QUINOLIZIDINE ALKALOIDS FROM Maackia amurensis RUNNERS

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Maackia amurensis Rupr. et Maxim. (Amur maackia) belongs to the family Leguminosae (bean), is indigenous to the continential part of the southern Russian Far East, and is distributed in river basins of the Ussuri and middle Amur, river valleys, and low hills [1].

Chemical and pharmacological research on *M. amurensis* produced from extracts of its heartwood the polyphenolic preparation Maksar, which has hepatoprotective activity [2]. Runners of *M. amurensis* are waste from production of Maksar. However, this part of the plant is known to be rich in quinolizidine alkaloids. Therefore, it is a valuable source of them.

Many researchers have studied the qualitative composition of quinolizidine alkaloids from representatives of the bean family. However, the alkaloid composition of *M. amurensis* growing in the Russian Far East is relatively unknown [3, 4].

We studied the composition and relative content of quinolizidine alkaloids in runners (2-4 years old) of *M. amurensis* (Primorskii krai). According to GC—MS, the runners contained more than 17 quinolizidine alkaloids. We previously identified in *M. amurensis* 8 alkaloids that were arbitrarily divided into the following groups: cytisine (cytisine, *N*-methylcytisine), sparteine (sparteine, pachycarpine, anagyrine, argentamine), ammodendrine (ammodendrine, maackiamine) [5].

Runners of M. amurensis were collected in 2003 during leaf emergence (5 June 2003) and budding (27 June 2003) about 3 km to the east of the mouth of the Ryazanovka river (Ryazanovsk lake) in Khasansk region of Primorskii krai. Alkaloids were extracted from plant material by EtOH (70%) and were extracted by CH_2Cl_2 as the free bases after purification with Et_2O [6].

During various development phases (phenophases), the qualitative composition of the quinolizidine alkaloids was practically identical. During leaf emergence and budding, the alkaloids were represented mainly by ammodendrine, camensidine, and cytisine. The relative contnet of total quinolizidine alkaloids during these periods varied from 0.09 to 0.26%. Figure 1 shows the results.

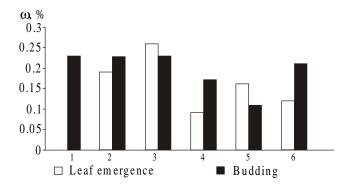


Fig. 1. Relative content of quinolizidine alkaloids in runners of *M. amurensis*: 2003 runners (1), 2002 runners (apical) (2), 2002 runners (side) (3), 2001 runners (apical) (4), 2001 runners (side) (5), 2000 runners (6).

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GC—MS identified in *M. amurensis* for the first time the quinolizidine alkaloids 1',2'-dehydromaackiamine, *N*-formylammodendrine, 1',2'-dehydroammodendrine, 11,12-dehydrolupanine, 5,6-dehydrolupanine, *N*-acetylcytisine, aphylline, and camoensidine [7-10]. Unknown alkaloids were identified by comparing mass spectra published in the literature and the NIST library and by GC—MS on an Agilent GC/MSD 5973N instrument (USA) with an HP-5 MS capillary column (30 m × 0.25 mm × 0.25 µm) using a 100-260°C temperature gradient at 10°C/min, vaporizer temperature 250°C, detector 230°C, flow ratio in vaporizer 1:50, He carrier gas at linear flow rate 37 cm/m and volume rate 1 mL/min. Mass spectra were obtained by electron impact at ionization energy 70 eV, detector potential 1435 V, scan range 33-450 m/z, scan rate 3.49 s. Mass spectra were averaged over the whole width with background subtraction.

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REFERENCES

- 1. O. B. Maksimov, N. I. Kulesh, and P. G. Gorovoi, *Rastit. Resur.*, 28, 3, 157 (1992).
- 2. O. B. Maksimov, O. E. Krivoshchekova, L. S. Stepanenko, et al., RF Pat. No. 1510147 (1994); *Byull. Izobret.*, No. 22, 3 (1994).
- 3. G. K. Nikonov, Tr. Vses. Nauchno-Issled. Inst. Lek. Aromat. Rast., 11, 38 (1959).
- 4. A. I. Shreter, *Medicinal Flora of the Soviet Far East* [in Russian], Moscow (1975).
- 5. A. I. Molchanova, L. I. Sokolova, P. G. Gorovoy, and E. V. Zarembo, in: *Abstracts of 3rd International Symposium on Separations in Biosciences SBS '03*, Moscow (2003), 91.
- 6. I. Murakoshi, E. Kidoguchi, J. Haginiwa, S. Ohmiya, K. Higashiyama, and H. Otomasu, *Phytochemistry*, **21**, 6, 1313 (1982).
- 7. K. Saito, T. Yoshino, T. Sekine, S. Ohmiya, H. Kubo, H. Otomasu, and I. Murakoshi, *Phytochemistry*, **28**, 9, 2533 (1989).
- 8. S. Ohmiya, H. Otomasu, J. Haginiwa, and I. Murakoshi, *Phytochemistry*, 23, 11, 2665 (1984).
- 9. I. Murakoshi, E. Kidoguchi, M. Kubota, J. Haginiwa, S. Ohmiya, and H. Otomasu, *Phytochemistry*, **21**, 9, 2385 (1982).
- 10. S. Ohmiya, H. Kubo, Y. Nakaaze, K. Saito, I. Murakoshi, and H. Otomasu, *Chem. Pharm. Bull.*, **39**, No. 5, 1123 (1991).