LAETANINE, ICARISIDE E₃, (-)-PINORESINOL AND MANTOL O-B-D-GLUCOPYRANOSIDE FROM AQUEOUS EXTRACT OF PHOEBE TAVOYANA (MEISSN) HOOK

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Abstract. Phoebe tavoyana (Meissn) Hook often grows scatterly in tropical rain forest in Viet Nam. The plant is used in traditional medicine to treat acne and the bark is used to prevent rheumatism. In continuous course of study on chemical composition of Phoebe genus, this paper describes the extraction and structure evaluation of four compounds including laetanine (1), icariside E₃ (2), (-)-pinoresinol (3) and maltol O-β-D-glucopyranoside (4) from an aqueous extract of the leaves of Phoebe tavoyana (Meissn) Hook. These compounds were isolated based on thin layer and column chromatographies. Their chemical structures were determined by analyses of their ESI-MS, 1D-NMR and 2D-NMR spectral data, and compared with those reported in the literature. This is the first report of compound 2 and 4 from the genus Phoebe.

Keywords: Phoebe tavoyana, alkaloid, lignan.

Classification numbers: 1.1.1, 1.4.7.

1. INTRODUCTION

Phoebe is a genus of tall, flowering plants belonging to the Laurel family, Lauraceae, which contains about 200 species, mainly distributed in Asia and America. They are found in large numbers in the Borneo peninsula and Malaysia. In Viet Nam, the genus Phoebe includes about 12 species and distributed throughout the country. Phoebe is widely used in folk remedies such as healing wounds or sores, eliminating pimples and rheumatism. Phytochemical studies revealed attractive alkaloids, particularly, oxoaporphine, and aporphine alkaloids; terpenoids, lignans were recognized as main compounds of this genus as well as in P. tavoyana [1 - 3]. In Viet Nam, seven alkaloids including corydydine, N-methylaurolitsine, N-methylaurotetanine, pronuciferine, stepharine, norcorydine and anonaine, some steroids and lignans such as phoebenoside A, phoebenoside B, dendranthemoside A, lyoniresinol, (+)-3-O-L-rhamnopyranoside-5-methoxyisolariciresinol, and (+)-lyoniresinol 3α-O-β-D-glucopyranoside were isolated from P. tavoyana [1 - 3]. To continue the phytochemical studies on Phoebe, this paper reports the isolation and characterization of 4 compounds from P. tavoyana.
2. MATERIALS AND METHODS

2.1. Plant material

The leaves of *Phoebe tavoyana* (Meisn.) Hook. were collected at Me Linh, Vinh Phuc province, Viet Nam in May, 2016 and identified by Dr. Nguyen The Cuong, Institute of Ecology and Biological Resources, Vietnam Academy of Science and Technology (VAST). A voucher specimen (NCCT-P59) was deposited at the Biological Resources Research Department, Institute of Marine Biochemistry, VAST.

2.2. General experimental procedures

NMR spectra were recorded on a Bruker 500 MHz spectrometer. ESI mass spectra were recorded on an Agilent 6530 Accurate-Mass Q-TOF LC/MS system. Column chromatography was performed using a silica gel (Kieselgel 60, 70 - 230 mesh and 230 - 400 mesh, Merck) or RP-18 resins (150 μm, YMC), thin layer chromatography (TLC) using a pre-coated silica gel 60 F254 (0.25 mm, Merck), RP-18 F254S plates (0.25 mm, Merck), sephadex LH-20 (25 - 100 μm, Merck), and Diaion HP-20 (250 - 850 μm Supeclo).

