methoxyanthranilic acid (XIX), we used p-toluidine, which was nitrated with nitrating mixture, diazotized, and converted into 4-hydroxy-2-nitrotoluene. After methylation with dimethyl sulfate, (XVII) was obtained. Compound (XVII) was reduced with $SnCl_2$, the product was isolated, and the resulting 2-acetamido-4-methoxytoluene (XVIII) was oxidized with $KMnO_4$. Saponification of the acetyl group gave (XIX).


XVII XVIII XIX

By condensing the anthranilic acids obtained with α-pyrrolidone in the presence of $POCl_3$ or $SOCl_3$ [9], we obtained the corresponding methoxy-substituted analogs of deoxyvasicinone (XX–XXII). We may note that by varying the sequence of the addition of the reactants it is possible to increase the yield of deoxyvasicinones. As the condensing agent here even $SOCl_2$ can be used, although the best condensing agent for the reaction of anthranilic acids with lactams is considered to be $POCl_3$ [9].

By reduction with zinc in hydrochloric acid, from the deoxyvasicinones (XX–XXII) we obtained the corresponding methoxy-substituted deoxypeganines (XXIII–XXV). Boiling compounds (XX–XXII) in 47% HBr yielded the phenolic deoxyvasicinones (XXVI–XXVIII). By reducing compounds (XXVI–XXVIII) with zinc in hydrochloric acid followed by demethylation in 47% HBr, from compounds (XXIII–XXV) we obtained the hydroxy-substituted deoxypeganine analogs (XXIX–XXXI).



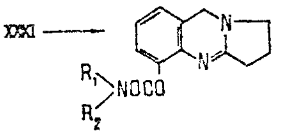
XX. R = 6-OCH_3
XXI. R = 7-OCH_3
XXII. R = 8-OCH_3
XXVI. R = 6-OH
XXVII. R = 7-OH
XXVIII. R = 8-OH

XXIII. R = 6-OCH_3
XXIV. R = 7-OCH_3
XXV. R = 8-OCH_3
XXIX. R = 6-OH
XXX. R = 7-OH
XXXI. R = 8-OH

Compounds (XXIX—XXXI) are best obtained via (XXVI—XXVIII); their synthesis via (XXIII—XXV) requires additional purification, since the products are always contaminated with the corresponding deoxyvasicinones (XXVI—XXVIII).

Among all the phenolic compounds obtained (XXVIII) and (XXXI) possess weak phenolic properties and are extracted by organic solvents from alkaline solution. This is apparently due to the existence of an intramolecular hydrogen bond of the phenolic hydroxyl with the nitrogen.

To elucidate the link between the structure of quinazolines and their physiological action, we obtained a number of carbamates of (XXXI) (XXXII—XXXIV).



XXXII. $R_1 = R_2 = CH_3$
XXXIII. R_1 = H, $R_2 = CH_2-CH_3$
XXXIV. R_1 = H, $R_2 = (CH_2)_3CH_3$

We determined the physicochemical constants of all the compounds synthesized. The IR spectra of (XX—XXII) contain absorption bands in the 1500—1635 cm^{-1} region that are characteristic for the double bond (—N=C, C=C) of a quinazoline nucleus, and the band of the amide carbonyl appears at 1665—1680 cm^{-1} [9]. A broad band in the 3000-3200 cm^{-1} region in the spectra of compounds (XXVIII) and (XXXI) shows the presence of an intramolecular hydrogen bond.

In the mass spectra of compounds (XX—XXII and XXVI—XXVIII) the main peaks are those of the M^+ ions while in the case of compounds (XXIII—XXV and XXIX—XXXI) they are the $(M - 1)^+$ peaks. A detailed discussion of the mass spectra of the compounds obtained will be given in a separate paper.

On comparing the PMR spectra of (I) and (XX—XXII) (in $CDCl_3$), it can be seen that the presence of a methoxy substituent in the aromatic ring affects the chemical shifts and multiplicities of the aromatic protons while having almost no influence on the methylene protons in positions 9-11. Because of the existence of ortho and para effects in (XX) and (XXII), the signal of the proton at C-5 shifts upfield by 0.55-0.75 ppm. In the case of (XXI), almost no influence of the methoxy group is observed.

