## ALKALOIDS OF PETILIUM EDUARDI

R. Shakirov, R. N. Nuriddinov, and S. Yu. Yunusov

Khimiya Prirodnykh Soedinenii, Vol. 1, No. 6, pp. 384-392, 1965.

The epigeal part of Petilium eduardi (a.Rgl.) Vved., collected in the initial flowering stage in the surroundings of Shargun (Gissar range) contains 1.1% of a mixture of alkaloids, and that collected at Babatag contains 1.25%. From the fraction of the total soluble in ether (isolated from <u>P. eduardi gathered</u> in the Shargun region) we have obtained the alkaloid imperialine [1, 2] and a new alkaloid edpetilidine,  $C_{27}H_{45}O_2N$  [3]. Edpetilidine is a tertiary base. Three Cmethyl groups have been found in this alkaloid, but it contains no N-methyl group. It gives crystalline hydrochloride, hydrobromide, hydriodide, and methiodide.

The IR spectrum of the base exhibits absorption bands characteristic for a hydroxy group (3425 cm<sup>-1</sup>), and C-methyl group (2925 and 1455 cm<sup>-1</sup>). It lacks absorption frequencies corresponding to carbonyl groups, ether linkages, and water of hydration. Consequently, the two oxygen atoms in the base must be present in the form of hydroxyl groups. The mixture of bases from the mother liquors of imperialine and edpetilidine was separated with respect to solubility in petroleum ether. The fraction soluble in petroleum ether gave eduardine,  $C_{27}H_{43}O_2N$  [3]. This base was also isolated in the form of the hydrochloride from the fraction of bases soluble in ether.

Eduardine is a tetiary base containing no N-methyl group and not forming crystalline salts. The IR spectrum of the base exhibits absorption frequencies characteristic for hydroxyl ( $3530 \text{ cm}^{-1}$ ), carbonyl ( $1700 \text{ cm}^{-1}$ ), and C-methyl groups (1450, 2930 cm<sup>-1</sup>). Of the two oxygen atoms, one is present in the form of a hydroxyl group and the other in the form of a carbonyl group.

On separating the chloroform fraction of the total alkaloids with respect to solubility and basicity, we isolated edpetiline, with the composition  $C_{33}H_{53}O_8N$  [3, 5, 6].

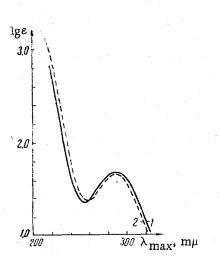
The ethereal fraction of the total alkaloids from <u>P. eduardi</u> collected in Babatag gave imperialine. The alkaloids remaining in the mother liquor were separated with respect to the solubility of their hydrochlorides in chloroform. From their soluble fraction a mixture of crystals was isolated, the separation of which gave eduardine.

A new alkaloid with mp 269-271°C ( $C_{27}H_{45}O_2N$ ) was isolated from the eduardine mother liquors; we have called it <u>edpetilidinine</u>. It readily forms hydrochloride and hydrobromide salts. The IR spectrum of the base lacks absorption bands for a carbonyl group, an ether group, and water of hydration; it exhibits absorption bands characteristic for hydroxyl (3425 cm<sup>-1</sup>) and C-methyl (1465, 2930 cm<sup>-1</sup>) groups. Thus, the two oxygen atoms in edpetilidinine are present in the form of hydroxyl groups. The mother liquor from eduardine and edpetilidinine gave, when treated with hydrochloric acid, a hydrochloride with mp 250-252°C, which yielded a base with mp 267-269°C [ $\alpha$ ]<sub>D</sub> -44.62° ( $C_{27}H_{43}O_4N$ ). The base, which is secondary, gives some highly crystalline salts, an acetyl derivative, an oxime, and a N methyl derivative. The composition and properties of the alkaloid and its salts and derivatives agree well with those for peimisine [7], which shows their identity.

