SUMMARY

1. The oxidation of cembrene with chromium trioxide in aqueous sulfuric acid (the Jones reagent) and in aqueous acetone has given norcembra-2,7,11-trien-4-one, norsolanadione, (3E, 8E)-5-isopropyl-8-methyltrideca-3,8-diene-2,12-dione, and five new compounds the structures of which have been established on the basis of their spectra.

2. Oxidation with chromium trioxide in aqueous acetone, in contrast to oxidation with the Jones reagent, takes place stereospecifically—the $C_{11}-C_{12}$ double bond of cembrene is not affected.

LITERATURE CITED

1. A. J. Haagen-Smit, T. N. Wang, and N. T. Mirov, J. Am. Pharm. Assoc., 40, 557 (1951).
2. N. T. Mirov and P. M. Iloff, J. Am. Pharm. Assoc., 44, 425 (1955).
3. P. M. Iloff and N. T. Mirov, J. Am. Pharm. Assoc., 45, 77 (1956).
4. V. A. Pentegova, O. Motl, and V. Herout, Collection Czech. Chem. Commun., 26, 1362 (1961).
5. A. I. Lisina, Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 3, 120 (1962).
6. M. A. Chirkova, Author's Abstract of Candidate's Dissertation, Novosibirsk (1962).
7. W. G. Dauben, E. F. Thiessen, and P. R. Resnick, J. Am. Chem. Soc., 84, 2015 (1962).
8. H. Kobayashi and S. Akiyoshi, Bull. Chem. Soc. Japan, 36, 823 (1963).
9. V. A. Raldugin, A. I. Rezvukhin, and V. A. Pentegova, Khim. Prirodn. Soedin., 553 (1971).
10. W. G. Dauben, J. Agric. Food Chem., 22, 154 (1974).
11. V. A. Raldugin, N. K. Kashtanova, and V. A. Pentegova, Khim. Prirodn. Soedin., 604 (1971).
12. V. A. Raldugin and V. A. Pentegova, Khim. Prirodn. Soedin., 174 (1976).
13. D. L. Roberts and R. L. Rowland, J. Org. Chem., 27, 3989 (1962).
14. J. L. Courtney and S. McDonald, Tetrahedron Lett., 459 (1967).
15. R. R. Johnson and J. A. Nicholson, J. Org. Chem., 30, 2918 (1965).
16. K. B. Wiberg, in: Oxidation in Organic Chemistry (ed. K. B. Wiberg), Academic Press, New York, Part A (1965), p. 69.
17. W. Waters, Mechanisms of Oxidation of Organic Compounds, Methuen, London/Wiley, New York (1964).

ALKALOIDS OF Haplophyllum perforatum

V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov

UDC 547.944/945

We are studying for the first time the alkaloids of the epigeal part of the plant Haplophyllum perforatum growing in the Dzhungarian Ala-Tau, Kazakh SSR. The plant, collected in the flowering period, was extracted with methanol. The methanolic extract was separated into acid, neutral, and basic fractions. From the basic fraction, comprising 0.32% of the weight of the dry plant, we obtained evoxine (I) [1], and the new alkaloids glycoperine (II) [2], and methylevoxine (III) [3], and from a neutral fraction the lignane eudesmin, the known alkaloids flindersine (IV) [4] and 7-isopentenyloxy-γ-fagarine (V) [5], and a new base—haplamine (VI) [6], which proved to be the main component (0.143% of the dry weight of the plant) of the mixture of bases. No alkaloids were found in the acid fraction. The total amount of bases obtained was 0.48% of the weight of the dry plant, and of these 1/3 was represented by the alkaloids isolated from the neutral fraction of the extract. Thus, the combined alkaloids of this plant can be evaluated both qualitatively and quantitatively only after separation of the basic and the neutral fractions of the extract.

Of the substances isolated, only evoxine and the lignane eudesmin had been obtained from this plant previously [7, 8]. Furthermore, we did not detect skimmianine, which is present in the plant H. perforatum

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 320-328, May-June, 1976. Original article submitted July 1, 1975.

growing in Babatage [9] and in the Kitab region of the Kashkadar'ya oblast [7]. The combined alkaloids of H. perforatum from different growth sites are completely different, which is a convincing example of the dependence of the qualitative and quantitative compositions of the alkaloids of plants of one species on the growth site [10].