Alkaloid	OCH_3	C-5	C-9	C-10	C-11
DOV (I)		8,12 dd	3,07 t	2,18 m	4,08 t
6-OCH_3DOV(XX)	3,84 s	7,44 dd	3,08 t	2,27 m	4,13 t
7-OCH_3DOV(XXI)	3,81 s	8,03 d	3,07 t	2,21 m	4,09 t
8-OCH_3DOV(XXII)	3,88 s	7,65 dd	3,11 t	2,18 m	4,07 t

EXPERIMENTAL

Mass spectra were recorded on MKh-1303 instrument, IR spectra on a UR-10 spectrometer, and NMR spectra on a JNM-4H-100/100 MHz instrument with HMDS as internal standard. The elementary compositions of the compounds obtained were determined with the aid of MKh-1310 high-resolution mass spectrometer [20]. The homogeneity of the compounds obtained was checked by thin-layer chromatography in the following systems: chloroform—methanol (9:1) (1), and (4:1) (2) and toluene—acetone—methanol—ammonia (41.5:49.5:4)* (system 3), the adsorbent being type KSK SiO_2.

4-Methoxyisonitrosoacetanilide was obtained by the method of Bachman and Picha [11], mp 181-182°C.

5-Methoxyisatin (VII). With stirring, 10 g of 4-methoxyisonitrosoacetanilide was added in portions to 40 ml of 90% H_2SO_4 at 65°C. Stirring was continued at 70°C for 30 min, and then the mixture was cooled to 30°C and was poured onto 600 g of crushed ice. After an hour, the deposit was filtered off with suction, washed three times with ice water, dried in the air, and crystallized from glacial acetic acid; mp 200-201°C (according to the literature [11]: 200—201°C); yield 6.2 g (67.7%).

2-Methoxyisonitrosoacetanilide (VI) was obtained by Pietra's method [14]; mp 147-148°C.

7-Methoxyisatin (VIII). With stirring, 10 g of 2-methoxyisonitrosoacetanilide was added in portions to 40 ml of 90% H_2SO_4 at 70°C. Stirring was continued at 85°C for 30 min. After the working up procedure described above, 1.5 g of (VIII) was obtained. Recrystallization from glacial acetic acid yielded 0.8 g of pure product with an amber color; mp 238-240°C (according to the literature [17]: 240-242°C).

5-Methoxy-2-nitrotoluene (XIII) was obtained by a literature method; mp 54-56°C.

2-Acetamido-5-methoxytoluene (XV). A solution of 10 g of (XIII) in 360 ml of ethanol was treated with 66.5 g of $SnCl_2 \cdot 2H_2O$ in 210 ml of concentrated HCl. The mixture was boiled under reflux on the water bath for 6 h. Then the solution was cooled and the ethanol was driven off under reduced pressure, after which the residue was made alkaline with 20% KOH and was extracted with chloroform. The chloroform solution was dried (Na_2SO_4) and filtered, and the solvent was evaporated off. A light yellow oil (6.5 g) remained. To this were added 10 ml of acetic anhydride and 2 ml of pyridine and the mixture was heated on the water bath for 2 h. After cooling, the reaction product was diluted with chloroform (200 ml), and the chloroform solution was washed with water (3 × 50 ml), dried (Na_2SO_4), filtered, and evaporated. The residue crystallized on standing; mp 145—146°C; yield 5.5 g.

3-Methoxy-2-nitrotoluene (XIV) was obtained by the method of Kuffner et al. [3]; mp 84—86°C (according to the literature [13a]: 88—89°C).

2-Acetamido-3-methoxytoluene (XVI) was obtained in a similar manner to (XV); mp 165—167°C (according to the literature [13b]: 167—168°C).

5-Methoxyanthranilic Acid (IX). A. With stirring, 3 ml of 30% H_2O_2 was added dropwise to 2 g of crude 5-methoxyisatin in 20 ml of 5% NaOH. The reaction took place with spontaneous heating and foaming. After cooling, the reaction mixture was acidified with 10% HCl to an acid reaction and was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in ethanol, and the solution was filtered and diluted with ether, which led to the deposition of 0.7 g of the hydrochloride. Another 0.2 g was obtained from the mother liquor. The product was recrystallized from ethanol—ether (1:2), the melting point of the hydrochloride of (IX) being 213-214°C. This was converted into the free (IX) by alkalinization with 1% NaOH to pH 6.5—7. The acid was filtered off and purified by sublimation; mp 150—151°C (according to the literature [11]: 151°C).