The mother liquors from the hydrochloride yielded a base with mp  $228-231^{\circ}$ C (C<sub>27</sub>H<sub>41</sub>O<sub>3</sub>N), identified as imperialone [1]. From the chloroform fraction of the total bases edpetiline, C<sub>33</sub>H<sub>33</sub>O<sub>8</sub>N, was isolated. This base forms a poorly crystallizing hydrochloride, hydrobromide, hydriodide, oxime, and tetraacetyl derivative. The UV spectrum of edpetiline is very similar to the UV spectrum of imperialine (figure). However, the spectrum of edpetiline in the near IR region differs strongly from that of imperialine and has broad intense absorption bands (1140 and 1000 cm<sup>-1</sup>) characteristic of the hydroxyl groups of glucoalkaloids. The similarity of the curves and absorption maxima in the UV spectra of edpetiline forms an amino alcohol with mp 265-266°C,  $[\alpha]_D$  -34.01°, and a neutral substance. The properties of this base are identical with those of imperialine. The neutral substance readily reduces silver oxide forming a silver mirror, which shows the presence of an aldose in this substance.

Since a comparison of the empirical formulas of edpetiline and imperialine show a difference of  $C_6H_{10}O_5$  it may be assumed that a monosaccharide is liberated on hydrolysis. To confirm this, the neutral substance was chromatographed on paper with a reference sample of D-glucose by the radial and the ascending methods [8]. The same R<sub>f</sub> values were found for the neutral substance and for glucose. Moreover, the neutral substance gave an osazone identical with an authentic sample of D glucose osazone [9].

As is well known, an osazone with mp 207-208 °C can be formed from glucose, fructose, and mannose. However, the Rf values found for the neutral substance correspond only to that of glucose. Consequently, the second hydrolysis product is glucose. The structure of the amino alcohol imperialine has been studied by many investigators, but the most probable structure for this alkaloid is that proposed by Chu and his coworkers. [1, 2, 10].



UV spectra of 1) imperialine and 2) edpetiline.

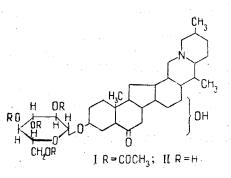
Imperialine has a modified steroid structure, and contains two hydroxyl groups and one carbonyl group. The secondary hydroxyl group undergoes acetylation but the teritary does not. The secondary hydroxyl group is located on the third carbon atom but the position of the teritary hydroxyl group has not been established.

In edpetiline, the glucose is attached to the secondary hydroxyl group, which is confirmed by the production of a tetraacetyl derivative of edpetiline. In these circumstances, the hydroxyl groups of the carbohydrate part of the molecule are acetylated and the tertiary hydroxyl group in the aglucone moiety of the edpetiline molecule, which is incapable of acetylation, remains unaffected.

Determination of the difference in the molecular rotations of edpetiline and imperialine has shown that glucose is attached to the imperialine by a  $\beta$ -glycosidic bond [11, 12].

To confirm the structure of edpetiline, imperialine was condensed with tetraacetylbromoglucose. From the reaction products a crystalline base was isolated with mp 224-226 °C, identical with the tetraacetyledpetiline (I) [3, 5] obtained from natural edpetiline.

On saponification with alcoholic alkali, the tetraacetyl derivative gave a crystalline base with mp 272-276°C corresponding to edpetiline (II) [3]. This was confirmed by a comparison of their IR and UV spectra and R<sub>f</sub> values.



## Experimental

Isolation of the total alkaloids. 14 kg of the epigeal part of the plant <u>P. eduardi</u> collected in the region of Shargun was extracted with chloroform in a continuous process. The chloroform solution was concentrated, washed with water, and treated with 5% sulfuric acid.

The acid solution, after washing with ether, was treated with ammonia, and the free alkaloids were extracted with ether (122.37 g), and chloroform (22.68 g).

The aqueous washing solution was treated with 5% sulfuric acid to an acid reaction and was then washed with ether, made alkaline with 25% ammonia, and extracted with chloroform. This gave 9.01 g of a mixture of alkaloids. The total yield of the mixture was 154.06 g, or 1.1% of the weight of the dry plant.

Separation of the mixture of alkaloids. On treatment with acetone, 122.37 g of the total bases obtained from the ethereal fraction gave 26.08 g of a mixture of crystalline bases with mp 210-232°C which, when separated into fractions by fractional recrystallization from acetone, gave 15.98 g of a base with mp 265-266°C and crude edpetilidine with mp 216-222°C.

