

องค์ประกอบทางเคมีจากตะแบกกราย

Chemical Constituents from *Terminalia pierrei* Gagnepain

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บทคัดย่อ

การแยกส่วนสกัดเฮกเซนของเปลือกต้นตะแบกกรายด้วยวิธีทางโครมาโทกราฟี นำไปสู่การแยกสารได้ 3 สาร คือ friedelin (1), β -sitosterol (2) และ D-mannitol (3) ขณะที่ส่วนสกัดเฮกเซนของใบและกิ่งก้านให้ lupeol (4) และ (+)-sesamin (5) โครงสร้างของสารประกอบทั้ง 5 ระบุได้โดยวิธีการทางสเปกโทรสโกปี

Abstract

Chromatographic separation of the hexane extract of bark of *Terminalia pierrei* led to the isolation of three compounds, friedelin (1), β -sitosterol (2) and D-mannitol (3). Hexane extract of leaves and twigs yielded lupeol (4) and (+) - sesamin (5). The structure of these five compounds was determined by spectroscopic methods.

คำสำคัญ: ตะแบกกราย องค์ประกอบทางเคมี โครมาโทกราฟี

Keywords: *Terminalia pierrei*, chemical constituents, chromatography

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Introduction

Terminalia pierrei Gagnepain (synonym = *T. dafeuillana* Pierre ex Lanessan) is one of the 17 species in the genus *Terminalia* (Combretaceae) found in Thailand.^{1,2} Some species, such as *T. arjuna*, *T. alata*, *T. bellirica*, *T. catappa*, *T. chebula*, and *T. calamansanai*, have been investigated for their chemical constituents. However, there are many species that have not been investigated. This paper reports chemical constituents isolated from bark, leaves and twigs of *T. pierrei*.

Methods

General procedures

Melting points were uncorrected. IR spectra were recorded on a Shimadzu FTIR-8601 spectrometer. ¹H and ¹³C spectra were recorded in CDCl₃ solution on a Jeol JNM-EX 90A spectrometer with TMS as internal standard. Optical rotation was measured on a Jasco DIP-1000 digital polarimeter. Silica gel 60H (70-230 mesh) was used for column chromatography.

Extraction and Isolation

Powdered, dried bark (6.3 kg) of *T. pierrei* was extracted with hexane (4L x 3) at room temperature. The filtrates were combined and the solvent were removed *in vacuo* to yield a hexane extract (19.2 g) which was chromatographed on silica gel and eluted with hexane, hexane-EtOAc (4:1-3:2-2:3-4:1), EtOAc, and MeOH to give 8 fractions, F_B 1 - F_B 8. The F_B 2 (8.1 g) was further separated by flash column chromatography eluted with increasing concentrations of EtOAc in hexane followed by MeOH. The early fractions eluted with hexane-EtOAc (9:1) furnished friedelin (1, 17 mg).

Subsequent fraction eluted with hexane-EtOAc (8:2) yield β-sitosterol (2, 253 mg). Further separation of F_B 3 (1.71 g) using the method described above gave an additional amount of 2 (241 mg), while further separation of F_B 4 (1.672 g) afforded D-mannitol (3, 514 mg). The two compounds were obtained from fractions eluted with hexane-EtOAc (9:1) and hexane respectively.

Powered, dried leaves and twigs (9 kg) of *T. pierrei* were extracted with hexane (10 L x 4) at room temperature. Removal of the solvent from the combined filtrates gave the hexane extract (98.3 g). Chromatographic separation of this extract (20.7 g) was carried out on silica gel and eluted with increasing concentration of EtOAc in hexane and finally with MeOH gave 8 fractions, F_{LT} 1-F_{LT} 8. Fractions F_{LT} 3 and F_{LT} 4 were further separated by flash column chromatography eluted with increasing concentrations of EtOAc in hexane followed by MeOH. The early fractions eluted with hexane-EtOAc (9:1) of F_{LT} 3 furnished lupeol (4, 25 mg), while (+)-sesamin (5, 287 mg) was obtained from early fractions eluted with hexane-EtOAc (8:2) of F_{LT} 4.

Friedelin (1) : colorless needles; mp 262-264°C (lit.³ 265-267°C); IR (KBr) ν_{\max} 2929, 2860, 1716, 1460, 1379 cm⁻¹; ¹H NMR (CDCl₃) δ 2.34 (2H, *m*, *H*-2), 1.20 and 1.05 (each 3H, *s*, *H*-28, 27), 0.99 (6H, *s*, *H*-30, 26), 0.92, 0.84 and 0.72 (each 3H, *s*, *H*-29, 25, 24); ¹³C NMR (CDCl₃) δ 213.0, 59.5, 58.2, 53.1, 42.8, 42.1, 41.5, 41.3, 39.7, 39.2, 38.3, 37.4, 36.0, 35.6, 35.3, 35.0, 32.8, 32.4, 32.1, 31.8, 30.5, 30.0, 28.1, 22.3, 20.3, 18.6, 18.2, 17.9, 14.6, 6.8.

