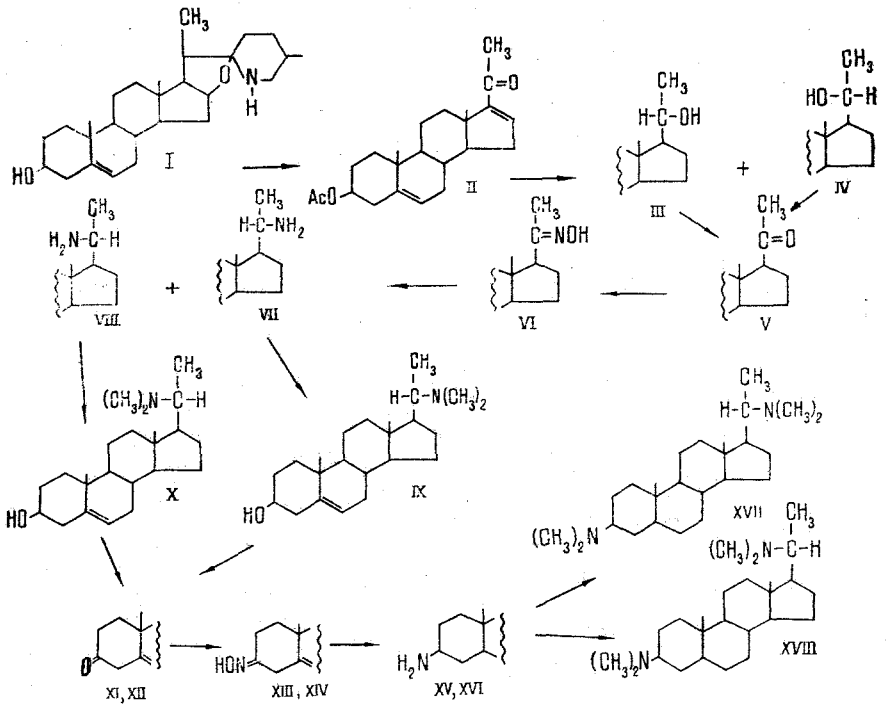

bands of a carbonyl group at 1680 cm^{-1}. The reduction with sodium in ethanol of the oxime (VI) obtained from (V) gave reaction products from which 20α-aminopregn-5-en-3β-ol (VII) and 20β-aminopregn-5-en-3β-ol (VIII) were isolated. The subsequent methylation of (VII) and (VIII) led to 20α-dimethylaminopregn-5-en-3β-ol (IX) and 20β-dimethylaminopregn-5-en-3β-ol (X).

Then compounds (IX) and (X) were oxidized by analogy with (III) and (IV); the oximes were obtained, and these were then reduced and subjected to Hess methylation. In this way the following compounds were obtained: 20α-dimethylaminopregn-5-en-3-one (XI), 20β-dimethylaminopregn-5-en-3-one (XII); the oximes of compounds (XI) and (XII) — (XIII) and (XIV), respectively; 3β-amino-20α-dimethylaminopregnane (XV), 3β-amino-20β-dimethylaminopregnane (XVI), 3β,20α-bisdimethylaminopregnane (XVII), and 3β-20β-bisdimethylaminopregnane (XVIII) [3] (Scheme). It must be mentioned that when the oximes (XIII) and (XIV) were reduced, the hydrogenation of the double bond at C_5–C_6 took place simultaneously, as was confirmed by the absence of a signal from an olefinic proton in their NMR spectra. The characteristics of the NMR spectra of compounds (I-IV, IX, X, XVII, and XVIII) are given below (chemical shifts, δ scale, ppm; s, singlet; d, doublet; m, multiplet):

	II	*III*	*IV*	*IX*	*X*	*XVII*	*XVIII*
18-CH_3, s	0,97	0,62	0,71	0,58	0,59	0,58	0,60
19-CH_3, s	1,02	0,97	0,98	0,75	0,74	0,70	0,71
21-CH_3, d		1,18	1,10	0,85	0,63	0,79	0,65
CH–OH, m		3,63	3,69	3,49	3,50		
$-O-CO-CH_3$, s	1,98	1,98	2,00				
$H_3C-CO-C=C$, s	2,21						
$HC-O-CO-CH_3$, m	4 57	4,53	4,54				
HC=C, m	6,65; 5,32	5 31	5,31	5,29	5,27		
$N(CH_3)_2$, s				2,10	2,06	2,28; 2,08	2,35; 2,06

On comparing the chemical shifts of the protons of the 18-CH_3 and 21-CH_3 groups in the NMR spectrum of (III) with those of (IV), a difference of 9 Hz in the chemical shifts of the C-18 methyl protons and of 8 Hz in those of the C-21 methyl protons is observed. This confirms the fact that (III) differs from (IV) by the configuration of the C_{20} asymmetric center.

When compounds (XVII) and (XVIII) were treated with methyl iodide, quaternary salts were obtained which possess physiological activity.

EXPERIMENTAL

The homogeneity of the substances was checked by chromatography in a thin layer of type G silica gel and alumina (activity grade II) in the following solvent systems: 1) cyclohexane–

ethyl acetate (10:3); 2) benzene–ether (3:1); 3) benzene–ether (4:1); 4) chloroform–ethanol–ammonia (1:1:0.25); 5) hexane–chloroform–ethanol–ammonia (10:5:7:0.35); 6) chloroform–ethanol (5:7).

The IR spectra were taken on a UR-20 spectrometer (KBr), the NMR spectra on a JNM-4H-100 MHz instrument (HMDS, $CDCl_3$, δ scale), and the mass spectra on a MKh-1303 instrument fitted with a system for direct introduction into the ion source. Molecular weights were determined mass-spectrometrically. Specific rotations were determined in chloroform.