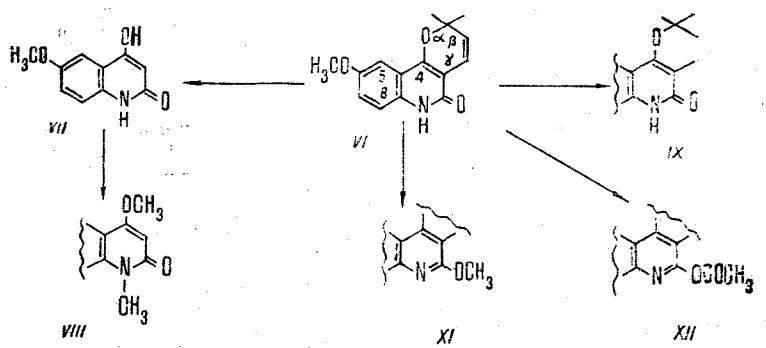
Since doubt has been expressed in the literature concerning the native nature of evoxine [11], we extracted the alkaloids without the use of an acid. However, as in the case of methanolic extraction, we obtained (I). These facts show that evoxine is a natural alkaloid and not an artefact.

We have previously proposed for haplamine the structure of 6-methoxyflindersine (VI) on the basis of the spectral characteristics of the alkaloid and of its decomposition product (VII) [6]. The latter was synthesized from p-anisidine and diethyl malonate by a known method [12]. According to TLC and its melting point and IR spectrum, the synthetic 4-hydroxy-6-methoxy-2-quinolone was identical with substance (VII). Their O,N-dimethyl derivatives (VIII) also gave no depression of the melting point. Thus, it was shown that the methoxy group in haplamine is present in position 6.

The presence of an α,α-dimethylpyran ring was confirmed by the formation of a dihydro derivative (IX) (Scheme 1), the spectral characteristics of which are close to those of dihydroflindersine (X). In the NMR spectrum of (IX) (Fig. 1), as in the spectrum of (X) [13], in place of the signals of olefinic protons two two-proton triplets are observed at 7.53 and 8.32 ppm (J = 6.5 Hz), which is typical for the protons of the γ- and β-methylene groups of an α,α-dimethyldihydropyran ring [14]. The other signals observed in the NMR spectrum of haplamine [6] are retained in the spectrum of (IX). Under the conditions of mass spectrometry, the molecular ion of dihydrohaplamine with m/e 259 decomposes with the formation of the stable ions $(M-43)^+$, $(M-55)^+$, and $(M-56)^+$, which is characteristic for substances containing an α,α-dimethyldihydropyran ring unsubstituted in the β position [15]. The IR spectra of haplamine taken in an KBr tablet and in chloroform solution show a strong absorption band at 1660 cm^{-1} (amide carbonyl) and a weak maximum at 3155 cm^{-1} (NH group). Consequently, haplamine has the lactam structure both in the crystalline state and in solution. The considerable displacement in the low-frequency direction of the absorption band of the NH group, which is typical for cyclic amides [16] is due to strong intermolecular hydrogen bonds, which are retained in solutions in solvents of low polarity [17].

The methylation of haplamine with methyl iodide formed not a N-methyl derivative, as in the case of flindersine [18], but an O-methyl derivative (XI), mol. wt. 271 (mass spectrometry) (see Scheme 1), the IR spectrum of which lacked the absorption band of an amide carbonyl. On this basis, structure (XI) was proposed for the methylation product, and this was confirmed by its partial synthesis from haplamine. The action of phosphoric trichloride on haplamine formed the 2-chloro derivative, the treatment of which with sodium methoxide yielded 2-O-methylhaplamine, identical with the product of the methylation of haplamine according to its melting point, TLC, and IR spectrum.