A mixture of a sample of the crystals having mp 265-266°C with imperialine melted at 265-266°C. This base and imperialine both gave  $R_f$  0.80 on paper chromatography in the butanol-acetic acid-water (4:1:5) system.

82 g of the mother liquor from imperialine and edpetillidine was dissolved in 200 ml of 5% sulfuric acid, and, with cooling, the solution was made alkaline with 25% ammonia. The alkaline solution deposited a voluminous precipitate of alkaloids, which were extracted with petroleum ether and ether; evaporation of the petroleum ether solution gave

0.31 g of crude eduardine with mp 232-242°C.

The ethereal extract was evaporated until the appearance of turbidity. After separation of the precipitate, the ethereal solution was evaporated under vacuum. The resulting white powder (58 g) was dissolved in 5% hydrochloric acid with cooling and was exhaustively extracted with chloroform.

The acidic solution was made alkaline with 25% ammonia and the alkaloids were extracted with ether. The residue from the ethereal solution was treated with acetone; 1.5 g of imperialine was deposited.

The acidic chloroform extract was made alkaline with 25% ammonia and evaporated under vacuum. The resulting white solid powder, on treatment with acetone, gave 1.4 g of crude eduardine with mp 232-242°C.

From 9.01 g of the chloroform fraction of the total alkaloids extracted from the wash water was obtained 1.5 g of crude edpetiline with mp 259-265 °C (from methanol).

22.68 g of the chloroform fraction of the total alkaloids was separated with respect to basicity. For this purpose, the material was dissolved in 40 ml of 1 N sulfuric acid and the solution was made alkaline with 5-ml portions of 1 N caustic potash. Each fraction was extracted with chloroform. Eight fractions were obtained. The seventh and eighth fractions gave 0.5 g of crude edpetiline (from acetone). The extraction of the alkaloids from 7.2 kg of the epigeal part of <u>P. eduardi</u> collected in Babatag was carried out in the same way as from the epigeal part of <u>P. eduardi</u> gathered in Shargun.

The wash water gave 4 g of total alkaloids and the chloroform fraction 5.4 g. Concentration of the ethereal part gave 37.76 g of crude imperialine which, after recrystallization from methyl alcohol, had mp 265-266°C. The mixture of bases from the mother liquor from the imperialine amounted to 43.44 g. The total yield of combined alkaloids was 90.60 g, or 1.25% of the weight of the dry plant.

The mixture of alkaloids (43.44 g) was dissolved with cooling in 5% hydrochloric acid and the solution was exhaustively extracted with chloroform. The acid solution was made alkaline with 25% ammonia and the alkaloids were extracted with ether. The residue of the ethereal extract gave another 8 g of crude imperialine (from acetone).

The solid residue obtained from the chloroform extract of the acid solution, after being made alkaline with 25% ammonia, evaporation, and treatment with acetone, gave 2.65 g of a mixture of crystals with mp 225-236°C, from which 1.22 g of eduardine and 0.69 g of edpetilidinine were isolated by fractional recrystallization from alcohol.

The eduardine mother liquor after the separation of the edpetilidinine was evaporated. The residue was dried under vacuum and dissolved in acetone, and the solution was treated with an alcoholic solution of hydrochloric acid. This gave 1.28 g of the crystalline hydrochloride of peimisine with mp 245-248°C. After recrystallization from a mixture of acetone and methyl alcohol, the peimisine hydrochloride melted at 250-252°C.

The mother liquor from the peimisine hydrochloride was evaporated to dryness, dissolved in chloroform, and decomposed with ammonia, and the chloroform was distilled off. The solid residue gave 0.6 g of base with mp 221-224°C (from acetone).

A mixture of 15.71 g of the base from the eduardine and edpetilidinine mother liquors was dissolved in a small amount of chloroform and separated into fractions by extraction with 5% sulfuric acid. The 17 fractions of the acid solutions obtained were individually made alkaline with 10% ammonia and exhaustively extracted with chloroform. The residue from the 5th-8th fractions, after distilling off the chloroform, yielded 0.2 g of a crystalline base 8 with mp 252-257°C (from acetone), which, after three recrystallizations from a mixture of acetone and methyl alcohol (9 : 1) had mp 253-257°C.

