Chemical Constituents of *Taraxacum formosanum*

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Three new compounds, taraxacine-A (1), taraxacine-B (2) and taraxafolin (3) together with twenty-five known compounds, which include two \( \beta \)-carboline alkaloids, two indole alkaloids, two chlorophylls, two flavonoids, one coumarin, two triterpenoids, one monoterpenoid, one ionone, four steroids and eight benzenoids, were isolated and characterized from the fresh aerial parts of *Taraxacum formosanum*. Structures of new compounds were determined by spectral analysis.

Key words: *Taraxacum formosanum*; Compositae; \( \beta \)-carboline alkaloid

*Taraxacum formosanum* is a herbaceous plant belonging to a family Compositae, distributed mainly in the littoral areas of north Taichung in Taiwan. Some species of the genus, *Taraxacum*, have been used in folk medicine to treat lactation, and as diuretic, antimastopathy and anti-inflammatory agent. Earlier pharmacological studies on this plant revealed that the crude extract showed an *in vitro* bactericidal effect against *Staphylococcus aureus* and inhibitory action against *Mycobacterium tuberculosis* and *Leptospira*. It is also a safe herb with an LD \(_{50}\) of 59 g/kg in mice and has a record of relatively few side effects. However, *T. formosanum* was hitherto uninvestigated for its chemical constituents. As a part of our ongoing phytochemical work on Chinese medicinal plants, we have examined the aerial parts of *T. formosanum*, which resulted in the isolation of three new and twenty-five known compounds. This paper deals with the structural determination of two new \( \beta \)-carbolines, taraxacine-A (1) and taraxacine-B (2), and one phenylpropanoid, taraxafolin (3) by means of spectral analysis. This is the first report of the isolation of \( \beta \)-carboline alkaloids from the genus of *Taraxacum*.

Results and Discussion

Taraxacine-A (1) was obtained as pale yellow syrup, which gave a positive reaction with Dragendorff’s reagent, indicating it to be an alkaloid. The molecular formula was established as \( \text{C}_{13}\text{H}_{10}\text{N}_{2}\text{O}_{3} \) by high resolution electron impact (HR-EI)-MS. The UV absorptions at 216, 232, 270, 287 (sh), 303, 333 and 346 nm characteristic of a \( \beta \)-carboline alkaloid. Its IR absorption bands suggested the presence of amine \((3200\ \text{cm}^{-1})\), carboxyl \((1721\ \text{cm}^{-1})\), and aromatic \((1437\ \text{cm}^{-1})\) groups. Presence of carboxylic acid group was also supported by a prominent fragment ion \([\text{M} – \text{CO}_2\text{H}]^{+}\) peak at \( m/z \) 199 in EI-MS spectrum. The \( ^1\text{H}-\text{NMR} \) spectrum showed four adjacent aromatic proton system at \( \delta \ 8.31\ (1\text{H}, \text{d}, J = 8.0\ \text{Hz}, \text{H-5}), 7.97 \ (1\text{H}, \text{d}, J = 8.0\ \text{Hz}, \text{H-8}), 7.85 \ (1\text{H}, \text{t}, J = 8.0\ \text{Hz}, \text{H-7}), \text{and } 7.54 \ (1\text{H}, \text{t}, J = 8.0\ \text{Hz}, \text{H-6}), \) and a singlet at \( \delta \ 9.07 \) (H-4) corresponding to heteroaromatic proton and a methoxy signal at \( \delta \ 4.24 \) (3H, s, 1-OCH\(_3\)). Two broad singlets at \( \delta \ 13.46, \) and 10.14 \((\text{each } 1\text{H}, \text{br s}, \text{D}_2\text{O exchangeable})\) were attributed to –OH, and NH, respectively. The downfield shift of H-4 signal to \( \delta \ 9.07 \) suggested that a carbonyl group was attached to C-3. It was confirmed by the nOe signal between H-4 and H-5. From the foregoing spectral analyses, the structure 2 was assigned to taraxacine-B.

