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ISOFLAVONOIDS FROM HEARTWOOD OF *Maackia amurensis* RUPR. ET MAXIM.

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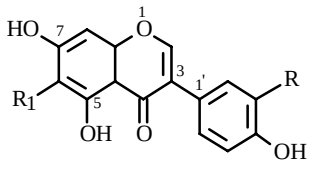
Orobol, tektorigenin, (-)-medicarpin, (±)-vestitol, and a new isoflavanone, the structure of which was established by chemical transformations and spectral data, were isolated from heartwood of Maackia amurensis.

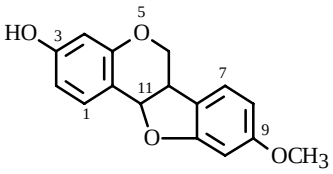
Key words: *Maackia amurensis*, orobol, tektorigenin, (-)-medicarpin, (±)-vestitol, (±)-3-hydroxyvestitone.

We have previously isolated isoflavones, stilbenes [1], isoflavostilbenes [2], stilbenolignan [3], and dimeric stilbenes [4, 5] from heartwood of Amur maackia.

We now present results of further studies of the chemical composition of alcohol extracts of Amur maakia wood. Separation of the ethylacetate fraction of the alcohol extract yielded five compounds of moderate polarity (**1**-**5**). According to UV and IR spectra, PMR, and mass spectrometry, these compounds are orobol (**1**), tektorigenin (**2**), (-)-medicarpin (**3**), (±)-vestitol (**4**), and (±)-3-hydroxyvestitone (**5**). Compounds **1**, **2**, **4**, and **5** were first isolated from *Maackia amurensis* Rupr. et Maxim.



1: R = OH
2: R = H, R_1 = OCH_3



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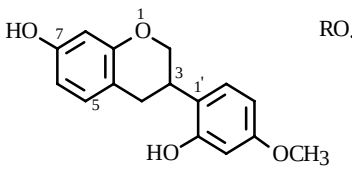

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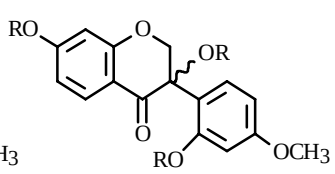

5: R = H
6: R= Ac

Pterocarpanes, including medicarpin, were previously obtained by Japanese researchers from the closely related species *Maackia amurensis* var. buergeri [6]. In our specimen, the only pterocarpane observed was medicarpin as a minor component. Our spectral data and other physicochemical properties of **1**-**4** agree with the literature data.

A new 3-hydroxyisoflavanone was recently isolated from *Dalbergia odorifera* (Leguminosae). Its structure was determined as 3,7,2′-trihydroxy-4′-methoxyisoflavanone (3-hydroxyvestitone) [7]. However, we also obtained ^{13}C spectra and synthesized the acetyl derivative (**6**) of **5** in order to establish its structure because the literature confirming its structure was unavailable. It should be noted that isoflavanones hydroxylated in the 3-position are rather rare. According to our information, secundifloran [8] and secundiflorol A [9] from *Sophora secundiflora*, bolusanthin [10] from *Bolusanthus* sp. (Bolus), and ferreirinol [11] from *Swartzia poliphylla* are also known.

The separation of (±)-vestitol and (±)-3-hydroxyvestitone was very difficult. Only repeated chromatography of the fraction containing the total of these compounds with a very gradual increase in the amount of the polar solvent gave the pure compounds. (±)-3-Hydroxyvestitone was isolated as colorless crystals. The IR spectrum (dioxane) showed absorption bands at 3376, 3480, and 3579 cm^{-1}. This is consistent with the presence of three hydroxyls.

Acetylation gave the triacetate **6**, which also contains three hydroxyls.

The ^1H NMR spectrum contains two doublets at 4.34 and 4.91 ppm, each from one proton. The spin—spin coupling

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constant (SSCC) is 11.8 Hz, which suggests that the doublets correspond to geminal protons on C-2. The magnitude of the chemical shift indicates that the hydroxyl is on C-3.

The position of the substituents on ring B in **5** and **6** was found by using the nuclear Overhauser effect. The multiplicity in this instance (d, J = 2.1, 2.2 Hz; dd, J = 8.7, 8.8 Hz, J = 2.1, 2.2 Hz) with saturation of the protons of the methoxyl indicates that the methoxyl on ring B is located in the 4′-position of both compounds.

The ^{13}C NMR spectrum has a signal at weak field at 190.3 ppm that belongs to the C=O on C-4 and signals at 74.3 (C-2) and 74.8 (C-3) ppm that are typical of isoflavonones hydroxylated in the 3-position.

We include all physicochemical and spectral data that we obtained for the isolated compounds because these data are very scattered in the literature, incomplete, and published long ago [12-17].

EXPERIMENTAL

The specimens were collected in November 1997 in the suburbs of Vladivostok in Primorskii Krai. The plant was identified by Prof. P. G. Gorov.

