LITERATURE CITED

1. K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prir. Soedin., 367 (1976).
2. K. Samikov, R. Shakirov, and S. Yu. Yunusov, Khim. Prir. Soedin., 673 (1977).
3. R. N. Nuriddinov and S. Yu. Yunusov, Khim. Prir. Soedin., 334 (1968).
4. R. N. Nuriddinov, A. I. Saidkhodzhaev, and S. Yu. Yunusov, Khim. Prir. Soedin., 333 (1968).
5. S. Ito, Y. Fukazawa, and M. Miyashita, Tetrahedron Lett., 36, 3161 (1976).
6. I. Fried, P. Grabowich, E. F. Sabo, and A. I. Cohen, Tetrahedron, 20, 2297 (1964).
7. M. L. Mihalovic, L. Lorens, M. Rogic, A. Melera, and M. Stefanovic, Tetrahedron, 22, 2345 (1966).
8. T. M. Moynehan, K. Schofield, R. A. V. Jones, and A. R. Katritsky, J. Chem. Soc., 2637 (1962).
9. F. Bohlmann, Chem. Ber., 91, 2157 (1958).

PHYTOCHEMICAL INVESTIGATION OF Datura innoxia

S. F. Aripova and S. Yu. Yunusov

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The alkaloids in the various organs of the plant Datura innoxia cultivated in the Darmina sovkhoz [collective farm], Chimkent province, Kazakh SSR, have been studied. Ten individual bases and two terpenoids were isolated. The percentages of the main alkaloids have been determined. It has been shown that the epigeal part of the plant can be used to obtain scopolamine hydrobromide.

The high physiological activity of the tropane alkaloids from plants of the genus Datura, family Solanaceae, is generally known. Thus, scopolamine hydrobromide – the main alkaloid of plants of this genus – is widely used in psychiatry, surgery, neurology, and opthalmic practice and as an antiemetic and tranquilizer for sea and air sickness as a component of Aeron tablets. Datura leaves are components of powders (Astmatal) and cigarettes (Astmatin) used in bronchial asthma [1].

Scopolamine hydrobromide is obtained from the seeds of D. innoxia cultivated in the Darmina sovkhoz [collective farm] (Chimkent province, Kazakh SSR) of Lekrasprom SSSR (All-Union Combine for the Production, Preparation, and Processing of Medicinal Plants of the USSR Ministry of the Medical Industry). In order to determine the possibility of using other organs of the plant for industrial purposes and to study its alkaloid composition, we have investigated the leaves, stems, and roots (in the budding and flowering period) and also the seeds (in the fruit-bearing period). The total alkaloids were extracted with chloroform from raw material previously wetted with dilute ammonia solution. After the appropriate working up, the following amounts of total alkaloids (% on the raw material) were obtained: from the leaves, 0.31; from the stems, 0.29; from the roots, 0.28; from the seeds, 0.28.

In all cases the main alkaloids were hyoscyamine and hyoscine, which were obtained in the form of perchlorates. Their proportions in the total were (%): in the seeds, 71.4; in the leaves, 55.2; in the stems, 56.3; in the roots, 50.0. The mother liquors from the perchlorates were separated on a column of alumina with elution successively by hexane, ethyl acetate, chloroform, and chloroform–methanol (0.5, 1, 5, and 10%).

As a result of the separation of the total alkaloids of the epigeal part and the seeds, 10 individual bases were isolated: hyoscine, hyoscyamine, apohyoscine, apoatropine, tropine, pseudotropine, 3,6-dihydroxytropane, oscine(scopoline), and bases 9 and 10.

