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# A NEW BENZENOID OF *Elaeagnus grandifolia*

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*A new benzenoid, 2,3-(methylenedioxy)-6-methylbenzene-1,4,5-triol (1) and seven known compounds (2–8) were isolated from the stems of* Elaeagnus grandifolia *Hayata. The structure of the new benzenoid was elucidated by chemical and physical evidence.*

**Keywords**: *Elaeagnus grandifolia*, triol, benzenoid.

There are about 90 species of *Elaeagnus* around the world. The majority are native to the temperate and subtropical regions in Asia, of which nine species can be found in Taiwan [1]. Many species of *Elaeagnus* are considered folk medicinal plants, e.g., *E. umbellate* [2], *E. pungens* [3], *E. angustifolia* [4], and *E. multiflora* [5]. Triterpenoids, steroids, and flavonoids have been isolated from several species of *Elaeagnus*, e.g., *E. ungens* [6], *E. umbellate* [6], *E. bockii* [7], *E. orientalis* [8], and *E. pungens* [9, 10]. Earlier investigations on the chemical constituents of stems of *E. grandifolia* with 16 compounds, including four flavonoids, 5-hydroxy-7,4′-dimethoxyflavone, 5-hydroxy-7,3′,4′-trimethoxyflavone, 5,3′-dihydroxy-7,4′-dimethoxyflavone, and 5,4′-dihydroxy-7,3′-dimethoxyflavone; two amides, *N-trans*-feruloyltyramine and *N-trans*-caffeoyltyramine; five benzenoids, *p*-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, syringaldehyde, *trans*-methyl *p*-coumarate, and thalictoside; one purine, uridine; and four steroids, *β*-sitosterol, stigmasterol, *β*-sitostenone, and stigmastenone [11]. In the course of screening for biologically and chemically novel agents from *Formosan eleagnaceous* plants [11–13], *E. grandifolia* Hayata was chosen for further phytochemical investigation. Investigation of the stems of *E. grandifolia* Hayata has led to the isolation and characterization of 8 compounds, one new benzenoid: 2,3-(methylenedioxy)-6-methylbenzene-1,4,5-triol (**1**); four known benzenoids, salicylic acid (**2**) [14], vanillic acid (**3**) [15], ferulic acid (**4**) [16], and isoferulic acid (**5**) [17]; and three lignans, (+)-medioresinol (**6**) [18], (+)-pinoresinol (**7**) [19], and (+)-syringaresinol (**8**) [20]. In this paper, we report the isolation and structural elucidation of this new benzenoid.

2,3-(Methylenedioxy)-6-methylbenzene-1,4,5-triol (**1**) was isolated as a white powder from MeOH. Its molecular formula, $C_8H_8O_5$, was established by HR-ESI-MS. The UV spectrum of **1** contained absorption bands typical of the methylene-dioxybenzene [14]. Its showed the presence of a hydroxy (3500 $cm^{-1}$), a phenyl (1590 and 1510 $cm^{-1}$), and a methylenedioxy group (1070 and 920 $cm^{-1}$) from its IR spectrum [21].

The $^1H$ NMR spectrum of compound **1** revealed the presence of a methyl group at δ 2.08 and methylenedioxy protons at δ 5.83. The $^{13}C$ NMR and DEPT experiments of compound **1** exhibited eight resonance lines, consisting of one methyl carbon, one methylene carbon, and six quaternary carbons. The structural assignment of compound **1** was further supported by 2D NMR experiments. The HSQC experiment revealed that the carbon signals at δ 101.9 for the methylene group and δ 15.7 for the $CH_3$-6 correlated with the proton signals at δ 5.83 for $OCH_2O$ and δ 2.08 for $CH_3$-6, respectively. Based on these correlations, the structure of compound **1** was determined to be a new benzenoid, which was further confirmed by the HMBC experiment (Table 1).

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**Salicylic acid (2)** as in [14], white needles ($CHCl_3$), mp 159–161°C.

**Vanillic acid (3)** as in [15], colorless needles (MeOH), mp 210–212°C.

**Ferulic acid (4)** as in [16], brown powder.

**Isoferulic acid (5)**, white powder. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.79 (3H, s, 6-$OCH_3$), 6.23 (1H, d, J = 16.0, H-2), 6.83 (1H, d, J = 8.2, H-8), 6.96 (1H, dd, J = 8.2, 2.0, H-9), 7.04 (1H, d, J = 2.0, H-5), 7.56 (1H, d, J = 16.0, H-3) [17].