Like flindersine [18], haplamine is not acetylated under the usual conditions. When compound (VI) was heated with acetic anhydride in the presence of p-toluenesulfonic acid, the 2-O-acetyl derivative (XII) was obtained (see Scheme 1), as was shown by the presence in the IR spectrum of (XII) of an absorption band at 1765 cm^{-1} corresponding to the characteristic vibrations of a $Ar-OCOCH_3$ group. In the NMR spectrum of 2-O-acetylhaplamine (Fig. 2), the protons of the benzene ring appear in the form of sharp signals at (ppm) 2.40 (doublet, 1 H, J_{ortho} = 9 Hz–H-8); 2.92 (quadruplet, 1 H, J_{ortho} = 9 Hz, J_{meta} = 3 Hz–H-7); and 3.32 (doublet, 1 H, J_{meta} = 3 Hz–H-5). These facts show that the signal in the weak field does not always refer to H-5 [13].



Scheme 1. Transformations of haplamine (VI).

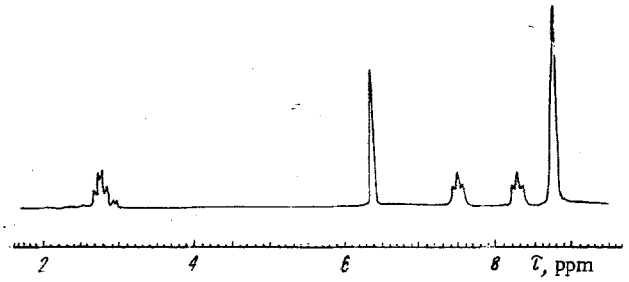


Fig. 1. NMR spectrum of dihydrohaplamine (IX) (CF_3COOH).

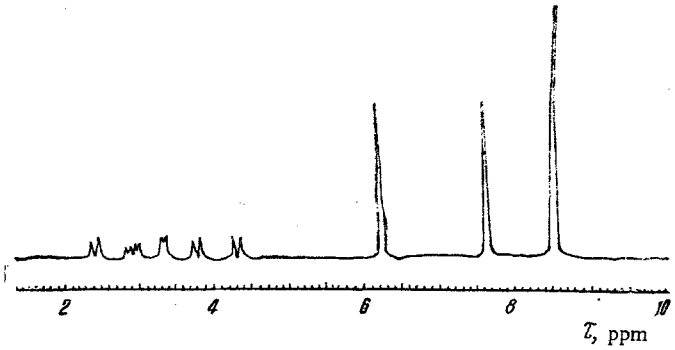
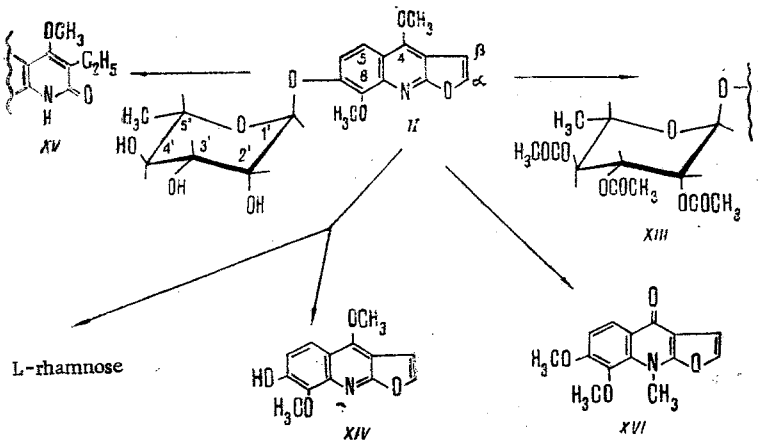


Fig. 2. NMR spectrum of 2-O-acetylhaplamine (XII) (CCl_4).

Such an assignment is correct only in those cases where an alkoxy substituent is present in position 7 or 8, but not 6. The other signals in the spectrum of (XII) are observed at (ppm) 3.73 and 4.26 (doublets, 1 H each, J=10 Hz, C–CH=CH–C), 6.25, 7.63, and 8.60 [singlets, 3 H, 3H, and 6 H, respectively– $OCH_3 \cdot ArOCOCH_3$ and $C(CH_3)_2$].

