

Present work. Shade dried flowers were extracted successively with light petrol., C_6H_6 , Et_2O , acetone and $EtOH$. The light petrol. extract yielded an aliphatic alcohol (0.244%), m.p. 80–81°, ν_{max} (KBr): 3400 (OH), 1737 (CO), 1472, 1462, 723, 712 cm^{-1} . The C_6H_6 extract yielded caviunin⁷ (0.0028%), $C_{15}H_{14}O_2(OH)_2(OCH_3)_4$. M.p., m.m.p., co-chromatography, UV, IR, NMR and MS measurements corroborated the identification. The Et_2O extract by column chromatography (silica gel) followed by preparative TLC (kieselgel G) gave two flavones apigenin (0.0028%) and luteolin (0.0022%) which were identified by m.p., m.m.p., co-chromatography (3 solvents), UV and IR spectral measurements. The acetone extract yielded (+)-pinitol (0.22%), $C_6H_6(OH)_5(OCH_3)_3$, m.p. 185–186°, $[\alpha]_D^{25} +67^\circ$ (c 1.0, H_2O); [lit.⁸ m.p. 185–186°, $[\alpha]_D^{25} +66.8^\circ$ (c 2.5, H_2O)]. The ethanol extract yielded dalpanin⁹ (0.47%) which has been characterized as an isoflavanone-*C*-glucoside.

Comment. The present investigation shows for the first time the presence of flavones in a *Dalbergia* species, co-occurring with isoflavanoids.

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CONSTITUENTS OF *MACHAERIUM PEDICELLATUM* HEARTWOOD

KOICHI OGIYAMA and MORITAMI YASUE

Faculty of Agriculture, Yamagata University, Tsuruoka, Japan

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Plant. *Machaerium pedicellatum* Vog., Leguminosae. *Source.* Imported to Japan from Bolivia. *Uses.* Fancy plywood. *Previous work.* On the heartwood of sister species *Machaerium*.^{1–7}

¹ KUROSAWA, K., OLLIS, W. D., REDMAN, B. T., SUTHERLAND, I. O., BRAGA DE OLIVEIRA, A., GOTTLIEB, O. R. and MAGALHÃES ALVES, H. (1968) *Chem. Commun.* 1263.

² KUROSAWA, K., OLLIS, W. D., REDMAN, B. T., SUTHERLAND, I. O., GOTTLIEB, O. R. and MAGALHÃES ALVES, H. (1968) *Chem. Commun.* 1265.

³ GREGSON, M., KUROSAWA, K., OLLIS, W. D., REDMAN, B. T., ROBERTS, R. J., SUTHERLAND, I. O., BRAGA DE OLIVEIRA, A., EYTON, W. B. and GOTTLIEB, O. R. (1968) *Chem. Commun.* 1390.

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⁵ OLLIS, W. D. and GOTTLIEB, O. R. (1968) *Chem. Commun.* 1396.

⁶ EYTON, W. B., OLLIS, W. D., FINEBERG, M., GOTTLIEB, O. R., SALIGNAC DE SOUZA GUIMARÃES, I. and TAVERIRA MAGALHÃES, M. (1965) *Tetrahedron* **21**, 2697.

⁷ BRAGA DE OLIVEIRA, A., GOTTLIEB, O. R., OLLIS, W. D. and RIZZINI, C. T. *Phytochemistry* (1971) **10**, 1863.