2.3 Extraction and isolation

The dried leaf powder of *P. tavoyana* (3.2 kg) were extracted with MeOH (3 × 5 L) using sonicator to yield 200 g of extract. The MeOH extract was suspended in water and successively partitioned with CH₂Cl₂, ethyl acetate (EtOAc) to obtain CH₂Cl₂ (PT1), EtOAc (PT2), and water (PT3) fractions. The PT3 was chromatographed on a Diaion HP-20 column eluting with water to remove sugars, then increasing concentration of methanol in water (25, 50, 75, and 100 %, each 1 L to obtain four fractions, PT3A - PT3D, respectively. PT3C was subjected on silica gel CC eluted with CH₂Cl₂/MeOH (8/1, v/v) to give 6 fractions from FPTW3A to FPTW3F, respectively. The fraction FPTW3F was chromatographed on sephadex eluted with MeOH/water solvent (1:1) to obtain two sub-fractions FPTW3F1 and FPTW3F2. The fraction FPTW3F2 was chromatographed on silica gel CC eluted with dichlomethane / acetone/water (1:4:0.3, v/v/v) to yield compound 1 (7 mg). Fraction FPTW3E was chromatographed on RP-18 eluted with acetone/water solvent (1:4, v/v) to obtain 3 sub-fractions FPTW3E1, FPTW3E2, FPTW3E3. The FPTW3E2 fraction was chromatographed on sephadex eluted with MeOH/water (1: 2) solvent to obtain compound 2.

The fraction FPTW3C was loaded on RP-18 CC, eluted with acetone: water (1:3.5, v/v) to obtain 3 fractions FPTW3C1, FPTW3C2, FPTW3C3. The fraction FPTW3C2 was chromatographed on silica gel CC eluted with EtOAc/MeOH/water (5: 10: 1, v/v/v) to give 2 sub-fractions FPTW3C2A, FPTW3C2B and compound 3. The FPTW3C2A fraction was chromatographed on sephadex eluted with MeOH/water (1:1) solvent to yield compound 4 (5 mg).

**Laetanine (1)**

White amorphous powder; ESI-MS: m/z 314 [M+H]+, C₁₈H₁₉NO₄.

¹H-NMR (500 MHz, methanol-d₄) δH (ppm): 6.59 (1H, s, H-3), 6.74(1H, s, H-8), 8.03 (1H, s, H-11), 3.61 (3H, s, OCH₃-1), 3.90 (3H, s, OCH₃-9), 3.75 (1H, dd, 4.5, 13.5 Hz, H-6a), 2.99 (2H, m, H-5), 3.34 (1H, m, H-5), 2.73 (1H, dd, 4.5, 13.5 Hz, H₆-7), 2.62 (1H, d, 13.5 Hz, H₅-7), 2.67/2.98 (2H, m, H-4).

¹³C-NMR (125 MHz, methanol-d₄) δC (ppm): 144.5 (C-1), 127.7 (C-1a), 126.9 (C-1b), 150.9 (C-2), 115.5 (C-3), 130.5 (C-3a), 28.9 (C-4), 43.8 (C-5), 54.9 (C-6a), 36.9 (C-7), 130.2
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(C-7a), 115.8 (C-8), 147.8 (C-9), 147.2 (C-10), 113.0 (C-11), 124.9 (C-11a), 60.3 (C-1-OCH₃), 56.7 (C-9-OCH₃).

![Chemical structure of compound 1-4.](image)

**Icariside E3 (2)**

White amorphous powder; ESI-MS: m/z 525 [M+H]⁺, C₂₅H₃₁O₁₁, [α]D = -61.0° (c 1.0, MeOH).

¹H NMR (500 MHz, methanol-d₄) δH (ppm): 6.73 (1H, s, H-2), 6.73 (1H, s, H-6), 2.65 (1H, t, H-7), 1.83 (1H, m, H-8), 3.57 (1H, t, H-9), 6.58 (1H, d, 1.5 Hz, H-2’), 6.59 (1H, d, J≈ 8.0 Hz, H-5’), 6.49 (1H, d, 1.5, 8.0 Hz, H-6’), 2.71 (1H, dd, 9.5, 14.0 Hz, H-6”), 2.99 (1H, dd, 5.0, 13.5 Hz, H-7”), 3.99 (1H, m, H-8”), 3.76 (1H, m, H-9”), 3.81 (3H, s, OCH₃), 3.71 (3H, s, OCH₃), Glu: 4.63 (1H, d, 7.5 Hz, H-1”), 3.45 (1H, m, H-2”), 3.14 (1H, m, H-3”), 3.40 (1H, m, H-4”), 3.41 (1H, m, H-5”), 3.69 (1H, m, H-6”), 3.80 (1H, m, H-6”).