B. Crude 2-acetamido-5-methoxytoluene (XV) (5 g) was suspended in 300 ml of water, 10 g of $KMnO_4$ was added, and the mixture was heated on the water bath until the solution was completely decolorized, and then another 10 g of $KMnO_4$ was added and heating was continued until this was decolorized. After cooling, the mixture was filtered, the filtrate was evaporated to small bulk, and the residue was cooled with ice and acidified with cold concentrated HCl. This led to the deposition of 3.5 g of a white precipitate. The crude product was suspended in 15 ml of concentrated HCl and the mixture was heated under reflux on the steam bath for 2 h. On cooling, acicular crystals deposited; yield 2.1 g; mp 213—214°C; a mixture with the hydrochloride of (IX) obtained previously gave no depression of the melting point.

3-Methoxyanthranilic Acid (X). A. A solution of 0.8 g of (VIII) in 10 ml of 5% NaOH was oxidized with 1.5 ml of 30% H_2O_2 in a similar manner to (VII). This gave 0.35 g of the

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hydrochloride of (X) with mp 202–203°C.

B. To 10 g of crude (XVI) was added 670 ml of water, and it was oxidized with $KMnO_4$ as described for (XV). This gave 4.5 g of 2-acetamido-3-methoxybenzoic acid. This was saponified with 35 ml of concentrated HCl by heating in the steam bath for 2 h. On cooling, the solution deposited prismatic crystals of the hydrochloride of (X) with mp 197–199°C, which were converted into (X) in a similar manner to that described above, the melting point of the (X) being 170°C (according to the literature [13c]: 170–171°C), identical according to a mixed melting point with the (X) obtained from 7-methoxyisatin.

4-Methoxy-2-nitrotoluene (XVII) was synthesized by the method of Southwick and Casanova [2], a faintly yellow oil being obtained.

2-Acetamido-4-methoxytoluene (XVIII). A solution of 133 g of $SnCl_2 \cdot 2H_2O$ in 720 ml of concentrated HCl was added to a solution of 20 g of 4-methoxy-2-nitrotoluene in 720 ml of ethanol, and the mixture was heated on the boiling water bath for 6 h. Then the ethanol and the acid were evaporated off to small bulk, and the crystals that deposited were separated off, treated with 10% KOH, and extracted with chloroform. The filtrate was also made alkaline and extracted with chloroform. The chloroform extracts were combined and the solvent was driven off. The residue was recrystallized; mp 46°C; yield 14.6 g.

The 2-amino-4-methoxytoluene obtained (10 g) was heated with 20 ml of acetic anhydride and 3 ml of pyridine on the boiling water bath for 2 h, and then the excess of acetic anhydride was eliminated and the residue was diluted with chloroform. The chloroform solution was washed three times with water and dried (Na_2SO_4), and the solvent was driven off. The residue was recrystallized; yield 10 g; mp 92-93°C.

4-Methoxyanthranilic Acid (XIX). The crude 2-acetamido-4-methoxytoluene (8.5 g) was suspended in 570 ml of water, and 17 g of $KMnO_4$ was added. The experiment was then continued as in the preparation of (IX). This gave 6.5 g of precipitate. Then 45 ml of concentrated HCl was added to the crude product and the mixture was heated on the steam bath for 2 h. On cooling, it deposited acicular crystals of the hydrochloride of (XIX); yield 1.3 g; mp 178–180°C.

6-Methoxydeoxyvasicinone (XX). A mixture of 3.2 g of the hydrochloride of (IX) and 2.2 g of α-pyrrolidone was treated with 8 ml of $POCl_3$ and heated on the boiling bath for 1 h. After cooling, it was decomposed with 10 ml of H_2O, made alkaline with 25% NH_4OH and extracted with chloroform. The chloroform solution was dried with Na_2SO_4, filtered, and evaporated. The residue was recrystallized from hexane; mp 110°C; yield 1.75 g (50%); TLC – systems 1 and 2. Mol. wt. 216 (mass-spectrometrically).