The chloroform fraction of the total alkaloids of <u>P. eduardi</u> was separated under the same conditions as the chloroform fraction of the total alkaloids from the P. eduardi collected in Shargun. This yielded 4.4 g of edpetiline.

Edpetilidine. The crude edpetilidine with mp 216-222°C was recrystallized from methyl alcohol and then had mp 227-228°C was recrystallized from methyl alcohol and then had mp 227-228°C,  $[\alpha]_D = 48.19^\circ$  (c 2.234; pyridine). Rf 0.85 (butanol saturated with 5% acetic acid).

Found, %: C 77.3; 77.2; H 10.8; 10.9; N 3.37; 3.48. Calculated for C<sub>27</sub>H<sub>45</sub>O<sub>2</sub>N, %: C 78.01; H 10.91; N 3.37.

Hydrochloride. On being mixed with an alcoholic solution of hydrogen chloride, an acetone solution of edpetilidine formed a hydrochloride with mp 283-285°C (from acetone).

Found, %: C1 7.95; 7.98. Calculated for C27H45O2N HCL %: Cl 7.85.

<u>Hydrobromide</u>. The action of hydrobromic acid on an acetone solution of edpetilidine gave the hydrobromide with mp 270-272°C (from acetone).

Hydriodide. The addition of hydriodic acid to an acetone solution of edpetilidine gave the hydriodide, mp 262-263°C (from acetone).

Nitrate. The treatment of edpetilidine with 10% nitric acid gave the nitrate with mp 225°C (decomp., from water).

Found, %: N 5.73; 5.93. Calculated for C<sub>27</sub>H<sub>45</sub>O<sub>2</sub>N · HNO<sub>3</sub>, %: N 5.85.

Methiodide. A mixture of 0.9 g of edpetilidine, 70 ml of methyl alcohol, and 15 ml of methyl iodide was boiled on a water bath for 4 hours. When the solution was concentrated under vacuum, crystals with mp 292-294°C (from methanol) were deposited.

Found, %: I 21.99, 22.44. Calculated for C<sub>27</sub>H<sub>45</sub>O<sub>2</sub>N · CH<sub>3</sub>I, %: I 22.76.

Eduardine. The crude eduardine with mp 232-242°C was recrystallized from ethyl alcohol and then had mp 247-251°C,  $[\alpha]_D = 53.02°$  (c 0.977; methanol), Rf 0.83 (butanol saturated with 5% acetic acid).

Found, %: C 78.3; H 10.7; N 3.44; 3.46. Calculated for C<sub>27</sub>H<sub>43</sub>O<sub>2</sub>N, %: C 78.39; H 10.47; N 3.38.

Peimisine. The peimisine was recrystallized from methyl alcohol: mp 267-269°C,  $[\alpha]_D - 44.62°$  (c 0.986; ethyl alcohol).

Found, %: C 73.9; 74.0; H 9.78; 9.85. N 3.19; 3.24; equiv. 449.1. Calculated for C<sub>27</sub>H<sub>43</sub>O<sub>4</sub>N, %: C 72.76; H 9.72; N 3.14; equiv. 445.6.

Hydrochloride. On mixing with an alcoholic solution of hydrogen chloride, an acetone solution of peimisine formed a hydrochloride with mp 250-252°C, [from acetone – methyl alcohol (: 1)].

Found, %: Cl 7.53; 7.25. Calculated for C<sub>27</sub>H<sub>43</sub>O<sub>4</sub>N · HCl, %: Cl 7.36.

<u>Hydrobromide</u>. The addition of hydrobromic acid to an acetone solution of peimisine gave the hydrobromide with mp 257-259°C [from a mixture of acetone and methyl alcohol (1: 1)].

Hydriodide. Peimisine was dissolved in acetone and the solution was mixed with hydriodic acid; the crystals obtained had mp 254-256°C (from acetone).

Nitrate. The action of nitric acid on an acetone solution of peimisine gave the nitrate with mp 230-232°C (from acetone).