Taraxafolin (3) was isolated as optically active colorless syrup with a molecular formula of \( \text{C}_{11}\text{H}_{14}\text{O}_{5} \), deduced from its HR-EI mass spectrum. Its UV absorption bands at 234 (sh), 249 (sh), 291, and 326 nm indicated the presence of aromatic ring. IR absorption bands at 3331, and 1713 cm\(^{-1}\) inferred the hydroxyl, and carbonyl groups, respectively. Accordingly, a D\(_2\)O exchangeable broad singlet integrated for two protons was observed at \( \delta \ 7.85 \) in \( ^1\text{H}-\text{NMR} \) spectrum. The \( ^1\text{C}-\text{NMR} \) spectrum of 3 also showed the presence of two methoxyl groups at \( \delta \ 3.61 \) (3H, s), and 3.12 (3H, s), a methylene group at \( \delta \ 2.69 \) (1H, dd, \( J = 15.2, 9.2\ \text{Hz} \)), and 2.50 (1H, dd, \( J = 15.2, 4.8\ \text{Hz} \)), and an oxymethylene group at \( \delta \ 4.45 \) (1H, dd, \( J = 9.2, 4.8\ \text{Hz} \)), corresponding to a \(-\text{CH}(\text{OCH}_3)\text{-CH}_2\text{COOCH}_3 \) moiety. The presence of trisubstituted phenyl ring was confirmed by an ABX pattern signals at \( \delta \ 6.82 \) (1H, \( d, J = 2.0\ \text{Hz} \)), 6.80 (1H, \( d, J = 8.0\ \text{Hz} \)), and 6.68 (1H, \( d, J = 8.0, 2.0\ \text{Hz} \)), attributable to H-2’, 5’, and 6’, respectively.

The \( ^{13}\text{C}-\text{NMR} \) spectrum, combined with \( ^1\text{H}-\text{detected heteronuclear multiple quantum coherence} \) (HMOC) and heteronuclear multiple bond connectivity (HMBC) experiments, suggested a methyl 3-(3’-4’-dihydroxyphenyl)-3-methoxy propionate nucleus for compound 3. In the HMBC spectrum, the signals at \( \delta \ 4.45 \) showed \( ^2\text{J},^3\text{J}-\text{correlations with methoxy carbon (\( \delta_c \ 55.9 \)) and with C-6’ (\( \delta_c \ 118.7 \)) and C-2 (\( \delta_c \ 43.4 \)).

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suggested that methoxyl group was attached to C-3. It was further confirmed by the EI-MS, which showed a fragmentation ion, [M-CH3COOCH3]+ at m/z 153. The negative optical rotation of 3 inferred the S stereochemistry for C-3. 5 Consequently, the structure of (S)-taraxafolin was assigned as 3.

The known compounds, 3-carboxy-1,2,3,4-tetrahydro-β-carboline, 2 1,2,3,4-tetrahydro-1,3,4-triexo-β-carboline, indole-3-carboxaldehyde, indole-3-carboxylic acid, 13 hydro-(13 R)-p-hydroxyphenyl acetic acid methyl ester, 19 phenylalanine, benzoic acid, 18 methyl paraben, 17 p-hydroxyphenyl acetic acid methyl ester, 19 (3R,6R,7E)-3-hydroxy-4,7-megastigma-dien-9-one, 20 2,6,6-trimethyl-4-hydroxy-1-cyclohexene-1-carboxaldehyde, 21 β-sitosterol, 20 β-sitosteryl-3-0-glucoside, 20 and stigmasteryl-3-0-glucoside, 20 were also isolated and identified by comparison of their spectral data with corresponding literature values.

**Experimental**

Melting points were measured on a Yanagimoto MP-S3 micromelting point apparatus and were uncorrected. The UV spectra were recorded on a Jasco P-1010 polarimeter. 