**(+)-Medioresinol (6)**, brown powder ($CHCl_3$), $[\alpha]_D^{25}$ +11.9° (*c* 0.50, $CHCl_3$). UV (MeCN, $\lambda_{max}$, nm): 210, 282, 292. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.10 (2H, m, H-1, 5), 3.88 (2H, m, H-4ax, 8ax), 3.90 (6H, s, 2 × $OCH_3$), 3.91 (3H, s, $OCH_3$), 4.27 (2H, m, H-4eq, 8eq), 4.73 (2H, dd, J = 11.6, 4.4, H-2, 6), 5.49 (1H, s, OH), 5.60 (1H, s, OH), 6.58 (2H, s, H-2″, 6″), 6.82 (1H, dd, J = 8.4, 2.0, H-6′), 6.89 (1H, d, J = 8.4, H-5′), 6.90 (1H, d, J = 2.0, H-2′) [18].

**(+)-Pinoresinol (7)**, yellow powder ($CHCl_3$), $[\alpha]_D^{25}$ +18.6° (*c* 0.40, $CHCl_3$). UV (MeCN, $\lambda_{max}$, nm): 235, 285. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.09 (2H, m, H-1, 5), 3.89 (2H, dd, J = 9.2, 3.8, H-4ax, 8ax), 3.91 (6H, s, 2 × $OCH_3$), 4.25 (2H, dd, J = 9.2, 7.0, H-4eq, 8eq), 4.74 (2H, d, J = 4.5, H-2, 6), 5.96 (2H, s, 2 × OH), 6.82 (2H, dd, J = 8.0, 2.0, H-6′, 6″), 6.89 (2H, d, J = 2.0, H-2′, 2″), 6.90 (2H, d, J = 8.0, H-5′, 5″) [19].

**(+)-Syringaresinol (8)**. $^1$H NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.11 (2H, m, H-1, 5), 3.91 (12H, s, 4 × $OCH_3$), 3.91 (2H, dd, J = 9.6, 3.6, H-4ax, 8ax), 4.28 (2H, dd, J = 9.6, 6.8, H-4eq, 8eq), 4.74 (2H, d, J = 4.3, H-2, 6), 5.50 (2H, s, 2 × OH), 6.59 (4H, s, H-2′, 2″, 6′, 6″) [20].


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# A NEW BENZENOID OF *Crithmum maritimum*

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*A new benzenoid, junzhibutanol (**1**), along with eight known compounds (**2–9**), were isolated from the stems of* Crithmum maritimum *L. Compounds **2–8** were isolated from this source for the first time. The structure of the new benzenoid was elucidated by chemical and physical evidence.*

**Keywords**: Sea fennel, *Crithmum maritimum* L., Apiaceae, benzenoid.

Sea fennel (*Crithmum maritimum* L.) is a perennial halophyte also known as samphire, crest marine, marine fennel, and rock samphire, which grows spontaneously on sandy beaches, maritime rocks, breakwaters, and piers of all the world's coastlines, being particularly abundant along the coasts of Mediterranean countries [1]. In many parts of the world, sea fennel is used as a food ingredient for several traditional recipes. It is especially known for its good sensory traits, owing to its high essential oils content [2]. In the past, sea fennel was used in folk medicine to prevent scurvy and for vermifuge and diuretic effects [1]. Today, sea fennel enjoys a good reputation as a traditional remedy in some Mediterranean regions. For example, in Spain, pickled leaves are eaten as a digestive and for its antiscorbutic and diuretic properties [3]. In Northern regions, the sea fennel decoction is used in folk medicine to take care of the urogenital apparatus and liver, whereas in southern Italy, the same decoction is considered a useful remedy for treating whooping cough and cold [4, 5]. At the same time, for inhabitants of central Italy, the leaf juice is traditionally used for its depurative, diuretic, and carminative effect, whereas the fruits infusion is used for its stomachic, digestive, and carminative properties [6]. Sea fennel leaves contain a significant amount of compounds such as ascorbic acid, carotenoids, tannins, and flavonoids [7–10]. Low amounts of apigenin, rutin, quercetin-3-galactoside are also reported [11]. These observations provide useful information for potential chemopreventive drug design. The MeOH extract of its stems was subjected to solvent partitioning and chromatographic separation to afford eight pure compounds. The chemical constituents in the stems of *C. maritimum* were separated with column chromatography. Investigation of the stems of *C. maritimum* has led to the isolation and characterization of nine compounds, one new benzenoid: junzhibutanol (**1**); eight known compounds, salicylic acid (**2**) [12], vanillic acid (**3**) [13], ferulic acid (**4**) [14], isoferulic acid (**5**) [15], (+)-medioresinol (**6**) [16], (+)-pinoresinol (**7**) [17], (+)-syringaresinol (**8**) [18], and (+)-(3*R*,8*S*)-falcarindiol (**9**) [19]. Compounds **1–8** were obtained for the first time from this plant and identified by direct comparison with authentic sample and literature [12–19].