On the basis of the spectral characteristics of glycoperine and its triacetyl derivative (XIII), the acid hydrolysis of (II) to L-rhamnose and haplopine (XIV), and also a determination of the configuration of the glycosidic bond by means of Klyne's rule, the structure of 4,8-dimethoxyfuranoquinoline 7-α-L-rhamnopyranoside has previously been proposed for the base, and this has been confirmed by the partial synthesis of (XIII) [2]. The saponification of (XIII) by Zemplén's method [19] gave glycoperine.

Like other alkaloids of the dictamnine series, on Adams reduction glycoperine gives a tetrahydro derivative (XV) (Scheme 2), mol. wt. 395 (mass spectrometry). When (II) was methylated with methyl iodide and sodium hydride in dimethyl sulfoxide [20], isoskimmianine (XVI) was obtained in place of the expected trimethoxy derivative (see Scheme 2).



Scheme 2. Transformations of glycoperine (II).

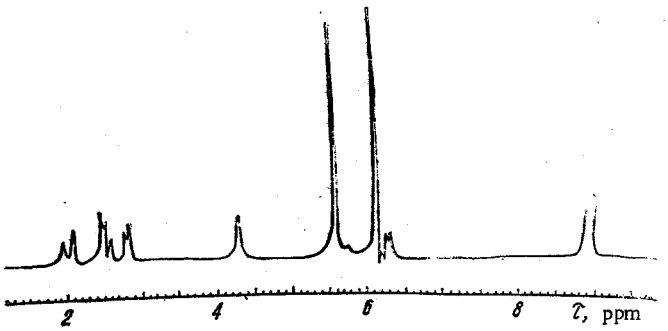


Fig. 3. NMR spectrum of glycoperine (II) (CF_3COOH).

In the NMR spectrum of glycoperine (Fig. 3), the signal of the proton at the anomeric center appears at 4.36 ppm in the form of a slightly broadened singlet the half-width of which is 3.3 Hz. This shows the equatorial position of the protons at C-1' and C-2'. Consequently, in the glycoperine molecule the α-L-rhamnose is present in the 1C conformation [21].

On the basis of the facts given above, structure (II) has been established for glycoperine.

The new alkaloid methylevoxine (III) was isolated from the mother liquors obtained after the separation of glycoperine and evoxine. From a comparative study of the spectra of methylevoxine and evoxine and of methylevoxine and its acetyl derivative, and from the production of haplopine when (III) was fused with alkali, the structure of methylevoxine has been established as 4,8-dimethoxy-7-(2'-hydroxy-3'-methoxy-3'-methylbutyloxy)furanoquinoline [3].

EXPERIMENTAL

The homogeneity of the substances was established by chromatography in a thin layer of silica gel in the toluene–ethyl acetate–formic acid (5:4:1) and benzene–methanol (4:1) systems. The UV spectra were taken on a Hitachi spectrometer, the IR spectra on a UR-10 instrument (tablets with KBr), the mass spectra on an MKh-1303 mass spectrometer, and the NMR spectra on a JNM-4H-100/100-MHz instrument, the τ scale being used.

Isolation of the Combined Alkaloids. The comminuted epigeal part of the plant (13 kg) was treated with methanol until the alkaloids had been extracted completely. The concentrated methanolic extract was diluted with water, acidified with 10% sulfuric acid, and extracted with chloroform (A). After the acid solution had been made alkaline with ammonia, the alkaloids were extracted with ether (6.5 g) and chloroform (9.7 g) (basic fraction). The concentrated chloroform solution (A) was shaken with 10% acid (C) and then with a 4% solution of sodium hydroxide. Distillation of the chloroform yielded the neutral fraction. When the acid solution (C) was made alkaline, a precipitate deposited (19 g) (basic fraction). The alkaloids were extracted from the alkaline solution with ether (3.57 g) and chloroform (3.21 g) (basic fraction). The total weight of the basic fraction was 41.98 g (0.32% of the weight of the dry plant).