The MeOH extract of the heartwood was treated with *n*-hexane, followed by Et₂O. The Et₂O soluble fraction was chromatographed on SiO₂, giving the following compounds: β -Amyrin acetate (yield 0.034%; based on wood), C₃₂H₅₂O₂, m.p., m. m.p., [α]_D, IR and NMR; alkali hydrolysis to β -amyrin, C₃₀H₅₀O, m.p., m. m.p., [α]_D, IR and NMR; *R*-3,4-dimethoxydalbergione (yield 0.592%), C₁₇H₁₆O₄, m.p., [α]_D, IR, UV and NMR;⁶ reductive acetylation to *R*-3,4-dimethoxydalbergione quinol diacetate, C₂₁H₂₂O₆, m.p., [α]_D, IR, UV and NMR; kuhlmannene (yield 0.007%), C₁₇H₁₈O₄, m.p., UV, IR and NMR;⁴ *R*-3,4-dimethoxydalbergione quinol (yield 0.474%), C₁₇H₁₈O₄, UV, IR and NMR;⁶ diacetate C₂₁H₂₂O₆, m.p., m. m.p., [α]_D and IR; oxidation with air to *R*-3,4-dimethoxydalbergione, m.p., m. m.p. and IR; *O*-methylalbergin (yield 0.095%), C₁₇H₁₄O₄, m.p., UV, IR and NMR;⁸ kuhlmannin (yield 0.017%), C₁₇H₁₄O₄, m.p., UV, IR and NMR;⁴ dalbergin (yield 0.095%), C₁₆H₁₂O₄, m.p., UV, IR and NMR;⁸ methylation to *O*-methylalbergin, m.p., UV and IR.

In addition to the above known compounds three new isoflavans, machaerol-*A*, -*B* and -*C* were isolated. Machaerol-*A* (yield 0.004%), (Found: C, 65.10; H, 5.85. C₁₈H₂₀O₆ requires: C, 65.06; H, 6.02%), 332 M⁺, m.p. 160–162°, $\lambda_{\text{max}}^{\text{EtOH}}$ 295 nm, log ϵ 3.74; diacetate C₂₂H₂₄O₈, m.p. 145–147°, NMR [δ 6.88 (*d*, 1H, 8Hz), 6.64 (*d*, 1H, 8Hz), 6.60 (*s*, 1H), 6.52 (*s*, 1H) four aromatic protons; 3.77 (*s*, 3H), 3.74 (*s*, 3H), 3.71 (*s*, 3H) three OMe groups; 2.21 (*s*, 3H), 2.25 (*s*, 3H) two OAc groups; 4.22 (*q*, 1H, 10 Hz, 3.5 Hz), 3.9 (*t*, 1H, 10 Hz), 3.5 (*m*, 1H), 2.9 (*d*, 2H, 7.5 Hz) five protons at C₂, C₃ and C₄ of the isoflavan structure²]. Although the molecular formulae and mps of machaerol-*A* and its acetate are identical with those of lonchocarpan and its acetate,⁹ the NMR spectrum and MS fragmentation show marked differences. Machaerol-*B* (yield 0.047%), (Found: C, 63.02; H, 5.87. C₁₉H₂₂O₇ requires: C, 62.98; H, 6.08), *m/e* 362 M⁺, m.p. 70–80°, $\lambda_{\text{max}}^{\text{EtOH}}$ 284 nm log ϵ 3.65; dimethyl ether C₂₁H₂₆O₇, m.p. 77–79°C, NMR [δ 6.75 (*d*, 1H, 8 Hz), 6.85 (*d*, 1H, 8 Hz), 6.32 (*s*, 1H) three aromatic protons; 3.88 (*s*, 3H), 3.86 (*s*, 3H), 3.84 (*s*, 6H), 3.80 (*s*, 3H), 3.76 (*s*, 3H) six OMe groups; 4.32 (*q*, 1H, 3 Hz, 10 Hz), 3.94 (*t*, 1H, 10 Hz), 3.60 (*m*, 1H), 2.88 (*d*, 2H, 8 Hz) five protons at C₂, C₃ and C₄ of the isoflavan structure]. Machaerol-*C* (yield 0.223%) (Found: C, 62.09; H, 5.72. C₁₈H₂₀O₇ requires: C, 62.07; H, 5.75), *m/e* 348 M⁺, m.p. 170–172°, $\lambda_{\text{max}}^{\text{EtOH}}$ 284 nm, log ϵ 3.55, trimethyl ether C₂₁H₂₆O₇, m.p. 77–79° (identical with machaerol-*B*-dimethyl ether). Further investigation is in progress.

The wood of *Machaerium pedicellatum* frequently causes dermatitis among operators during machining. The violently irritating compounds have been found to be *R*-3,4-dimethoxydalbergione and *R*-3,4-dimethoxydalbergione quinol.

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