¹³C-NMR (125 MHz, methanol-d₄) δC (ppm): 140.3 (C-1), 111.8 (C-2), 153.1 (C-3), 143.6 (C-4), 138.5 (C-5), 120.4 (C-6), 33.1 (C-7), 35.5 (C-8), 62.2 (C-9), 133.3 (C-1’), 113.7 (C-2’), 148.4 (C-3’), 145.3 (C-4’), 115.6 (C-5’), 122.6 (C-6’), 39.2 (C-7’), 42.8 (C-8’), 67.1 (C-9’), 56.4 (C-3-OCH₃), 56.3 (C-3’-OCH₃), 105.6 (C-1”), 75.9 (C-2”), 78.1 (C-3”), 71.3 (C-4”), 77.9 (C-5”), 62.5 (C-6”).

(-)-Pinoresinol (3): Colorless oil, [α]D²⁵: -84.4° (c 0.1, CHCl₃). ESI-MS (m/z): 341 [M+H-H₂O]⁺.

¹H NMR (500 MHz, CD₃OD) δH (ppm): 3.13 (1H, m, H-1/H-5), 4.70 (1H, d, 4.5, H-2/H-6), 6.96 (1H, d, 1.5, H-2’/H-2”), 6.76 (1H, d, 8.0, H-5’/H-5”), 6.81 (1H, dd, 1.5, 8.0, H-6”/H-6”), 3.86 (3H, s, OCH₃/3’/OCH₃”), 4.23 (1H, m, H₃a/H₃b), 3.83 (1H, m, H₃a/H₃b).

¹³C-NMR (125 MHz, CD₃OD) δC (ppm): 55.2 (C-1/C-5), 85.6 (C-2/C-6), 71.2 (C-4/C-8), 134.1 (C-1’/C-1”), 110.6 (C-2”/C-2’”), 146.8 (C-4”/C-4”), 115.5 (C-5’/C-5’”), 119.6 (C-6”/C-6”), 56.2 (C-3’-OCH₃/C-3’-OCH₃).

**Maltol O-β-D-glucopyranoside (4)**

White amorphous powder; ESI-MS: m/z 289 [M+H]⁺, C₁₂H₁₆O₁₈.
$^1$H-NMR (500 MHz, CD$_3$OD) $\delta_{H}$ (ppm): 6.46 (1H, d, 6.0 Hz, H-5), 8.02 (1H, d, 6.0 Hz, H-6), 2.49 (3H, s, -CH$_3$), 4.85 (1H, d, H-1'). Glu: 3.41 (1H, dd, H-2'), 3.41 (1H, dd, H-3'), 3.37 (1H, dd, 2.0, 9.5 Hz, H-4'), 3.27 (1H, m, H-5'), 3.86 (1H, m, H-6'), 3.69 (1H, dd, 3.5, 12.0, H$_{-6''}$).

$^{13}$C-NMR (125 MHz, CD$_3$OD) $\delta_{C}$ (ppm): 164.2 (C-2), 143.6 (C-3), 177.2 (C-4), 117.3 (C-5), 157.1 (C-6), 105.5 (C-1'), 75.4 (C-2'), 78.6 (C-3'), 71.2 (C-4'), 78.0 (C-5'), 62.6 (C-6').

3. RESULT AND DISCUSSION

Compound 1 was separated as the white amorphous powder. The $^1$H-NMR showed two methoxyl protons at $\delta_{H}$ 3.90 (3H, s) and 3.61 (3H, s), respectively. Seven aliphatic protons were observed at the high chemical shift from $\delta$ 2.60 to 3.75 ppm, expected of protons of H-4, H-5, H-6a, and H-7. A singlet proton at $\delta$ 6.59 was determined to be the signal at H-3, confirming that C-1 and C-2 were substituted. Two singlet signals seen at $\delta$ 8.03, 6.74 were assigned to the protons at H-11 and H-8. These values were typical of a 9,10 substitution pattern of aporphine moiety. The H-5 proton appeared at the lower field compared to H-4 due to the neighboring N-atom adjacent to C-5.