Separation of the Basic Fraction. The precipitate (19 g) was crystallized from methanol (1:25). This gave 6.3 g of glycoperine with mp 221-222°C. Treatment of the mother solution with acetone led to the separation of more glycoperine (1.6 g). The concentrated acetone solution deposited crystals (5.61 g) of evoxine with mp 154-155°C. The mother solution (3.5 g) was chromatographed on alumina. The chloroformic eluates yielded methylevoxine (0.5 g), the chloroform-methanolic eluates yielded evoxine (0.71 g), and the methanolic extracts yielded glycoperine (0.49 g). The combined ether-soluble and chloroform-soluble alkaloids (basic fraction), by separation according to solubility in acetone and methanol, evoxine (2.06 g) and glycoperine (2.59 g) were obtained. A total of 10.98 g of glycoperine (0.084% of the weight of the dry plant), 8.38 g of evoxine (0.064%), and 0.5 g of methylevoxine (0.005%) were obtained.

Separation of the Neutral Fraction. The neutral fraction was separated according to its solubility in acetone. The acetone-soluble fraction, containing alkaloids, was dried and treated with ether. The ethereal solution in the cold deposited crystals (9.2 g) of eudesmin, mp 107-108°C (methanol and acetone). The ethereal mother liquor was treated with petroleum ether. The concentrated petroleum ether solution deposited crystals (2.46 g) of haplamine. The mother solution was chromatographed on alumina. Ethereal eluates yielded 7-isopentenyloxy-γ-fagarine (0.26 g), eudesmin (0.11 g), flindersine (1.96 g), and haplamine (0.53 g). The

petroleum-ether-insoluble fraction yielded haplamine (15.65 g) by treatment with ether. The neutral fraction yielded a total of 18.64 g of haplamine (0.143% of the weight of the dry plant), 9.31 g of eudesmin (0.07%), 1.96 g of flindersine (0.015%), and 0.26 g of 7-isopentenyloxy-γ-fagarine (0.002%).

Acetone Extraction. An acetone extract of the epigeal part of the plant (600 g) was filtered and concentrated. From the residue (50 g) by column chromatography on alumina using gradient elution (hexane, petroleum ether, diethyl ether, chloroform, ethanol), haplamine (0.51 g), evoxine (0.29 g), and glycoperine (0.03 g) were isolated.

Flindersine (IV) formed colorless needles with mp 185-186°C (decomp; ethanol).

Dihydroflindersine (X) had mp 228-229°C (ethanol). The spectral characteristics of (IV) and (X) coincided with those published in the literature [13, 18, 22].

Haplamine (VI) formed slightly yellowish crystals with mp 201-202°C (decomp; ethanol). Found, %: N 5.80; OCH_3 11.99. $C_{15}H_{15}NO_3$. Calculated, %: N 5.45; OCH_3 12.45.

Dihydrohaplamine (IX). In ethanolic solution (40 ml), 0.5 g of haplamine was hydrogenated over a platinum catalyst for 12 h. The concentrated filtrate deposited crystals of (IX) (0.49 g), mp 231-232°C. IR spectrum: 1650, 3155 cm^{-1} (NHCO group). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 216.5; 233; 278; 287; 334 (log ε 4, 48; 4.51; 3.92; 3.89; 3.91); λ_{min} 222; 262.5; 283; 299 nm (log ε 4.46; 3.62; 3.87; 3.21).

Cleavage of Haplamine. A mixture of carefully ground haplamine (0.5 g) in 30% caustic potash solution (25 ml) was boiled for 8 h in such a way that about 10 ml of distillate was obtained per hour. The volume of the reaction mixture was kept constant by the addition of water. When the alkaline filtrate was acidified with concentrated hydrochloric acid, a precipitate of (VII) (0.23 g) with mp 317-320°C (glacial acetic acid) was formed. IR spectrum, cm^{-1}: 1668 (amide carbonyl), 2800-3200 (NH and OH). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 232, 275, 284, 337 nm (log ε 4; 44; 3.68; 3.59; 3.54); λ_{min} 260, 281, 297 nm (log ε 3.46; 3.58; 2.68). Mass spectrum: m/e (%) 191 (M, 100), 176 (42), 149 (20), 134 (36), 106 (36).

