

POLYPHENOLS FROM *Maackia amurensis* ROOT BARK

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In continuation of a comprehensive study of *Maackia amurensis* Rupr. et Maxim. (Leguminosae) [1], we investigated the chemical composition of its root-bark extracts.

At present roots of two *Maackia* species have been investigated. Diadzein, formononetin, maackiain, and their glycosides, and the prenylated flavanones maackiaflavanone and 5-hydroxysophoranone were observed in roots of *Maackia amurensis* subsp. *buengeri* [2]. Prenylated isoflavanes called tenuifolins A and B [3] and manuifolins G, H, and K [4] were isolated from roots of *M. tenuifolia*. We previously established that the chemical composition of woods from Primorskaya maackia and *M. buengeri* differ substantially [1]. Our data have indisputable chemotaxonomic interest because further investigations may enable the close relationship of these species to be distinguished.

Plant material was collected in April 1999 by O. B. Maksimov in Vladivostok suburbs. Root bark (200 g) was exhaustively extracted with ethanol to give the alcohol extract (45.8 g), a portion of which (9.82 g) was diluted with water and extracted successively with hexane (0.23 g), benzene (1.32 g), and ethylacetate (2.63 g). The aqueous alcohol remainder was dried (5.60 g). Hydrolysis of the dry solid (40 mg) detected seven polyphenolic aglycons.

The compounds were separated by chromatography and purified by the literature methods [1]. Compounds **1-5** were isolated from the benzene fraction. Preliminary analysis of the UV, IR and NMR spectra showed that **1** and **2** could be assigned to prenylated flavanoids; **3** and **4**, to pterocarpanes; **5**, to isoflavones.

Mass spectra were measured in an LKB-9000 S mass spectrometer by direct probe introduction into the ion source at 18 and 70 eV.

Maackiaflavanone (1, 67 mg). Cream-colored powder, $C_{26}H_{30}O_6$, EIMS ($m/z, I_{rel}$): 438 (31) $[M]^+$, 437 (27), 408 (23), 340 (24), 285 (20), 284 (92), 283 (77), 205 (20), 178 (18), 176 (40), 164 (42), 149 (23), 84 (19), 78 (100), 43 (26). UV spectrum (MeOH, λ_{max} , nm): 288, 335sh. PMR [300 MHz, δ , ppm (CH_3)₂CO- d_6 , J/Hz]: 1.72 (6H, s, 2CH₃), 1.78 (6H, s, 2CH₃), 2.82 (1H, dd, J = 3.0, 17.0, H-3_{ax}), 2.93 (1H, dd, J = 13.0, 17.0, H-3_{eq}), 3.32 (4H, t, J = 7.0, 2CH₂), 3.77 (3H, s, OCH₃), 5.23 (1H, m, CH=), 5.32 (1H, m, CH=), 5.45 (1H, OH), 5.65 (1H, dd, J = 13.0, 3.0, H-2), 6.01 (1H, s, H-6), 6.43 (1H, s, H-3'), 7.21 (1H, s, H-6'), 8.20, 8.37 (2H, br.s, 2OH), 12.05 (1H, br.s, OH-5).

5-Hydroxysophoranone (2, 58.8 mg). Cream-colored powder, $C_{30}H_{36}O_5$, EIMS ($m/z, I_{rel}$): 476 (59) $[M]^+$, 256 (15), 243 (65), 221 (41), 220 (50), 205 (72), 192 (42), 165 (100), 157 (13). UV spectrum (MeOH, λ_{max} , nm): 290, 332. NMR [300 MHz, δ , ppm, (CH_3)₂CO- d_6 , J/Hz]: 1.61, 1.62, 1.71, 1.72, 1.73, 1.74 (18H, s, 6CH₃), 2.75 (1H, dd, J = 3.0, 17.0, H-3_{ax}), 3.15 (1H, dd, J = 12.5, 17.2, H-3_{eq}), 3.22 (2H, br.d, J = 7.0, CH₂), 3.39 (4H, br.d, J = 7.0, 2CH₂), 5.21 (1H, m, CH=), 5.35 (1H, m, 2×CH=), 5.41 (1H, dd, J = 3.0, 12.5, H-2), 6.02 (1H, s, H-6), 7.16 (2H, s, H-3',6'), 9.7 (1H, br.s, OH), 12.1 (1H, br.s, C₅-OH).

The structures of **3-5** were determined as medicarpin (15 mg) [1], maackiain (30 mg), and formononetin (10 mg) [5]. The spectral data and other physicochemical properties agree with those in the literature.

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REFERENCES

1. N. I. Kulesh, O. B. Maksimov, V. A. Denisenko, and V. P. Glazunov, *Khim. Prir. Soedin.*, **26** (2001).
2. N. Matsuura, R. Nakai, M. Iinuma, T. Tanaka, and K. Incue, *Phytochemistry*, **36**, 255 (1994).
3. J.-F. Zeng, G.-L. Li, X. Xu, and D.-Y. Zhu, *Phytochemistry*, **43**, 893 (1996).
4. J.-F. Zeng, H.-X. Wei, G.-L. Li, and D.-Y. Zhu, *Phytochemistry*, **47**, 903 (1998).
5. M. Takai, H. Yamaguchi, T. Saitoh, and S. Shibata, *Chem. Pharm. Bull.*, **20**, 2488 (1972).