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Base 9 was an amorphous substance in the mass spectrum of which there was the peak of the molecular ion with m/z 321 and a fragmentary peak with m/z 238, corresponding to the splitting out of 83 m/z, and peaks with m/z 222 $(238 - 16)^+$, 154, 138, 122, 94, and 83 formed from the tropine moiety of the base. The following signals of protons were detected in the NMR spectrum: 1.82 (6H, s, $2CH_3{-}C{=}$); 1.74 (6H, d, $2CH_3{-}CH{=}$); 2.43 (3H, s, NCH_3); 3.15 (2H, s, H-1.5); 5.07 (1H, m, H-3β); 5.42 (1H, m, H-6α); 6.83 (2H, m, $2CH{=}C$).

Base 10, with mp 157-159°C, gave in the mass spectrum the peak of the molecular ion with m/z 255 (M^+) and fragmentary peaks with m/z 172 $(M - 83)^+$ and 155 $(172 - 17)^+$. The splitting out of 83 m/z corresponded to the elimination of a tigloyl residue $-CH_3{-}CH{=}C(CH_3){-}C{=}O$, the presence of which in the structure was also shown by the NMR spectrum of the alkaloid: 1.8 (3H, d, $CH_3{-}CH$); 2.46 (3H, s, NH_3); 1.75 (3H, s, $CH_3{=}$); 3.08 (2H, m, $C_{1,5}H$); 4.04 (1H, m, H-3β); 5.6 (1H, m, H-6α); 6.95 (1H, m, $2H{=}C$); 4.76 (1H, m, H-7α).

What has been said above, and also a comparison with literature information, made it possible to establish that bases 9 and 10 were (±)6β-tigloyloxytropane-3α,7α-diol and (−)3α-6β-ditigloyloxytropane [2], which have been isolated from many Datura species.

According to the literature, 12 bases have been isolated from the wild species D. innoxia [3], but there is no information in the literature on the total amount of alkaloids and the amounts of the main representatives. From the introduced species that we investigated 10 bases were isolated, and differences were observed in the quantitative composition of the alkaloids: the introduced species lacked cuscohygrine and littorine, but oscine, apohyoscine, and 3,6-dihydroxytropane were isolated.

The total alkaloids of the seeds obtained by ethanolic extraction were separated into acid, neutral, and basic fractions. The acid fraction contained substances of nonbasic nature and all the weak bases. It amounted to 5% of the total mixture. The basic fraction consisted of a mixture of alkaloids. The neutral fraction was chromatographed on a column of silica gel. Hexane fractions eluted a mixture of crystals which were rechromatographed on a column of silica gel. Fractional crystallization from hexane–ether, hexane–acetone, and ether yielded individual compounds with mp 260-261°C (I) and 273-275°C (II).

From their melting points, compounds (I) and (II) were close to the daturadiol and daturaolone isolated from the wild species of Datura innoxia [4]. The PMR spectra of these substances contained the signals of eight methyl groups in the form of singlets, of an olefinic proton, and of hydrogen atoms geminal to hydroxy groups. The mass-spectrometric fragmentation of (I) and (II) corresponded to that of the daturadiol and daturaolone given in the literature. The presence of a 3-keto group in (II) in place of an OH group in (I) was confirmed by a multiplet at 2.72 ppm. Finally, the oxidation of (I) and (II) with the Jones reagent gave one and the same product – a diketone (III) with mp 197-199°C the properties of which corresponded to those of daturadione.

The ORD characteristics also agreed with this. Thus, we studied and compared the ORD curves of compound (III) (the diketone) and the methyl ester of the 3-acetate of sumaresinic acid (IV), a known triterpene of the β-amyrin series. The ORD curves for compounds (II) and (IV) possessed one characteristic feature: they were located in the region of positive rotations. The Cotton effects due to the $n \to \pi^*$ transition in the C=O group were identical in sign and similar in intensity.

The ORD curve of compound (III) (dioxane): $[\alpha]_{323} + 72°$, $[\alpha]_{286} + 420°$; and that of compound (IV) (dioxane): $[\alpha]_{323} + 100°$, $[\alpha]_{286} + 440°$. These results confirmed the presence of a keto group at C-6.