Methylation of Compound (VII). With vigorous shaking, four 10-ml portions of dimethyl sulfate and 1.7 ml of 20% caustic soda were added over an hour to a solution of (VII) (0.2 g) in 1 ml of 10% caustic soda, and then 1 ml of 20% caustic soda was added and the mixture was heated on the water bath for 30 min. It was then extracted with chloroform. The residue after the distillation of the solvent was crystallized from benzene–petroleum ether, mp 144-145°C. The yield of (VIII) was 0.07 g. IR spectrum: 1635 cm^{-1}. UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 232, 273, 282, 341 nm (log ε 4.64: 3.85; 3.82; 3.80). Mass spectrum, m/e (%): 219 (M, 100), 204 (84).

Synthesis of 4-Hydroxy-6-methoxy-2-quinolone (VII). Ethyl Ester of the p-Anisidide of Malonic Acid. A solution of p-anisidine (10 g) in malonic ester (100 ml) was heated at 190°C for 1 h. After the excess of malonic ester had been distilled off under vacuum, the residue was diluted with ethanol and then with water until a turbidity appeared and it was then cooled. Crystals of the ethyl ester of the p-anisidide of malonic acid deposited (7.1 g), mp 76-77°C (ether). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 253 nm (log ε 4.20). Mass spectrum, m/e (%): 237 (M, 100), 149 (67), 123 (86), 108 (78).

p-Anisidide of Malonic Acid. A mixture of the ethyl ester of the p-anisidide of malonic acid (6.3 g) in 10% caustic soda solution (63 ml) was heated on the water bath until the solid had dissolved completely. When the solution was acidified with concentrated hydrochloric acid, a precipitate of malonic acid p-anisidide deposited (3.78 g), mp 150-151°C (water). IR spectrum, cm^{-1}: 1670 (NHCO), 1720 (COOH), 3330 (NH and OH). NMR spectrum (CF_3COOH), ppm: 2.93 and 3.30 (doublets, 2 H each, two pairs of ortho aromatic protons), 6.46 (singlet, 3 H, OCH_3), 6.56 (singlet, 2 H, $COCH_2CO$).

4-Hydroxy-6-Methoxy-2-Quinolone (VII). Malonic acid p-anisidide (1.7 g) was added to polyphosphoric acid (10 g, d 2.2) heated to 130-135°C. Cyclization was performed at 135°C for 30 min. On cooling, the water-diluted reaction mixture deposited a precipitate which was washed with sodium bicarbonate solution. The yield of (VII) was 0.47 g, mp 317-320°C (glacial acetic acid).

4,6-Dimethoxy-1-methyl-2-quinolone (VIII) was obtained from the synthesized 4-hydroxy-6-methoxy-2-quinolone (0.28 g) under the conditions described for the preparation of the O,N-dimethyl derivative of the product of the alkaline cleavage of heplamine. Yield 0.09 g, mp 145-146°C (benzene–petroleum ether).

2-O-Methylhaplamine (XI). A mixture of haplamine (0.25 g), methyl iodide (3 ml), and anhydrous potassium carbonate (3 g) in dry acetone (50 ml) was boiled for 40 h. The residue obtained after the distillation of the solvent from the filtrate was chromatographed on alumina. The first ethereal eluates yielded 0.05 g of (XI) with mp 94-95°C (benzene–petroleum ether). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 223, 243, 257, 266, 325 nm (log ε 4.38; 4.32; 4.30; 4.27; 3.89). NMR spectrum (CCl_4), ppm: 2.54 (quadruplet, 1 H, J_{ortho} = 8.5 Hz, J_{para} = 1 Hz–H-8); 2.92 (broadened singlet, 1 H–H-5); 2.97 (quadruplet, 1 H, J_{ortho} = 8.5 Hz, J_{meta} = 2.5 Hz–H-7); 3.49 and 4.60 (two doublets, 1 H each, J = 10 Hz–C–CH = CH–C); 6.06 and 6.18 (singlets, 3 H each–2 OCH_3); 8.52 ppm [singlet, 6 H–$C(CH_3)_2$]. Mass spectrum, m/e (%): 271 (M, 39), 256 (100).