Found, %: N 5.66; 5.56. Calculated for C<sub>27</sub>H<sub>43</sub>O<sub>4</sub>N · HNO<sub>3</sub>, %: N 5.50.

Acetylation of peimisine. A mixture of 0.2 g of the base, 3 ml of dry pyridine, and 2 ml of acetic anhydride was left for 2 days at room temperature. After the pyridine had been distilled off under vacuum the residue was dissolved in ether and washed with 2% sulfuric acid. The ethereal solution was extracted with 10% ammonia and washed with water. The concentrated ethereal solution deposited 0.12 g of crystals with mp 224-227°C; after purfication from a mixture of ether and acetone (9 : 1) they had mp 238-240°C.

<u>Methylation of peimisine</u>. A mixture of 0.1 g of peimisine, 0.2 ml of formalin, and 0.1 ml of formic acid was heated for 4 hours. The reaction product was dissolved in 1% hydrochloric acid, and the solution was washed with ether, made alkaline with 10% caustic potash, and extracted with ether. On trituration with acetone, the residue formed crystals with mp 238-240°C. A mixture with peimisine melted at 211-232°C.

<u>Peimisine oxime</u>. A mixture of 0.1 g of the base, 30 mg of hydroxylamine hydrochloride, 80 mg of sodium acetate, and 6 ml of 65% alcohol was heated for 6 hr. The alcohol was distilled off under vacuum and the residue was dissolved in 5% sulfuric acid and washed with chloroform. The acid solution was made alkaline with ammonia and extracted with chloroform. The residue after the evaporation of the chloroform was recrystallized from a mixture of acetone and water (1:1), mp 190-191°C.

Found, %: N 5.78; 5.77. Calculated for C<sub>27</sub>H<sub>44</sub>O<sub>4</sub>N<sub>2</sub>, %: N 6.07.

Hydrochloride of the oxime. With an alcoholic solution of hydrogen chloride, an acetone solution of peimisine oxime gave a hydrochloride with mp 254°C (decomp., from acetone).

Imperialone. After recrystallization from acetone, the base with mp 221-224°C had mp 228-231°C. A mixture of this with imperialone gave no depression of the melting point.

Found, %: C 75.7 75.3; H 10.01; 9.86; N 3.24, 3.24, 3.17; equiv. 426.7. Calculated for C<sub>27</sub>H<sub>41</sub>O<sub>3</sub>N, %: C 75.8; H 9.66; N 3.27; equiv. 426.7.

Edpetilidinine. Fractional recrystallization of the mixture of crystalline bases with mp 225-236°C gave eduardine. The alcoholic mother liquor from eduardine, after concentration, gave edpetilidinine, which, after recrystallization from

methyl alcohol, alcohol, had mp 269-271°C,  $[\alpha]_D$  + 42.48 (c 0.306; alcohol). Rf 0.82 [butanol-acetic acid-water (4: 1: 5)].

Found, %: C 77.45; 77.45. H 10.84; 10.91 N 3.36; 3.44. Calculated for C<sub>27</sub>H<sub>45</sub>O<sub>2</sub>N, %: C 78.01; H 10.91; N 3.37.

The hydrochloride of edpetilidinine with mp 283°C (decomp) and the hydrobromide with mp 281-282° were obtained under the conditions described for the hydrochloride and hydrobromide of edpetilidine.

Found, %: Cl 7.87, 7.65. Calculated for C<sub>27</sub>H<sub>45</sub>O<sub>2</sub>N · HCl, %: C1 7.85.

Edpetiline. The recrystallization of crude edpetiline with mp 259-265 °C from methyl alcohol raised the mp to 272-276 °C,  $[\alpha]_D = 57.89$  (c 0.449; methyl alcohol),  $R_f 0.86$  [butanol – acetic acid – water (4 : 1 : 5)].

Found, %: C 66.8; 66.7 H 9.26; 9.41; N 2.39; 2.53. Calculated for C<sub>33</sub>H<sub>53</sub>O<sub>8</sub>N, %: C 66.9; H 9.02; N 2.36.