β -Sitosterol (2) : colorless needles; mp 137–138°C (lit⁴. 136–137°C); IR (KBr) ν_{\max} 3439 (OH), 2920, 2850, 1465, 1382, 1055 cm⁻¹; ¹H NMR(CDCl₃) d 5.35 (1H, d, $J = 4.3$ Hz, C = CH-), 3.50 (1H, br s, OH) 2.30–1.10 (30 H, m, -CH- and -CH₂-), 1.02 (3H, s, H-19), 0.99–0.78 (12H, m, H-21, 26, 27, 29), 0.70 (3H, s, H-18); ¹³C NMR (CDCl₃) d 140.8, 121.7, 71.8, 56.8, 56.1, 50.2, 45.9, 42.4, 39.8, 37.3, 36.5, 36.2, 34.0, 32.0, 31.7, 29.3, 28.3, 26.2, 24.3, 23.1, 21.1, 19.8, 19.4, 19.1, 18.8, 12.0, 11.9.

D-Mannitol (3) : colorless needles; mp 164–167°C (lit⁴. 166°C); [α]_D^{23.6} + 1.04 (c, 3 H₂O); IR (nujol) ν_{\max} 3360 (OH), 2941, 2872, 1419, 1078, 1020 cm⁻¹; ¹H NMR (D₂O) d 3.5–3.7 (m, -CH-, -CH₂-); ¹³C NMR (D₂O) d 73.5, 71.9, 65.8

Lupeol (4) : colorless needles; mp 209–210°C (lit³. 210°C); IR (KBr) ν_{\max} 3333 (OH), 3067, 2924, 2854, 1641, 1460, 1381, 881 cm⁻¹; ¹H NMR (CDCl₃) d 4.72 and 4.60 (each 1H, m, H-29), 3.20 (1H, m, H-3), 2.35 (1H, m, H-19), 1.60 (3H, s, H-30), 1.00, 0.90, 0.88, 0.80, 0.78, 0.76 (each 3H, s, H-26, 23, 27, 25, 28, 24); ¹³C NMR (CDCl₃) d 150.9, 109.3, 79.0, 55.3, 50.5, 48.3, 48.0, 43.0, 42.8, 40.8, 40.0, 38.9, 38.7, 38.1, 37.2, 35.6, 34.3, 29.9, 29.7, 28.0, 27.4, 25.2, 20.9, 19.0, 18.3, 18.0, 16.1, 16.6, 15.3, 14.5.

(+)-Sesamin (5) : colorless needles; mp 122–123°C (lit³. 123–124°C); [α]_D²⁹ + 51.5°C (c, 0.4 CHCl₃); IR (KBr) ν_{\max} 3040, 2940, 2870, 1490, 1430, 1096, 920 cm⁻¹; ¹H NMR (CDCl₃) d 6.83 (3H, m, ArH), 5.95 (2H, s, OCH₂O), 4.71 (2H, d, $J = 4.0$ Hz, H-2, 6), 4.23 (2H, dd, $J = 9.0$ and 6.6 Hz, H_c-4, 8), 3.87 (2H, dd, $J = 9.0$ and 3.2

Hz, H_a-4, 8), 3.05 (2H, m, H-1, 5); ¹³C NMR(CDCl₃) d 148.0, 147.1, 135.1, 119.3, 108.2, 106.5, 101.0, 85.8, 71.7, 54.4.

Results and Discussion

Chromatographic separation of a hexane extract of barks of *T. pierrei* collected from Wang Num Kaew botanic garden at Nakhon Ratchasima province, yielded three compounds, **1–3** (in yields of 0.0091, 0.0003, and 0.0082%, respectively). On the basis of spectroscopic methods, these compounds were identified as known compounds. Friedelin (**1**), the pentacyclic triterpene has been found in cork and bark of many plants. β -Sitosterol (**2**), the common sterol has been found in other *Terminalia* species such as *T. alata*, *T. arjuna*, *T. catappa*, and *T. tomentosa*. D-mannitol (**3**), the alditol has been found in *T. bellerica*.

A hexane extract of leaves and twigs of *T. pierrei* afforded another two known compounds, **4** and **5** (in yields of 0.0013 and 0.0187%, respectively). Compound **4** was identified as lupeol, one of the most widespread pentacyclic triterpenes and compound **5** was identified as (+)-sesamin, the furofuranoid lignan found in sesame oil and many other plants.

Acknowledgements

Support of this work by the Postgraduate Education and Research Program in Chemistry (PERCH) and by the Shell Centennial Education Fund is gratefully acknowledged.

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