We used KSK silica gel for column chromatography and a gradient of the solvent systems benzene—ethanol and benzene—acetone. Sorbfil plates and the solvent system toluene—ethylacetate—formic acid (10:8:2) were used for TLC.

Melting points were measured on a Boetius stage and are uncorrected. UV spectra were recorded on a Cary—Varian 219 in methanol; IR spectra, on a Specord M 82; mass spectra, in an LKB-9000 S mass spectrometer in a direct probe at ionization potentials 15 and 70 eV. NMR spectra were obtained at 300 MHz for ^1H and 63 MHz for ^{13}C (δ, ppm, 0 = TMS, acetone-d_6, $CDCl_3$).

Wood chips (4 kg) of *Maackia amurensis* were extracted with 95% ethanol for 24 h at 50°C. The extract was evaporated and concentrated and exhaustively extracted with hexane and ethylacetate. The ethylacetate fraction (140 g) was separated on a silica-gel column using a gradient of benzene—ethanol. Narrow fractions were rechromatographed on a silica-gel column using a gradient of benzene—acetone to isolate **1**-**5**.

Orobol (1): (21 mg), colorless needles, $C_{15}H_{10}O_6$, mp 268°C, UV spectrum (MeOH, λ_{max}, nm): 268, 293 sh., 320 sh. IR spectrum (dioxane, ν_{max}, cm^{-1}): 3275 (OH), 1656 (C=O, γ-pyrone), 1620, 1583, 1517 (C=C). Mass spectrum (EI, 70 eV) *m*/*z* (%): M^+ 286 (100), 153 (27), 150 (23), 137 (19), 134 (28), 120 (18).

^1H NMR (δ, ppm, acetone-d_6, J/Hz): 6.28 (1H, d, J = 2.2), 6.41 (1H, d, J = 2.2, H-8), 6.87 (1H, d, J = 8.5, H-5′), 6.94 (1H, dd, J = 2.2, 8.5, H-6′), 7.14 (1H, d, J = 2.2, H-2′), 8.15 (1H, s, H-2).

Tektorigenin (2): (65 mg), yellow crystals, $C_{16}H_{12}O_6$, mp 229°C, UV spectrum (MeOH, λ_{max}, nm): 214, 267, 338 sh; IR spectrum (dioxane, ν_{max}, cm^{-1}): 3310 (OH), 1653 (C=O), 1628, 1615, 1590, 1519 (C=C).

Mass spectrum (EI, 70 eV), *m*/*z* (%): M^+ 300 (20), 299 (100), 284 (42), 272 (19), 258 (8), 257 (33), 150 (27), 137 (16).

^1H NMR (δ, ppm, acetone-d_6, J/Hz): 3.88 (3H, s, OCH_3), 6.50 (1H, s, H-8), 6.91 (2H, d, J = 8.2, H-2′,6′), 7.46 (2H, d, J = 8.2, H-3′,5′), 8.19 (1H, s, H-2), 8.51, 9.21, 13.12 (3H, s, 3×OH).

(-)-Medicarpin (3) (11 mg), colorless needles, $C_{16}H_{14}O_4$, mp 126°C, $[\alpha]^{20}_{Hg589nm}$ -227°, UV spectrum (MeOH, λ_{max}, nm): 206, 229, 287, 317 sh; mass spectrum (EI, 70 eV), *m*/*z* (%): M^+ 270 (100), 269 (40), 255 (33), 161 (10), 149 (19).

^1H NMR (δ, ppm, acetone-d_6, J/Hz): 3.51 (1H, ddd, J = 4.2, 4.9, 6.4, 7.0, 11.0, 11.0, H-6 ax), 3.62 (1H, dd, J = 10.4, 11.0, H-6 ax), 3.76 (3H, s, OCH_3), 4.24 (1H, m, H-6 eq), 5.49 (1H, d, J = 6.4, H-11a), 6.42 (1H, d, J = 2.5, H-4), 6.46 (1H, dd, J = 2.5, 8.5, H-8), 6.55 (1H, dd, J = 2.5, 8.5, H-2), 7.12 (1H, d, J = 8.9, H-7), 7.37 (1H, d, J = 8.5, H-1). CD (MeOH): $[\theta]_{250}$ -55.5, $[\theta]_{297}$ -70.5, $[\theta]_{307}$ -30.0.

(±)-Vestitol (4) (63 mg), colorless needles, $C_{16}H_{16}O_4$, mp 156°C, $[\alpha]^{20}_{Hg589}$ 0.00°, UV spectrum (MeOH, λ_{max}, nm): 204, 229, 282, 286; IR spectrum (dioxane, ν_{max}, cm^{-1}): 3328 (OH), 1620, 1597, 1552 sh, 1512 (C=C); mass spectrum (EI, 70 eV), *m*/*z* (%): M^+ 272 (98), 271 (77), 151 (23), 150 (100), 149 (16), 138 (46), 137 (57), 123 (15).