Thus, the study of the introduced species Datura innoxia has shown that the plant in culture produces mainly the same substances as the wild species, which is due to the individuality of the species.

EXPERIMENTAL

The spectra of the substances were obtained on JNM-4H-100 MHz (δ-scale, $CDCl_3$, HMDS), UR-20 (KBr), MKh-1310, and JASCO-20 instruments. Alumina and KSK silica gel were used for thin-layer and column chromatography. The following solvent systems were used for TLC: chloroform–methanol–conc. ammonia solution (9:1:0.1); benzene–chloroform–methanol (5:3.5:1.5); cyclohexane–chloroform–diethylamine (5:3.5:1.0); and acetone–hexane (1:3).

SUMMARY

The alkaloids of Datura innoxia cultivated in the Darmi sovkhoz have been studied. As a result, 10 individual bases and two triterpenoids – daturadiol and daturaolone – have been isolated. The amounts of the main alkaloids have been determined. It has been shown that the epigeal part of the plant can also be used for obtaining scopolamine hydrobromide.

LITERATURE CITED

1. M. D. Mashkovskii, Drugs [in Russian], Meditsina, Moscow, Part 1 (1984), p. 239.
2. W. C. Evans and J. E. Lampard, Phytochemistry, 11, 3293 (1972).
3. W. C. Evans, A. Ghari, and V. A. Woolley, Phytochemistry, 11, 2527 (1972).
4. M. Kočor, J. St. Pyrek, C. K. Atal, K. L. Bedy, and B. K. Sharma, J. Org. Chem., 38, 3685 (1973).

ALKALOIDS OF THE EPIGEAL PART OF Aconitum talassicum. STRUCTURE OF ACTALINE

A. A. Nishanov, B. Tashkhodzhaev,
M. I. Sultankhodzhaev, B. T. Ibragimov,
and M. S. Yunusov

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The epigeal part of Aconitum talassicum M. Pop. has yielded, in addition to five alkaloids known previously, kobusine, pseudokobusine, and the new alkaloid actaline. The structure of the latter has been established on the basis of an x-ray structural analysis. Actaline is the first C_{20} diterpene alkaloid with a lycoctonine skeleton.

We have investigated the alkaloids of the epigeal part of Aconitum talassicum M. Pop., collected in the flowering phase in the environs of the village of Koksi (Talasskii Ala-Tau range, Kirghiz SSR).

The total amount of alkaloids was 0.7% of the weight of the air-dry plant. By separating the total alkaloids, in addition to the monoacetyltalatisamine, talatisamine, talatisidine, isotalatisidine and talatisine known previously [1, 2], we isolated three other bases.

A base with mp 272-274°C (acetone) had the composition $C_{20}H_{27}NO_2$, $[\alpha]_D + 80°$ (c 1; CH_3OH) and, according to its spectral characteristics, was an alkaloid of the hetisine type. The physicochemical constants and spectral characteristics of the base and its diacetate coincided with those of the alkaloid kobusine. For a definitive identification its methiodide was obtained. A comparison of the crystallographic characteristics of the methiodides of the base and of kobusine showed an identity of the parameters of the elementary cells (with an accuracy of 0.01 Å) and of the space groups, which confirmed the identity of the compounds [3].

The base with mp 268-270°C (acetone) had the composition $C_{20}H_{27}NO_3$. A comparison of spectral and physicochemical constants with literature figures permitted the conclusion that the base was pseudokobusine [4].

The base with mp 125-127°C (hexane) had the composition $C_{22}H_{31}NO_2$ (M 341.23543). Its IR spectrum showed the absorption bands of hydroxy (3475 cm^{-1}) and carbonyl (1680 cm^{-1} groups. The PMR spectrum contained the signals of tertiary C-methyl and N-ethyl groups and a terminal methylene group. In the mass spectrum of the alkaloid, the maximum peak was that of ion $M^+ - 15$. The base proved to be new and was called actaline. Since the

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