Junzhibutanol (**1**) was obtained as a colorless oil. Its molecular formula, $C_{12}H_{16}O_4$, was established by HR-ESI-MS. The UV spectrum of **1** contained absorption bands typical of the methylenedioxybenzene [20]. Its showed the presence of a hydroxyl (3400 $cm^{-1}$), a phenyl group (1660 and 1510 $cm^{-1}$), and a methylenedioxy (1040 and 935 $cm^{-1}$) group from its IR spectrum [20].

The $^1H$ NMR spectrum of compound **1** revealed the presence of two aromatic protons at δ 6.54 (2H, s, H-4, 6), methylenedioxy protons at δ 5.95, two methylene protons at δ 1.70 (2H, m, H-3′) and 1.79 (2H, m, H-2′), one methine proton at δ 4.50 (1H, m, H-1′), and one methyl proton at δ 0.91 (3H, t, J = 7.5, H-4′), indicating that **1** was probably a trisubstituted phenylalkanoid. A singlet at δ 3.91 (3H, s) was assigned to 7-OMe. The $^{13}C$ NMR and DEPT experiments of compound **1** exhibited 12 resonance lines, consisting of two methyl carbons, three methylene carbons, three methine carbons and four quaternary carbons. The structural assignment of compound **1** was further supported by 2D NMR experiments.

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**(+)-Medioresinol (6)** as in [16], brown powder ($CHCl_3$), $[\alpha]_D^{25}$ +11.9° (*c* 0.50, $CHCl_3$). UV (MeCN, $\lambda_{max}$, nm): 210, 282, 292. IR ($\nu_{max}$, $cm^{-1}$): 3500, 1610, 1500. $^1H$ NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.10 (2H, m, H-1, 5), 3.88 (2H, m, H-4ax, 8ax), 3.90 (6H, s, 2 × $OCH_3$), 3.91 (3H, s, $OCH_3$), 4.27 (2H, m, H-4eq, 8eq), 4.73 (2H, dd, J = 11.6, 4.4, H-2, 6), 5.49 (1H, s, OH), 5.60 (1H, s, OH), 6.58 (2H, s, H-2″, 6″), 6.82 (1H, dd, J = 8.4, 2.0, H-6′), 6.89 (1H, d, J = 8.4, H-5′), 6.90 (1H, d, J = 2.0, H-2′).

**(+)-Pinoresinol (7)** as in [17], yellow powder ($CHCl_3$), $[\alpha]_D^{25}$ +18.6° (*c* 0.40, $CHCl_3$). UV (MeCN, $\lambda_{max}$, nm): 235, 285. IR ($\nu_{max}$, $cm^{-1}$): 3400, 1610, 1500. $^1H$ NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 3.09 (2H, m, H-1, 5), 3.89 (2H, dd, J = 9.2, 3.8, H-4ax, 8ax), 3.91 (6H, s, 2 × $OCH_3$), 4.25 (2H, dd, J = 9.2, 7.0, H-4eq, 8eq), 4.74 (2H, d, J = 4.5, H-2, 6), 5.96 (2H, s, 2 × OH), 6.82 (2H, dd, J = 8.0, 2.0, H-6′, 6″), 6.89 (2H, d, J = 2.0, H-2′, 2″), 6.90 (2H, d, J = 8.0, H-5′, 5″).

**(+)-Syringaresinol (8)** as in [18].

**(+)-(3*R*,8*S*)-Falcarindiol (9)** as in [19], colorless oil, $[\alpha]_D^{25}$ + 15.02° (*c* 0.01, $CH_2Cl_2$). UV (MeCN, $\lambda_{max}$, nm): 230, 275, 291. IR ($\nu_{max}$, $cm^{-1}$): 3200, 2210, 1700. $^1H$ NMR (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.85 (3H, t, J = 6.8, H-17), 1.24 (8H, m, H-13–16), 1.34 (2H, m, H-12), 2.06 (2H, q, J = 7.2, H-11), 4.89 (1H, d, J = 5.2, H-3), 5.15 (1H, d, J = 8.0, H-8), 5.20 (1H, d, J = 10.0, H-1a), 5.41 (1H, d, J = 16.0, H-1b), 5.47 (1H, dd, J = 10.8, 8.0, H-9), 5.54 (1H, dt, J = 10.8, 7.2, H-10), 5.89 (1H, ddd, J = 16.0, 10.0, 5.2, H-2). $^{13}C$ NMR (100 MHz, $CDCl_3$, δ, ppm): 13.9 (C-17), 22.5 (C-16), 27.5 (C-11), 28.9 (C-14), 29.0 (C-13), 29.2 (C-12), 31.7 (C-15), 58.2 (C-8), 63.1 (C-3), 68.6 (C-6), 70.1 (C-5), 78.2 (C-7), 79.7 (C-4), 117.1 (C-1), 127.6 (C-9), 134.1 (C-10), 135.7 (C-2).

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