3β-Acetoxypregna-5,16-dien-20-one (II) was obtained from 6 g of solasodine as described by Suvorov et al. [3], mp 171-173°C (ethanol), R_f 0.40 (system 1), M^+ 354. Yield 3.7 g.

3β-Acetoxypregn-5-en-20α-ol (III) and 3β-Acetoxypregn-5-en-20β-ol (IV). Under conditions similar to those described by Suvorov et al. [3], 3.4 g of (II) was hydrogenated in ethanol in the presence of Raney nickel. This gave a mixture of two substances. It was separated on a column of alumina (activity grade II) with elution by benzene–ether (2:1), 5-ml fractions being collected. Fractions 1-25 gave substance (III) with mp 146-148°C (ethanol), R_f 0.20 (system 2), yield 1.72 g. Fractions 26-45 gave substance (IV) with mp 156-158°C (ethanol), R_f 0.18 (system 2), yield 1.36 g; M^+ (III, IV) 358.

3β-Acetoxypregn-5-en-20-one (V). Compounds (III) (1.53 g) and (IV) (1.25 g) were oxidized by the method of Cerny et al. [8]. They both gave the same product, (V), with mp 135-137°C (ethanol), R_f 0.93 (system 2). Yield 2.51 g, M^+ 356.

Oxime of 3β-Acetoxypregn-5-en-20-one (VI). Using a method described in the literature [9],* 1.21 g of (V) yielded 1.25 g of the oxime (VI) with mp 187-189°C (ethanol), R_f 0.62 (system 3).

20α-Aminopregn-3-en-3β-ol (VII) and 20β-Aminopregn-5-en-3β-ol (VIII). The oxime (VI) (2.15 g) was reduced as described by Romanchenko et al. [4], giving the amine (VII) with R_f 0.34 (system 4), yield 0.97 g, and also the amine (VIII) with R_f 0.29 (system 4), yield 0.94 g.

20α-Dimethylaminopregn-5-en-3β-ol (IX) and 20β-Dimethylaminopregn-5-en-3β-ol (X). The amine (VII) (0.95 g) was methylated by the Hess method [9]*, and substance (IX) was isolated from the reaction products with mp 169-171°C (ethanol), $[\alpha]_D$ −25.7° (c 0.77), R_f 0.37 (system 5). Yield 0.93 g.

Similarly, 0.92 g of (VIII) gave substance (X) with mp 176-178°C (ethanol), $[\alpha]_D$ −23.3° (c 0.77), R_f 0.41 (system 5). Yield 0.91 g; M^+ 345 (IX, X).

20α-Dimethylaminopregn-5-en-3-one (XI) and 20β-Dimethylaminopregn-5-en-3-one (XII). In a similar manner to the preparation of (V), 0.92 g of (IX) yielded 0.79 g of the ketone (XI) with mp 191-193°C (ethanol), R_f 0.52, and 0.88 g of (X) yielded 0.77 g, of the ketone (XII) with mp 193-195°C (ethanol), R_f 0.55 (system 5).

Oxime of 20α-Dimethylaminopregn-5-en-3-one (XIII) and Oxime of 20β-Dimethylaminopregn-5-en-3-one (XIV). Compounds (XI) (0.74 g) and (XII) (0.75 g) were converted into the oximes by the method for preparing the oxime (VI). The following were isolated: from (IX) the oxime (XIII) with mp 243-245°C (ethanol), R_f 0.45, yield 0.61 g, and from (XII) the oxime (XIV) with mp 246-248°C (ethanol), R_f 0.48 (system 5), yield 0.60 g.

3β-Amino-20α-dimethylaminopregnane (XV) and 3β-Amino-20β-dimethylaminopregnane (XVI). By reduction under the conditions for the preparation of compounds (VII and VIII), 0.56 g of (XIII) and 0.58 g of (XIV) were converted into the amines (XV) with R_f 0.37 (yield 0.47 g), and (XVI) with R_f 0.45 (system 5), yield 0.43 g, respectively.

3β,20α-Bisdimethylaminopregnane (XVII) and 3β,20β-Bisdimethylaminopregnane (XVIII). Compounds (XV) (0.44 g) and (XVI) (0.39 g) were methylated as for the methylation of the amines (VII and VIII). This gave substance (XVII) with mp 118-120°C (ethanol), $[\alpha]_D$ +18.8° (c 0.86), R_f 0.27, yield 0.38 g, and (XVIII) with mp 123-125°C (ethanol), $[\alpha]_D$ +8.3° (c 0.86), R_f 0.30 (system 6), yield 0.35 g, M^+ 374 (XVII, XVIII).

Quaternary Salts of (XVII) and (XVIII). A solution of 0.37 g of (XVII) in 5 ml of benzene was treated with 0.4 ml of methyl iodide, and the mixture was boiled for 9 h. From the reaction products was isolated the quaternary salt of (XVII) with mp 295-297°C (ethanol), R_f 0.52 (system 4), yield 0.23 g. The corresponding quaternary salt was obtained from 0.31 g of (XVIII) by the same method. It melted at 291-293°C (ethanol), R_f 0.57 (system 4), yield 0.21 g.

*As in the Russian original – Publisher.

SUMMARY

Solasodine has been converted for the first time into 20α-dimethylaminopregn-5-en-3β-ol (IX) and 20β-dimethylaminopregn-5-en-3β-ol (X) and also into the known compounds 3β,20α-bis-dimethylaminopregnane (XVII) and 3β,20β-bisdimethylaminopregnane (XVIII). Quaternary salts of (XVII) and (XVIII) have been obtained.

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