<u>Hydrochloride</u>. A solution of 0.02 g of the base in 0.5 ml of alcohol was treated with an alcoholic solution of hydrogen chloride to neutrality. The resulting solution was evaporated under vacuum and the residue was recrystallized from acetone. The hydrochloride softened at  $205^{\circ}$ C and melted at  $220^{\circ}$ C.

Found, %: C1 5.87; 5.62. Calculated for C<sub>33</sub>H<sub>53</sub>O<sub>8</sub>N · HCL, % Cl 5.65,

The hydrobromide and hydriodide of edpetiline were formed by the reaction of the corresponding acids on the base. These salts were obtained and purfied as for the hydrochloride. The hydrobromide softened at 208°C and melted at 226°C and the hydriodide at 195°C and 228°C respectively.

Edpetiline oxime. A mixture of 0.16 g of the base, 0.16 g of hydroxylamine hydrochloride, and 0.5 g of sodium acetate in 16 ml of 65% alcohol was heated for 6 hr. The alcohol was distilled off under vacuum. The residue was mixed with 100 ml of 2% sulfuric acid, washed with chloroform, and made alkaline with sodium carbonate solution. The reaction product was extracted with chloroform. The residue after the distillation of the chloroform was recrystallized from a mixture of alcohol and water (1: 2) and then from acetone. The crystals softenened at 226°C and melted at 259-262°C (decomp.).

Found, %: N 4.87; 4.73. Calculated for C<sub>33</sub>H<sub>54</sub>O<sub>8</sub>N<sub>2</sub>, %: N 4.61.

<u>Hydrolysis of edpetiline</u>. A solution of 0.25 g of the base in 10 ml of 10% sulfuric acid was heated for 10 hr. The acidic solution was treated with sodium acetate solution and extracted with ether. The residue after the distillation of the either (0.17 g) was recrystallized from methanol, mp 265-266°C,  $[\alpha]_D - 34.01^\circ$  (c 1.47, chloroform). A mixture of these crystals with imperialine melted at 265-266°C.

On ascending paper chromatography in the butan-1-o1 – acetic acid – water (4:1:5) system, the base isolated gave a spot with the same  $R_f$  value as a reference sample of imperialine (0.80). The detection agent was Dragendorff's solution.

The alkaline solution after the separation of the imperialine was neutralized with 1% sulfuric acid and evaporated to dryness. The dry residue was washed repeatedly with absolute alcohol. The alcoholic solution was evaporated. This yielded an oily neutral product which, in ascending paper chromatography in the acetone – butan-1-ol – water (7: 2: 1) system, gave a spot with the same Rf value as a reference sample of D-glucose (0.37) after 3 hr. On radial paper chromatography in the acetone – butan-1-ol – water (7: 2: 1) system, the neutral product and glucose gave the same Rf value (0.26). The detection agene was O-toluidine.

Osazone. A mixture of 4 ml of an aqueous solution of the neutral product, 0.16 g of phenylhydrazine hydrochloride, and 0.27 g of sodium acetate was heated for 1 hr on a water bath. The yellow crystals which were deposited had mp 207-208°C after recrystallization from alcohol. A mixture of these crystals with the osazone of D-glucose melted at 207-208°C.

Tetraacetyledpetiline (from natural edpetiline). A mixture of 0.5 g of the base, 7 ml of dry pyridine, and 10 ml of acetic anhydride was left for 5 days at room temperature. The pyridine was distilled off under vacuum and the residue was dissolved in 2% sulfuric acid. With cooling, the acid solution was made alkaline with 5% sodium carbonate solution, and the reaction product was extracted with ether. The concentrated ethereal solution containing traces of pyridine cry-stallized on evaporation under vacuum. Yield 0.7 g. The acetyl derivative, after recrystallization from a mixture of acetone and ether (1:5), had mp 224-226°C.

Found, %: C 63.9; 64.1; H 8.13; 7.96; equiv. 757.5. Calculated for C<sub>41</sub>H<sub>61</sub>O<sub>12</sub>N, %: C 64.8; H 8.07; equiv. 759.89.

The saponification products of tetraacetyledpetiline were found to contain 3.70, 3.73 mole of CH<sub>3</sub>COOH.