The $^{13}$C-NMR showed 18 carbon signals, including three aromatic carbons, four aliphatic carbons, nine quaternary carbons, and two methoxyl groups.

HSQC spectrum determined the correlation between proton and carbon; H-3/C-3, H-4/C-4, H-7/C-7, H-6a/C-6a, H-5/C-5, H-8/C-8, H-9-OMe/C-9-OMe, H-1-OMe/C-1-OMe and H-11/C-11.

The HMBC cross peaks from H-3 ($\delta_{H}$ 6.59) to C-2 ($\delta_{C}$ 150.6)/C-1 ($\delta_{C}$ 144.5)/C-1b ($\delta_{C}$ 126.9)/C-4 ($\delta_{C}$ 28.9); from H-4 ($\delta_{H}$ 2.67) to C-3 ($\delta_{C}$ 115.5)/C-3a ($\delta_{C}$ 130.2), C-5 ($\delta_{C}$ 43.8); from the methoxyl proton signals at $\delta$ 3.61 to C-1 ($\delta_{C}$ 144.5) determined the positions and chemical shift of C-2/C-1/C-3/C-4. The HMBC interactions between H-5 and C-4 ($\delta_{C}$ 28.9), C-3a ($\delta_{C}$ 130.2), C-6a ($\delta_{C}$ 54.9), allowing to determine the position and chemical shift of C-3a/C-5/C-6a. The HMBC interaction between H-7 ($\delta_{H}$ 2.62; 2.73) and C-6a ($\delta_{C}$ 54.9), C-1b ($\delta_{C}$ 126.9), C-7a ($\delta_{C}$ 130.5), C-8 ($\delta_{C}$ 115.8) determined the position and chemical shift of C-1b and C-7a. The interaction between H-8 ($\delta_{H}$ 6.74) and C-9 ($\delta_{C}$ 147.8), C-11a ($\delta_{C}$ 147.8), C-7 ($\delta_{C}$ 36.9) was similar to the appearance of HMBC interaction between H-11 (8.03) and C-10, -11a, C-7a, which determined the position and chemical shift of carbon in the remaining aromatic rings. Moreover, the ESI-MS of 1 showed an ion peak at m/z 314 [M+H]$^+$ corresponding to the molecular formula of C$_{18}$H$_{19}$NO$_4$. Based on these data, 1 was identified to be laetanane, an alkaloid previously reported from Hernandia voyronhi [4].

Compound 2 was obtained as white amorphous powder. The $^1$H-NMR showed five aromatic ring protons of different spin-spin interaction, including the ABX coupling protons at $\delta_{H}$ 6.49 (1H, dd, $J$ = 1.5, 8.0, H-6'), 6.58 (1H, d, $J$ = 1.5 Hz, H-2'), 6.59 (1H, d, $J$ = 8.0 Hz, H-5'); the AX coupling protons at $\delta_{H}$ 6.7H 6.73 (1H, s, H-2), 6.73 (1H, s, H-6). Two methoxyl group protons at $\delta_{H}$ 3.71 (3H, s), 3.82 (3H, s). Combined with $^{13}$C-NMR spectrum, 26 carbon signals, including seven quaternary carbon, four aromatic carbon, six aliphatic carbons, confirmed that the appearance of a lignan aryltetralins moiety. The glucopyranose moiety was suggested by the appearance of an anomeric proton at $\delta_{H}$ 4.63 (doublet, $J$ = 7.5 Hz) in the $^1$H-NMR and presence of six carbons at $\delta_{C}$ 105.6; 62.5; 78.0; 77.8; 75.9; 71.2 in the $^{13}$C-NMR.

