SUMMARY

The interconversions of the alkaloids of Sophora alopecuroides L. have been studied by feeding the plants with tritium-labelled alkaloids ([^{3}H]sophoridine, [^{3}H]pachycarpine, [^{3}H]cytisine, [^{3}H]isosophoridine, [^{3}H]allomatrine, and [^{3}H]N-methylcytisine). It has been established that the conformationally stable isomers of the alkaloids – isosophoridine and allomatrine – do not take part actively in the metabolism of the alkaloids. It has also been shown that the alkaloids of the sparteine group are converted into matrine alkaloids in the development of the plant. The methylation of cytisine to N-methylcytisine and the reverse transition have been shown experimentally in the plant organism.

LITERATURE CITED

1. A. Orechoff, Ber., 66, 948 (1933).
2. E. Orechoff, N. Proskurnina, and R. Konovalova, Ber., 68, 431 (1935).
3. T. E. Monakhova, N. F. Proskurnina, O. N. Tolkachev, V. S. Kabanov, and M. E. Perel'son, Khim. Prirodn. Soedin., 59 (1973).
4. T. E. Monakhova, O. N. Tolkachev, V. S. Kabanov, M. E. Perel'son, and N. F. Proskurnina, Khim. Prirodn. Soedin., 472 (1974).
5. J. K. Kuschmuradov, D. Gross, and H. R. Schütte, Phytochem., 11, 3441 (1972).
6. K. Mothes and H. R. Schütte, Biosynthese der Alkaloide, Akademie Verlag, Berlin (1968).
7. H. T. Schütte, H. Aslanov, and C. Schäfer, Arch. Pharm., 295, 34 (1962).
8. S. Shibata and U. Sankawa, Chem. Ind. (London), 1161 (1963).
9. K. Hasse, Abh. dtsch. Akad. Wiss. Berlin. Kä. Chem. Geol. Biol., No. 3, 187 (1966).
10. G. E. Saxton, Alkaloids, 3, 25 (1973).

BIOSYNTHEIS OF THE ALKALOIDS OF *Ammodendron karelinii*

Yu. K. Kushmuradov, H. R. Schütte
Kh. A. Aslanov, and S. Kuchkarov

UDC 547.944 / 945

There is information in the literature [1] according to which transitions of certain types of alkaloids into others take part in the plant organism. In the present paper we give information obtained in a study of the biosynthesis and interconversions of the alkaloids in the plant A. karelinii Fisch et Mey.

When young shoots of the plant were fed with [1,5-^{14}C]cadaverine, labelled anagyrine, pachycarpine, ammodendrine, N-methylcytisine, and cytisine were isolated.

Judging from the experimental results, a probable precursor of the quinolizidine [2, 3] and piperidine [4] alkaloids of this plant is [1,5-^{14}C]cadaverine (+, picrate, ++, hydriodide):

Alkaloid	Amount, mg	mp, °C	Specific radioactivity, counts/min/mmole	Proportion of inclusion, %
[1,5-^{14}C]cadaverine	20	—	$5.5 \cdot 10^9$	—
Anagyrine	4.5	253+	$7.42 \cdot 10^7$	1.34
Pachycarpine	154	235++	$4.27 \cdot 10^7$	0.77
Ammodendrine	20.14	73	$4.16 \cdot 10^7$	0.75
N-methylcytisine	7.5	136	$2.4 \cdot 10^6$	0.43
Cytisine	11.1	135	$2.98 \cdot 10^6$	0.05

V. I. Lenin Tashkent State University. Institute of Plant Biochemistry, Academy of Sciences of the GDR, Halle.

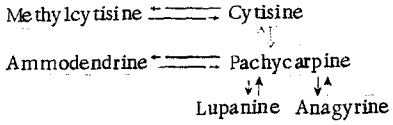
Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 247-250, March-April, 1977. Original article submitted December 2, 1976.

Possible routes for the biosynthesis of anagyrine, pachycarpone, ammodendrine, and cytisine in A. k karelinii are the same as in plants of the genus Lupinus [5].

In order to study the interconversions of the alkaloids in the plant, we fed young shoots of the plant A. karelinii with [^{3}H]lupanine, [^{3}H]anagyrine, [^{3}H]ammodendrine, and [^{3}H]pachycarpine. The results are given below (+, perchlorate; ++, hydriodide; +++, picrate):

Alkaloid	Amount, mg	mp, °C	Specific radioactivity, counts/min/mmole	Proportion of inclusion, %
		[^{3}H]lupanine		
[^{3}H]lupanine	41,2	211$^+$	2,71·10^9	—
Lupanine	8,5	44	1,6·10^5	5,5
Pachycarpine	52	235^{++}	3,98·10^7	1,46
		[^{3}H]anagyrine		
[^{3}H]anagyrine	45,9	315$^+$	5,78·10^9	—
Anagyrine	23	253	7,56·10^5	1,1
Lupanine	16,5	44	2,17·10^5	0,37
Pachycarpine	42,5	235^{++}	1,08·10^5	0,20
Pachycarpine N-oxide	14	153	7,3·10^7	0,12
		[^{3}H]ammodendrine		
[^{3}H]ammodendrine	31,7	73	1,2·10^9	—
Ammodendrine	14,5	73	3,41·10^5	2,84
Pachycarpine	73	235^{++}	6,8·10^7	0,56
Anagryine	18,2	253$^+$	2,8·10^7	0,23
		[^{3}H]pachycarpine		
[^{3}H]pachycarpine	35,1	235^{++}	6,55·10^9	—
Pachycarpine	34,4	208^{+++}	1,68·10^7	2,5
Pachycarpine N-oxide	8,5	153	9,81·10^5	1,5
Anagyrine	13,5	253$^-$	2,68·10^5	0,41
Ammodendrine	11	73	2,08·10^5	0,32