<u>Tetraacetyledpetiline (synthetic)</u>. With the constant passage of a gentle current of nitrogen, a three-necked roundbottomed flask was charged with 2 g of imperialine in 400 ml of absolute benzene and 2.9 g of freshly-prepared silver acetate. Over 1 hr, 100 ml of a 6% benzene solution of tetraacetylbromo-D-glucose was added in drops to the boiling mixture. Benzene was slowly distilled off from the reaction mixture to remove water. The amount of benzene in the flask was kept constant by the addition of fresh portions of dry benzene. Boiling of the reaction mixture and distillation of the benzene were continued for 4 hr. Then the benzene solution was separated from the silver salts by filtration and concentrated under vacuum.

The residue was dissolved with cooling in 100 ml of 2% sulfuric acid, and the solution was washed with ether, made alkaline with a solution of sodium carbonate, and extracted with ether. When the ethereal solution was concentrated, imperialine was deposited (0.99 g). The ethereal mother liquor, on concentration, gave crystals with mp 220-222°C, which, after recrystallization from a mixture of acetone and ether (1:5), had mp 224-226°C (I). A mixture of these crystals with tetraacetyledpetiline melted at 224-226°C. Yield 0.2 g. The mother liquor from the tetraacetyledpetiline after the elim ination of the solvent, formed 1.05 g of an amorphous product.

Production of edpetiline. a. A mixture of 0.12 g of substance (I) and 20 ml of a 10% methanolic solution of caustic potash was heated for 2 hours. The residue after distilling off the methanol was dissolved in 5% sulfuric acid with cooling. The acidic solution was made alkaline with ammonia, and the base was extracted with chloroform. The residue from the distillation of the chloroform crystallized on treatment with methanol, mp 272-276°C (methanol). A mixture with natural edpetiline melted at 272-276°C. UV spectrum (in alcohol):  $\lambda_{max}$  290 mµ (log  $\varepsilon$  1.7).

Found, %: C 66.2 66.0; H 9.06; 9.01; N 2.35; 2.35. Calculated for C<sub>33</sub>H<sub>53</sub>O<sub>8</sub>N, %: C 66.9; H 9.02; N 2.36.

b. 1.05 g of the mother liquor from the tetraacetyledpetiline was saponified under the same conditions as substance (I). The saponification products were extracted from the alkaline solution with ether and chlorofrom. The residue from the ethereal solution, on treatment with acetone, gave 0.35 g of imperialine, and the residue from the chloroform solution, on treatment with mathanol gave 0.25 g of edpetiline.

## Summary

1. Imperialine, imperialone, peimisine, and the new alkaloids edpetiline, eduardine, edpetilidine, and edpetilidinine have been isolated from the epigeal part of P. eduardi.

2. The hydrolysis of edpetiline has given D-glucose and imperialine.

3. The structural formula of edpetiline has been established by the condensation of imperialine with tetraacetylbromoglucose.

## REFERENCES

1. H.G. Boit, Ber., 87, 472, 1954; 90, 723, 1957.

2. T. T. Chu and J. Lon, Acta Chim. Sin., 21, 401, 241, 1955; 22, 210, 1956.

3. R. Shakirov, R. N. Nuriddinov, and S. Yu. Yunusov, DAN UZSSR, 9, 23, 1963.

4. V. M. Belikov, Usp. khim., 21, 496, 195.

5. R. Shakirov, R. N. Nuriddinov, and S. Yu. Yunusov, Uzb. khim. zh., 1, 38, 1965.

6. R. Shakirov, R. N. Nuriddinov, and S. Yu. Yunusov, DAN SSSR, 161, 3, 620, 1965.

7. T.Q. Chau, C.A. 7677, 1947.

8. I. M. Hais and K. Macek, Paper Chromatography [Russian translation], Moscow, 271, 1962.

9. A. N. Belozerskii and N. I. Poskuryakov, Practical Handbook of Plant Biochemistry [in Russian], Moscow, 12, 1951.

10. RZhKhim., 17 zh, 359, 1964.

11. W. Klyne, Biochem. J., 47, 1950.

12. J. Stanek, Chem. and Ind., 488, 1956.

2 July 1965

Institute of the Chemistry of Plant Substances AS Uzbek SSR