Synthesis of 2-O-Methylhaplamine. The 2-Chloro Derivative of Haplamine. A solution of haplamine (0.5 g) in phosphoric trichloride (10 ml) was heated on the water bath for 2 h, cooled, neutralized with ammonia, and extracted with chloroform. The residue after the solvent had been distilled off was chromatographed on alumina. The first ethereal eluates gave the 2-chloro derivative of haplamine (0.3 g), mp 111-112°C (ether). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ 245, 267, 277, 327 nm (log ε 4.38; 4.41; 4.49; 3, 74). Mass spectrum, m/e (%): 275 (M, 23), 260 (100).

2-O-Methylhaplamine (XI). A solution of the 2-chloro derivative of haplamine (0.2 g) in abs. methanol was mixed with a solution of sodium methoxide (0.2 g of sodium in 4 ml of methanol) and the mixture was boiled for 1 h. Then it was diluted with water and extracted with ether. The residue was chromatographed on alumina. The first benzene eluates yielded 0.02 g of (XI), mp 94-95°C.

2-O-Acetylhaplamine (XII). A mixture of haplamine (0.2 g), acetic anhydride (10 ml), and p-toluenesulfonic acid (0.03 g) was heated on the water bath for 3 h, and the mixture was cooled with ice, made alkaline with sodium carbonate, and extracted with ether. The residue after the distillation of the solvent was chromatographed on alumina. The first ethereal eluates gave 0.03 g of (XII) in the form of an oil.

Glycoperine (II), colorless needles, mp 224-225°C (methanol), $[\alpha]_D$ –66.3° (c 2.32- pyridine). Found %: N 3.58. $C_{19}H_{21}NO_8$. Calculated, %: N 3.58.

Tetrahydroglycoperine (XV) was obtained by the reduction of glycoperine (0.1 g) under the conditions described above dihydrohaplamine. The yield of (XV) was 0.08 g, mp 218-219°C (methanol). Mass spectrum, m/e (%): 395 (M; 0.8); 249 (81), 234 (100), 220 (40), 219 (44).

Acetylation of Glycoperine. A mixture of glycoperine (0.1 g), acetic anhydride (2 ml), and pyridine (6 drops) was heated on the water bath for 1 h and was then evaporated. The residue (0.11 g) was crystallized from benzene–petroleum ether, mp 181-182°C, $[\alpha]_D$ –76, 2° (c 2.57; ethanol).

Acid Hydrolysis of Glycoperine. A mixture of 0.9 g of glycoperine and 30 ml of a 0.1 N solution of sulfuric acid was heated on the water bath for 6 h. The acid solution was washed with chloroform, and the distillation of the chloroform then gave 0.38 g of haplopine (XIV), mp 203-204°C (methanol). The acid hydrolyzate after neutralization with barium carbonate was evaporated, and the residue was chromatographed on cellulose. This gave 0.25 g of a substance in the form of an oil which was identified by TLC and by paper chromatography as L-rhamnose; p-nitrophenylhydrazone with mp 185-186°C, giving no depression of the melting point with a sample of L-rhamnose p-nitrophenylhydrazone.

Methylation of Glycoperine. Glycoperine (0.2 g) was methylated by Hakomori's method [20]. The residue was chromatographed on silica gel. Ethereal eluates yielded crystals (0.05 g), mp 187°C (ethanol–water) which gave no depression of the melting point with a sample of isoskimmianine. Their IR spectra were identical.

Synthesis of Glucoperine (II). A mixture of 2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl chloride (2.6 g), obtained from L-rhamnose, haplopine (1 g), and anhydrous potassium carbonate (6 g) was boiled in dry acetone for 40 h. The filtrate was evaporated and the residue was chromatographed on silica gel. The ethereal eluates yielded (XIII) (0.23 g) in the form of needles with mp 181-182°C (benzene–petroleum ether), $[\alpha]_D$ –75.3° (c 2.69; ethanol). A solution of (XIII) (0.18 g) in abs. methanol (1 ml) was mixed with a 2 N solution of sodium methoxide (0.05 ml) and the mixture was left in the cold for 24 h. The precipitate that had deposited was crystallized from methanol. The yield of (II) was 0.09 g, mp 224-225°C. It gave no depression of the melting point with glycoperine, and their IR spectra was identical.