7-Methoxydeoxyvasicinone (XXI) was obtained similarly with mp 176–177°C from benzene–hexane (1:2); yield 70%; TLC – systems 1 and 2. Mol. wt. 216 (mass-spectrometrically).

8-Methoxydeoxyvasicinone (XXII). A. Obtained by the method described above; mp 155–156°C [from benzene–hexane (1:2)]; yield 55%; mol. wt. 216 (mass-spectrometrically).

B. With stirring, 5 ml of freshly distilled $SOCl_2$ was added dropwise to 4 g of α-pyrrolidone cooled with ice. After the vigorous reaction had died down, the mixture was left at room temperature for 2 h. Then 4.2 g of (X) was added and the mixture was heated on the boiling water bath for 1 h.

The reaction product was isolated as described above. Its melting point and a mixed melting point with (XXII) were 155–156°C; yield 3.85 g (72%).

6-Methoxydeoxypeganine (XXIII). A solution of 1 g of (XX) in 15 ml of 10% HCl was treated with 1.5 g of zinc dust, and the mixture was heated on the boiling water bath for 2 h. Then the hot solution was filtered. On cooling it deposited the hydrochloride of (XXIII), which was filtered off with suction, washed with acetone and dried. Then it was recrystallized from ethanol; mp 237–239°C; yield 0.9 g; TLC – system 3.

7-Methoxydeoxypeganine (XXIV) was obtained similarly; melting point of the hydrochloride 240–242°C (decomp.); TLC – system 3.

8-Methoxydeoxypeganine (XXV) was obtained similarly; melting point of the hydrochloride 205–206°C; TLC – system 3.

6-Hydroxydeoxyvasicinone (XXVI). A solution of 1 g of (XX) in 40 ml of 47% HBr was boiled under reflux in an oil bath at 120–125°C for 5 h. After cooling, it was made alkaline with 10% KOH, and the alkaline solution was washed with ether and was then saturated with NH_4Cl and extracted further with ether (2 × 100 ml). After the solvent had been driven off, the residue was divided into two parts. To the first was added ethanolic HCl, which gave the hydrochloride, with mp 260—262°C (decomp.), and to the second was added 40% KBr, giving the hydrobromide, with mp 294—295° (according to the literature [6]: 295°C).

7-Hydroxydeoxyvasicinone (XXVII) was obtained by a similar method from (XII); mp of the hydrochloride 252—254°C (decomp.); TLC — systems 2 and 3.

8-Hydroxydeoxyvasicinone (XXVIII) was obtained by a similar method from (XXII); mp 149—150°C; TLC — systems 2 and 3.

The Hydroxydeoxypeganines (XXIX—XXXI) were obtained by demethylation from (XXIII—XXV) in a similar manner to that described above. The products were purified by recrystallization of the hydrochlorides from ethanol. Melting point of the hydrochloride of (XXIX) 262°C (decomp.). Melting point of the hydrochloride of (XXX) 270—272°C (decomp.). Melting point of (XXXI) 159—160°C. Melting point of the hydrochloride of (XXXI) 295—296°C (decomp.); TLC — system 3.

By reduction with zinc dust in hydrochloric acid, (XXVI—XXVIII) gave products identical with (XXIX—XXXI) according to mixed melting points and TLC in system 3.

8-Hydroxydeoxypeganine Dimethylcarbamate (XXXII). With heating, 0.4 g of (XXXI) was dissolved in 10 ml of 5% NaOH, and 50 ml of a 10% solution of phosgene in toluene was added. The mixture was heated with stirring in the water bath at 50°C for 2 h. After cooling, the organic layer was separated off and the aqueous layer was treated with 10 ml of a 30% solution of dimethylamine. The mixture was left overnight. Tabular crystals deposited, with mp 159—162°C; yield 50 mg; TLC — system 3.