The protons and carbons were confirmed by HMBC spectra. The cross peaks from H-6 ($\delta_{H}$ 6.73) to C-7 ($\delta_{C}$ 33.1)/C-8' ($\delta_{C}$ 42.7)/C-4 ($\delta_{C}$ 143.6); from H-2 ($\delta_{H}$ 6.73) to C-7 ($\delta_{C}$ 33.1), C-4 ($\delta_{C}$ 143.6), C-6 ($\delta_{C}$ 120.3); from anomeric proton to C-4 ($\delta_{C}$ 143.6), determined the position and
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chemical shift of C-7, C-8, C-4 and sugar molecule positions attached to the aglycone at C-4. The HMBC correlations between H-8′ (δ_H 3.95) and C-6 (δ_C 120.4) determined the position and chemical shift of C-2 (δ_C 111.7) and C-6 (δ_C 120.4). The HMBC cross peak from 3-OCH_3 (δ_H 3.82) to C-3 (δ_C 153.1), from H-7 (δ_H 2.65) to C-1 (δ_C 140.3)/C-8 (35.5) confirmed the position of C-3, C-1, C-8. The position of hydroxyl group attached to C-9, C-9′ and quaternary carbon C-5 was determined based on the HMBC’s correlation between H-9 (δ_H 3.59) and C-7 (δ_C 33.1), C-8 (δ_C 35.5); H-9′ (δ_H 3.68, 3.78) with C-7′ (δ_C 39.2) and C-5 (δ_C 138.53). The HMBC correlation between H-6′ (δ_H 3.68) and C-7′ (δ_C 33.1)/C-2′ (δ_C 113.7)/C-5′ (δ_C 115.6)/C-4′ (δ_C 145.3), determining the position of C-7′, C-4′. Interaction between H-7′ (δ_H 2.99) and C-1′ (δ_C 133.3)/C-6′(δ_C 122.6)/C-9′ (δ_C 67.1), C-2′ (δ_C 113.7), identified the position and chemical shift of C-1′, C-6′, C-5′, C-9′, C-2′. The positions of methoxyl and hydroxyl groups at C-3′ was determined based on the HMBC correlation between the proton of the 3′-OCH_3 (δ_H 3.71) with C-3′ (δ_C 148.4). Moreover, The ESI-MS of 2 showed an ion peak at m/z 526 [M+H]^+ corresponding to the molecular formula of C_{29}H_{31}O_{11}.

The spectroscopic data of 2 was confirmed by comparison with Icariside E3 [5]. Consequently the structure of 2 elucidated as Icariside E3. This is the first report of this compound from genus Phoebe.