**Extraction and Isolation**

The fresh aerial parts of *T. formosanum* (4.68 kg) were extracted with MeOH (10×6) under reflux for 8 h and concentrated to give brown syrup (230.2 g). The syrup was suspended in H2O and subjected to column chromatography over silica gel and eluted with a gradient of n-hexane and EtOAc mixtures yielded 4',5'-dihydroxy-3'-hydroxy-(132-R)-p-hydroxyphenyl-beta(2.8 mg). The second fraction was repeatedly column chromatographed over silica gel with CHCl3. MeOH gradients to afford taraxacine-B (2) (3.0 mg), (S)-taraxafolin (3) (2.3 mg), 1,2,3,4-tetrahydro-1,3,4-triexo-β-carboline (2.0 mg), indole-3-carboxylic acid (10.0 mg), isosingenol-7-O-glucosyl-2'-0-glucoside (39.4 mg), aesculetin (1.4 mg), p-hydroxy-cinnamic acid (1.5 mg), benzoic acid (2.0 mg), and p-hydroxyphenyl acetic acid methyl ester (1.5 mg). The sixth fraction was also rechromatographed as above to obtain methyl paraben (1.0 mg).

**Taraxacine-B (1):** Pale yellow syrup. [H-NMR (CDCl3)] δ: 10.29 (1H, s, NH2), 8.90 (1H, d, J = 6.5 Hz, H-3), 8.54 (1H, d, J = 5.6 Hz, H-4), 8.31 (1H, d, J = 8.0 Hz, H-5), 7.85 (1H, t, J = 8.0 Hz, H-7), 7.72 (1H, d, J = 8.0 Hz, H-8), 7.56 (1H, d, J = 8.0 Hz, H-6), 4.30 (3H, s, OCH3). IR ν (KBr cm-1): 3300, 2924, 2853, 1460. UV λmax (MeOH) nm (log e): 212 (3.9), 246 (3.6), 257 (3.6), 273 (3.5), 300 (3.4), 367 (3.2). EI-MS m/z: 198.0794 (Calcd for C13H10N2O3). MS m/z: 198 (M+), 166, 140, 71, 57.

**Taraxacine-B (2):** Pale yellow syrup. [H-NMR (CDCl3)] δ: 3.36 (1H, br s, OH), 10.14 (1H, s, NH), 9.07 (1H, s, H-4), 8.32 (1H, d, J = 8.0 Hz, H-5), 7.97 (1H, d, J = 8.0 Hz, H-8), 7.85 (1H, t, J = 8.0 Hz, H-7), 7.54 (1H, t, J = 8.0 Hz, H-6), 4.24 (3H, s, OCH3). IR ν (KBr cm-1): 3200, 1721, 1437, 1341, 1255, 1105, 756. UV λmax (MeOH) nm (log e): 216 (4.3), 232 (4.3), 270 (4.4), 287 (4.0), 303 (3.8), 333 (3.5), 346 (3.5). EI-MS m/z: 242.0693 (Calcd for C12H15N2O3). MS m/z: 242 (M+), 227, 199, 149, 121, 95, 81, 67, 55.

**Taraxacine-C (3):** Colorless syrup. [H-NMR (CDCl3)] δ: 7.85 (1H, br s, OH), 6.82 (1H, d, J = 2.0 Hz, H-2), 6.80 (1H, d, J = 8.0 Hz, H-5), 6.68 (1H, d, J = 8.0 Hz, H-6), 4.45 (1H, dd, J = 9.2, 4.8 Hz, H-3), 3.61 (3H, s, OCH3), 3.12 (3H, s, OCH3), 2.69 (1H, dd, J = 15.2, 9.2 Hz, H-2), 2.50 (1H, dd, J = 15.2, 4.8 Hz, H-1). 13C-NMR (CDCl3) δ: 171.0 (C-1), 145.5 (C-3'), 145.2 (C-4'), 132.9 (C-1'), 118.7 (C-6'), 115.3 (C-5'), 113.9 (C-2'), 80.1 (C-3), 55.9 (CH-OCH3), 51.0 (COOCH3), 43.4 (C-2). IR ν (KBr cm-1): 3317, 1713, 1440, 1281, 1060, 757. UV λmax (MeOH) nm (log e): 234 (4.4, sh), 249 (4.3, sh), 291 (4.4), 326 (4.4). EI-MS m/z: 226.0842 (Calcd for C11H14O5). MS m/z: 226 (M+), 211, 194, 153, 134, 77. [α]D = −32.0° (c = 0.1, CHCl3).

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**References**