8-Hydroxydeoxypeganine Ethylcarbamate (XXXIII). Two drops of freshly distilled triethylamine was added to a suspension of 0.1 g of (XXXI) in 15 ml of absolute benzene. Then, with stirring, 10 ml of a 5% solution of ethyl isocyanate in absolute benzene was added dropwise. The mixture was heated under reflux on the water bath at 50—60°C for 2 h and was left overnight. Tabular crystals deposited with mp 184—187°C; yield 40 mg; TLC — system 3.

8-Hydroxydeoxypeganine butylcarbamate (XXXIV) was obtained from (XXXI) in a manner similar to that described above; mp 77°C; TLC — system 3.

SUMMARY

1. 3-Methoxy-, 4-methoxy-, and 5-methoxyanthranilic acids have been synthesized.

2. The 6-, 7-, and 8-monomethoxy-substituted analogs of deoxyvasicinone and of deoxypeganine, the 6-, 7-, and 8-monohydroxy-substituted analogs of deoxyvasicinone and of deoxypeganine, and also the dimethyl-, ethyl-, and butylcarbamoyl derivatives of 8-hydroxypeganine have been obtained.

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DEOXYDELSOLINE AND DIHYDROMONTICAMINE FROM *Aconitum monticola*

É. F. Ametova, M. S. Yunusov, and V. A. Tel'nov

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The epigeal part of *Aconitum monticola* Steinb. has yielded two C_{18} diterpene alkaloids which, on the basis of the results of a study of NMR, IR, and mass spectra, and also of chemical transitions, have been shown to be identical with synthetic deoxydelsoline and dihydromonticamine. This is the first time that these alkaloids have been found in a plant.

Continuing the separation of the total alkaloids from the epigeal part of *Aconitum monticola* Steinb. [1, 2], in addition to known alkaloids — songorine, songorine N-oxide [1], songoramine, norsongoramine, monticamine, monticoline [2], and delsoline [4, 5] — we have isolated two new bases. Base (I) had the composition $C_{22}H_{35}NO_5$, mp 156–157°C. Its IR spectrum contained the broad absorption band of hydroxy group in the 3300–3600 cm^{-1} region with two maxima at 3335 and 3550 cm^{-1}. The PMR spectrum, taken in pyridine, showed the following signals (ppm); 0.92 (t, 3 H, $N{-}CH_2{-}CH_3$), 3.14 and 32.8 (singlets, 3 H each, OCH_3); 3.75 (triplet, 1 H, C_{14}-βH).

The mass spectrum of the base is characteristic for the lycoctonine alkaloids with C_1-αOH, showing the following ion peaks: M^+ 393 (13%), M — 17 (100%), M — 15 (28%), M — 31 (2%), M — 33 (20%).

The facts given, and also a direct comparison of the base with the dihydromonticamine obtained by the reduction of monticamine [2] showed their identity. This is the first time that dihydromonticamine has been found in a plant.

Base (II) had the composition $C_{25}H_{41}NO_6$, mp 134–135°C. Its IR spectrum contained absorption bands of hydroxy groups at 3400 and 3550 cm^{-1}. The NMR spectrum taken in $CDCl_3$ showed signals due to the protons of four methoxy groups at 3.10, 3.12, 3.30, and 3.16 ppm (three-proton singlets, 4 OCH_3) and one-proton triplets at 1.41 ppm ($N{-}CH_2{-}CH_3$) and 3.48 ppm (J = 5 Hz; due to the β-proton at C_{14}). The mass spectrum of the base contained the following ion peaks: M^+ 451 (45%), M — 15 (100%), M — 31 (97%), M — 33 (93%). When the base was oxidized with potassium permanganate in an aqueous acetone medium, an oxo compound $C_{25}H_{39}NO_7$ (III) with mol. wt. 465, containing a lactam carbonyl in a six-membered ring (ν_{max} 1640 cm^{-1}) was obtained. The oxidation of (III) with periodic acid yielded a product (IV), the UV spectrum of which ($\lambda_{mas}^{C_2H_5OH}$ 225, 325 mμ; log ε 4.04, 2.57) was practically identical with that of dehydromethoxyoxosecodelphatine [3]. The IR spectrum of the product obtained — with a strong absorption band at 1160 cm^{-1} having additional weak splitting and a

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 504-507, July-August, 1982. Original article submitted September 4, 1981.

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