Compound 3 was received as a colorless oily substance. The $^1$H-NMR spectrum of 1 appeared the signal cluster of the three-position substituted aromatic ring with ABX interaction system at δ 6.79 (d, J = 8.0 Hz), δ 6.84 (dd, J = 2.0, 8.0 Hz) and δ 6.99 (d, J = 2.0 Hz). There are also signals of an oximetilen group at δ 6.47 (d, J = 4.5 Hz), an oximetilen group at δ 4.21 (m) and δ 3.79 (m), a metin group at δ 3.09 (m) and a methoxyl group at δ 3.84 (s). On the $^{13}$C-NMR and DEPT spectrum of 1, there are signals of 10 carbon atoms, including 6 at δ 110.6 (CH), 115.5 (CH), 119.6 (CH), 134.1 (C), 146.8 (C), 148.3 (C) belong to an aromatic ring, the remaining four signals included δ 56.2 (OCH_3), 55.2 (CH), 86.6 (CH-O), 72.2 (CH_2-O). The chemical shift values of H-C are accurately assigned and given based on HSQC spectra. In addition to the aromatic ring replaced by 3 positions as analyzed above, the existence of CH_2(O)-CH-CH_2(O) was determined by H-H coza spectroscopy based on the interaction between H-1 (δ 3.09) and H-2 (δ 4.67); H-5 (δ 3.09) with H-4 (δ 4.21 and 3.79); Besides, HMBC interaction between H-1 (δ 3.09) and C-5 (δ 55.2); H-2 (δ 4.67) with C-1 (δ 55.2) / C-4 (δ 72.2); H-4 (δ 4.21 / 3.79) with C-2 (δ 86.6) /C-5 (δ 55.2) as well as displacement value of CH_2O group (δ_C 72.2) a sharp shift towards the weak field allows for a close of this branch. Thus, the molecular formula of 3 will be C_{32}H_{28}O_{11}. However, when measuring the ESI-MS mass spectrometry of this compound, it appeared that the ion peak m/z 341 [M + H_2O]^+ corresponded to the molecular formula C_{29}H_{31}O_{11}. This result shows that the molecule of compound 3 is symmetrical with the second axis and was completely consistent with NMR spectra. The HMBC from H of OCH_3 to C-3′; from H-2 to C-1/C-1′; from H-1 to C-1′ demonstrated the structure of compound 3 as indicated above. In addition, The NMR spectroscopy and [α]D$^2$ = -84.4° (c 0.1, CHCl_3) of compound 3 were consistent with compound (-)-pinoresinol proved that substance 3 was (-)-pinoresinol or (-)-2,6-bis (4′-hydroxy-3′-methoxy-phenyl) -3,7-dioxabicyclo[3,3,0] octane. The spectroscopic data of 3 was confirmed by comparison with (-)-pinoresinol [6]. Consequently the structure of 3 was elucidated (-)-pinoresinol.

Compound 4 was obtained as a white amorphous powder. The $^1$H-NMR showed the signal of 2 aromatic protons at δ_H 6.46 (1H, d, 6.0), 8.02 (1H, d, 6.0), located at H-5 and H-6, confirming that the other carbons of the ring is substituted. $^{13}$C-NMR spectrum of compound 1, showing a total of 12 carbon signals, of which, there is one carbon signal of ketone group at C-4.
\( \delta_C \) 177.2, 3 signals of the quaternary carbon at \( \delta_C \) 164.2; 157.1; 143.6. These values indicated the appearance of a maltol ring in the molecule. Six typical carbon signals of glucopyranose molecule at \( \delta_C \) 105.5; 78.6; 78.0; 75.4; 71.2; 62.6.

The HSQC spectrum showed that the anomeric proton is at the chemical displacement range of the solvent, which had direct interaction with C-1' (105.5). On the other hand, the HMBC spectrum, there was an interaction between anomic proton and C-3 (143.6), confirmed that the sugar moiety linked to C-3 of the aglycone. HMBC interaction between H-5 (6.46) and C-4 (177.2), C-6 (157.1), C-3 (143.6) allowed determining the position and chemical shift of C-4 and C-6. HMBC interaction of proton H-6 (8.02) to C-2 (164.2), C-5 (117.3), C-4 (177.2). Besides, the interaction between -CH3 (2.49) and C-3, C-2, determining the position and chemical shift of C-5 and C-2. The proton coupling constant of H-1’ revealed this proton was axial orientation. All the NMR data of 4 were consistent with the corresponding data of maltol O-\( \beta \)-D-glucopyranoside. Furthermore, the ESI-MS of 4 exhibited an ion peak at m/z 289 [M+H]’ corresponding to the molecular formula of C_{12}H_{15}O_{18}. Hence, the structure of 4 was determined as maltol O-\( \beta \)-D-glucopyranoside [7]. This compound was firstly isolated from Phoebe genus.

4. CONCLUSIONS

Based on chromatography methods combined with spectroscopic evidences (MS-ESI, NMR), 4 compounds laetanine (1), icariside E3 (2), (-) pinoresinol (3) maltol O-\( \beta \)-D-glucopyranoside (4) were isolated from the methanol extract of Phoebe tavoyana (Meissn) Hook. Of which icariside E3 (2) and maltol O-\( \beta \)-D-glucopyranoside (4) were firstly isolated from this species. This research contributed to clarify the chemical composition of Phoebe in Vietnam.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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