The results obtained show that in the ontogenesis of the plant the alkaloids of the sparteine group are converted into ammodendrine, and the opposite transition is also observed, while in the given vegetation period the proportion of inclusion of ammodendrine in pachycarpene is considerably higher than in the case of the reverse transition. In addition, the interconversion of lupanine and anagyrine into pachycarpine was shown experimentally. In this case, lupanine is converted into pachycarpine far more readily. Consequently, in the plant A. karelinii the interconversions of these alkaloids evidently takes place in accordance with the following scheme



EXPERIMENTAL

For thin-layer chromatography we used Merck HF_{252} silica gel. Solvent systems 1) chloroform–benzene–methanol (20 : 5 : 3); 2) ethyl acetate–isopropanol–25% ammonia (50 : 35 : 25); 3) cyclohexane–diethylamine (7 : 3). Revealing agents: the Dragendorff reagent, iodine vapor, UV lamp.

The alkaloids lupanine, anagyrine, ammodendrine, and pachycarpine were labelled with tritium on a special Wilzbach–Tritierung apparatus, on a $BaCO_3$ support with the aid of uranium tritide. The labelled alkaloids were purified in the following way. The alkaloids were separated from the $BaCO_3$ support by decantation with methanol. The methanolic solution of the alkaloids was boiled for 30 min and the methanol was distilled off, after which the residue was redissolved in methanol. The operation was repeated five times.

The labelled alkaloids were rechromatographed three times by the preparative method on silica gel, and an autoradiogram (scannogram) was taken on a Dünnschicht-Scanner-II apparatus. The alkaloids isolated from the plants were identified by comparison with authentic samples.

Feeding A. karelinii with [1,5-^{14}C]cadaverine. Fresh shoots of the plant were immersed in Knopp's solution containing 23 mg of cadaverine dihydrochloride with a specific radioactivity of $1.8 \cdot 10^9$ counts/min/mmole which we synthesized as described previously [6]. After two days' exposure, the shoots were carefully washed with water and dried to constant weight. The weight of the air-dry plant was 41.7 g. The plant material was ground and extracted with methanol in a Soxhlet apparatus. The combined alkaloids (0.6 g) were separated into the individual bases by preparative chromatography on 200 × 200 mm plates with a fixed layer of silica gel. The chromatogram was revealed with the Dragendorff reagent. Zones with the same R_f values were combined, made alkaline with ammonia, and eluted with methanol. The methanolic extracts were distilled to dryness, made alkaline, and again extracted with chloroform. The amounts of alkaloids isolated were determined gravimetrically.

Feeding with [^{3}H]lupanine. Fresh shoots of the plant were immersed in Knopp's solution containing 41.2 mg of [^{3}H]lupanine with a specific radioactivity of $2.71 \cdot 10^9$ counts/min/mmole. The time of exposure and the method of isolating the combined alkaloids of the plants and separating them into their component fractions were similar to the preceding experiment. The following individual bases were obtained: anagyrine, lupanine, pachycarpine, and pachycarpine N-oxide.

Feeding with [^{3}H]anagyrine. Fresh shoots of the plant were placed in Knopp's solution containing 43.9 mg of [^{3}H]anagyrine with a specific radioactivity of $5.78 \cdot 10^{10}$ counts/min/mmole. The experiment was performed in the same way as the preceding one. The following bases were obtained: anagyrine, lupanine, pachycarpine, and pachycarpine N-oxide.

The feeding of the shoots of the plant with the labelled alkaloids [^{3}H]pachycarpine and [^{3}H]ammodendrine was performed under the same conditions as in the preceding experiment. Feeding with [^{3}H]pachycarpine led to the labelled alkaloids pachycarpine N-oxide anagyrine and ammodendrine, and feeding with [^{3}H]ammodendrine led to labelled pachycarpine and anagyrine.

SUMMARY

The biosynthesis of the alkaloids of Ammodendron karelinii Fisch. et Mey has been studied by feeding the plant with labelled [1,5-^{14}C]cadaverine. It has been shown that cadaverine is a precursor of anagyrine, pachycarpine, ammodendrine, N-methylcytisine, and cytisine. Possible routes of interconversions have been considered by feeding the plant with the tritium-labelled [^{3}H]pachycarpine, [^{3}H]lupanine, [^{3}H]anagyrine, and [^{3}H]ammodendrine.

LITERATURE CITED

1. A. P. Orekhov and N. F. Proskurnina, Zh. Obshch. Khim., 8, 308 (1938).
2. K. Hasse, Abh. dtsch. Akad. Wiss., Berlin, Kl, Chem. Geol. Biol., No. 3, 187 (1966).
3. H. R. Schütte, Abh. dtsch. Akad. Wiss., Berlin. Kl. Chem. Geol. Biol., No. 3, 199 (1966).
4. K. Mothes and H. R. Schütte, Biosynthese de Alkaloide, Berlin, Akademie Verlag (1968).
5. K. Mothes and H. R. Schütte, Angew. Chem., 75, 265 (1963).
6. H. R. Schütte, A. Unverricht, I. Lehfeld, N. Eberle, and U. Fischer, Z. Chem., 2, 336 (1962).