^1H NMR (δ, ppm, acetone-d_6, J/Hz): 2.79 (1H, ddd, J = 15.1, 2.1, 5.2, H-4 eq), 2.96 (1H, ddd, J = 15.5, 10.7, 0.9, H-4 ax), 3.48 (1H, dddd, J = 10.1, 10.7, 5.2, 3.7, H-3), 3.71 (3H, s, OCH_3), 3.97 (1H, t, J = 10.1, 10.4, H-2 ax), 4.24 (1H, ddd, J = 2.1, 3.7, 10.4, H-2 eq), 6.31 (1H, d, J = 2.4, H-8), 6.38 (1H, dd, J = 2.2, 8.2, H-6), 6.41 (1H, dd, J = 2.4, H-6′), 6.51 (1H, d, J = 2.4, H-2′), 7.03 (1H, d, J = 8.5, H-5′), CD (MeOH): $[\theta]_{330}$ -82.0, $[\theta]_{310}$ -82.0, $[\theta]_{285}$ -68.1.

(±)-3-Hydroxyvestitone (5) (91 mg), colorless crystals, mp 172°C, $C_{16}H_{14}O_6$, $[\alpha]^{20}_{Hg589nm}$ 0.00°, UV spectrum (MeOH, λ_{max}, nm): 230, 291.

IR spectrum ($CDCl_3$, ν_{max}, cm^{-1}): 3579, 3480, 3376 (OH), 1682 (C=O), 1615, 1583, 1505 (C=C), mass spectrum (EI, 70 eV), *m*/*z* (%): M^+ 302 (8), 301 (29), 284 (4), 283 (10), 274 (7), 166 (14), 151 (15), 138 (17), 137 (100), 121 (4).

^1H NMR (δ, ppm, acetone-d_6, J/Hz): 3.73 (3H, s, OCH_3), 4.34 (1H, d, J = 11.8, H-2 ax), 4.91 (1H, d, J = 11.8, H-2 eq), 6.37 (1H, d, J = 2.2, H-8), 6.39 (1H, d, J = 2.2, H-3′), 6.40 (1H, dd, J = 2.2, 8.7, H-5′), 6.60 (1H, dd, J = 2.2, 8.7, H-6), 7.35 (1H, d, J = 8.9, H-6′), 7.77 (1H, d, J = 8.7, H-5), 5.50 (1H, br. s, OH, C-3), 8.71 (1H, br. s, OH), 9.51 (1H, br. s, OH).

^{13}C NMR (δ, ppm, acetone-d_6, J/Hz): 55.2 (OCH_3), 74.3 (C-2), 74.8 (C-3), 190.3 (C-4), 130.4 (C-5), 111.6 (C-6), 163.7 (C-7), 103.2 (C-8), 165.3 (C-9), 113.4 (C-10), 117.6 (C-1′), 157.3 (C-2′), 102.9 (C-3′), 161.8 (C-4′), 105.6 (C-5′), 128.5 (C-6′), CD (MeOH): $[\theta]_{316}$ -49.2, $[\theta]_{362}$ -72.2.

Acetylation of 5. Compound **5** (27 mg) was acetylated in dry pyridine—Ac_2O at 60°C for 2 h. The reaction mixture was left overnight at room temperature. The solution was poured onto ice and exhaustively extracted with ethylacetate. The extract was washed with water, evaporated under vacuum, and dried. Yield of **6**, 21 mg.

Triacetate of (±)-3-hydroxyvestitone (6) (21 mg), white powder, $C_{22}H_{20}O_9$, IR spectrum ($CDCl_3$, ν_{max}, cm^{-1}): 1763, 1705 (C=O), 1650, 1615, 1585, 1507 (C=C).

Mass spectrum (EI, 70 eV), *m*/*z* (%): M^+ 428 (10), 386 (40), 326 (10), 301 (4), 284 (15), 250 (43), 166 (100), 151 (60), 137 (59).

^1H NMR (δ, ppm, $CDCl_3$, J/Hz): 2.11, 2.28, 2.31 (9H, s, 3×AcO), 3.76 (3H, s, OCH_3), 5.09 (1H, d, J = 11.4, H-2 ax), 5.11 (1H, d, J = 11.4, H-2 eq), 6.62 (1H, d, J = 2.7, H-3′), 6.72 (1H, d, J = 2.1, H-8), 6.73 (1H, dd, J = 2.7, 8.7, H-5′), 6.82 (1H, dd, J = 2.1, 8.7, H-6), 7.35 (1H, d, J = 8.7, H-6′), 7.97 (1H, d, J = 8.8, H-5).

^{13}C NMR (δ, ppm, acetone-d_6, J/Hz): 20.7×3 (AcO), 55.8 (OCH_3), 72.0 (C-2), 80.6 (C-3), 187.1 (C-4), 130.3 (C-5), 117.1 (C-6), 162.2 (C-7), 111.5 (C-8), 157.6 (C-9), 119.9 (C-10), 119.7 (C-1′), 151.2 (C-2′), 111.3 (C-3′), 161.6 (C-4′), 111.8 (C-5′), 129.5 (C-6′), 168.7 (AcO), 168.8 (AcO), 169.4 (AcO).

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