Methylevoxine (III) crystallized out on long standing in the form of colorless needles with mp 55-56°C.

Fusion of Methylevoxine with Caustic Soda. A mixture of methylevoxine (0.15 g), caustic soda (0.3 g), and water (one drop) was heated at 160-180°C for 3 min and was then cooled and dissolved in water (5 ml). The aqueous solution was washed with ether, and after being acidified with concentrated hydrochloric acid it was made alkaline with ammonia and extracted with chloroform. The residue after the distillation of the solvent was chromatographed on alumina. The chloroform eluates yielded haplopine with mp 203-204°C.

Acetylation of Methylevoxine. A mixture of methylevoxine (0.15 g), acetic anhydride (3 ml), and pyridine (four drops) was heated on the water bath for 3 h and was then evaporated. The residue was chromatographed on alumina. The ethereal eluates yielded the acetyl derivative of methylevoxine in the form of an oil. Mass spectrum, m/e (%): 403 (M; 100), 245 (38), 227 (54), 216 (20), 202 (20), 201 (10), 199 (10), 159 (38), 127 (14), 99 (64), 73 (58).

SUMMARY

1. From the epigeal part of the plant H. perforatum growing in the Dzhungarian Ala-Tau we have isolated the lignane eudesmin, the known alkaloids evoxine, flindersine, and 7-isopentenyloxy-γ-fagarine, and the new alkaloids haplamine, glycoperine, and methylevoxine. It has been shown that haplamine has the structure of 6-methoxyflindersine, glycoperine the structure of 7-hydroxy-4,8-dimethoxyfuranoquinoline 7-O-α-L-rhamnopyranoside, and methylevoxine the structure of 4,8-dimethoxy-7-(2'-hydroxy-3'-methoxy-3'-methylbutoxy)furanoquinoline.

LITERATURE CITED

1. F. W. Eastwood, J. K. Hughes, and E. Ritchie, Aust. J. Chem., 7, 87 (1954).
2. V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 680 (1974).
3. V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 272 (1975).
4. V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 262 (1974).
5. I. A. Bessonova, V. I. Akhmedzhanova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 677 (1974).
6. V. I. Akhmedzhanova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 109 (1974).
7. S. Yu. Yunusov and G. P. Sidyakin, Dokl. Akad. Nauk UzSSR, No. 12, 15 (1950); Zh. Obshch. Khim., 22, 1055 (1952).
8. D. M. Razzakova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 665 (1972).
9. T. T. Shakirov, G. P. Sidyakin, and S. Yu. Yunusov, Dokl. Akad. Nauk UzSSR, No. 6, 28 (1959).
10. S. Yu. Yunusov, Izv. Akad. Nauk UzSSR, 4, 11 (1948); Khim. Prirodn. Soedin., 104 (1966).
11. D. L. Dreyer, J. Org. Chem., 35, 2420 (1970).
12. R. Storer and D. W. Young, Tetrahedron, 29, 1215 (1973).
13. A. V. Robertson, Aust. J. Chem., 16, 451 (1963).
14. Z. Sh. Faizutdinova, I. A. Bessonova, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 267 (1967).
15. A. P. Johnson, A. Pelter, and P. Stainton, J. Chem. Soc.(C), 192 (1966).
16. L. Bellamy, Advances in Infrared Group Frequencies, Methuen, London (1968).
17. Yu. N. Sheinker and Yu. I. Pomerantsev, Zh. Fiz. Khim., 30, 79 (1956).
18. R. F. C. Brown, J. J. Hobbs, J. K. Hughes, and E. Ritchie, Aust. J. Chem., 7, 348 (1954).
19. G. Zemplén and E. Pacsu, Ber., 62, 1613 (1929).
20. S. Hakomori, Biochem. (Tokyo), 55, 205 (1964).
21. N. K. Kochetkov, The Chemistry of the Carbohydrates [in Russian], Moscow (1967), p. 38.
22. D. Lavie, N. Danieli, R. Weitman, and E. Glotter, Tetrahedron, 24, 3011 (1968).