ALKALOID FROM BARK OF *ALBIZZIA MYRIOPHYLLA*

Aiko ITO,[a] Ryoji KASAI,[a] Nguyen Minh DUC,[b] Kazuhiro OHTANI,[a] Nguyen Thoi NHAM,[b] and Kazuo YAMASAKI*,[a]

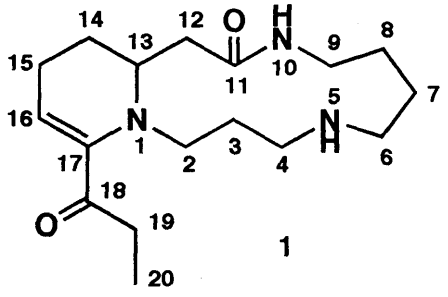
Institute of Pharmaceutical Sciences, Hiroshima University[a] School of Medicine, 1-2-3 Kasumi, Minami-ku, Hiroshima 734, Japan, and The Science Production Center of Vietnamese Ginseng,[b] Ho Chi Minh City University of Medicine and Pharmacy, 41 Dinh Tien Hoang, District 1, Ho Chi Minh City, Vietnam

A novel macrocyclic spermidine alkaloid, albizzine A has been isolated from bark of *Albizzia myriophylla*. The structure was established on the basis of spectral evidence.

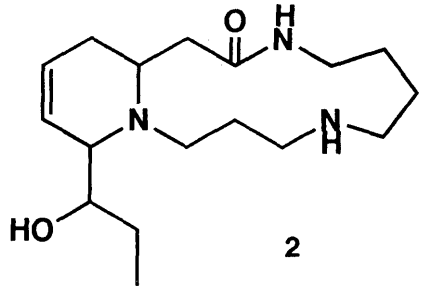
KEYWORDS *Albizzia myriophylla*; Leguminosae; albizzine A; macrocyclic spermidine alkaloid

In a previous paper,[1] we reported the isolation and structural determination of three closely related new lignan glycosides, named albizzioside A, B and C, from the bark of *Albizzia myriophylla*, which has recently been exploited as a substitute for licorice in the southern provinces of Vietnam under the name "Cay Song Ran". On further investigation of this plant, we isolated a new macrocyclic spermidine alkaloid. In this paper, we describe its structural elucidation.

From the methanol extract of the dried bark of *Albizzia myriophylla* (1.8 kg), compound **1** (oil, 32 mg) was obtained by a series of chromatography. Compound **1** had a molecular formula of $C_{17}H_{29}O_2N_3$, which was deduced from an $[M]^+$ peak at *m/z* 307.2260 in the HR-EI-mass spectrum. Though some chemical evidence has been adduced to arrive at the gross structures, the main evidence was found in exhaustive spectral data, particularly that of mass spectra, which were closely related to those of palustrine (**2**), isolated from *Equistum palustre* L.[2-4] A comparison of the mass spectral fragmentation pattern of **1** and **2** showed considerable similarities, *i.e.* common characteristic peaks at *m/z* 307 (M^+), 278 (M^+–29), 250 and 208, although the molecular ion (*m/z* 307) and the first fragment ion (*m/z* 278) of **1** were two mass units less than those of **2**. It also showed at *m/z* 278, 250, 208 in EI-MS (Chart **1**). The NMR spectra of **1**[5] (including H-H and C-H COSY) showed one double bond (δ 145.6 *s* and δ 130.1 *d*), but the multiplicity indicated that its position was different from that of **2**. It also showed a ketone signal (δ 205) instead of a hydroxymethine signal (C-18 of **2**). The structure of **1** was confirmed by HMBC spectra (Fig. 1). The C-18 carbonyl carbon (δ 205) showed cross-peaks between C-19 methylene protons (δ 2.87 and 2.76), C-20 methyl protons (δ 1.10), and C-16 olefinic proton (δ 6.78). Thus the structure of the side chain and the position of the double bond were determined as shown in Fig. 1. Additional



1



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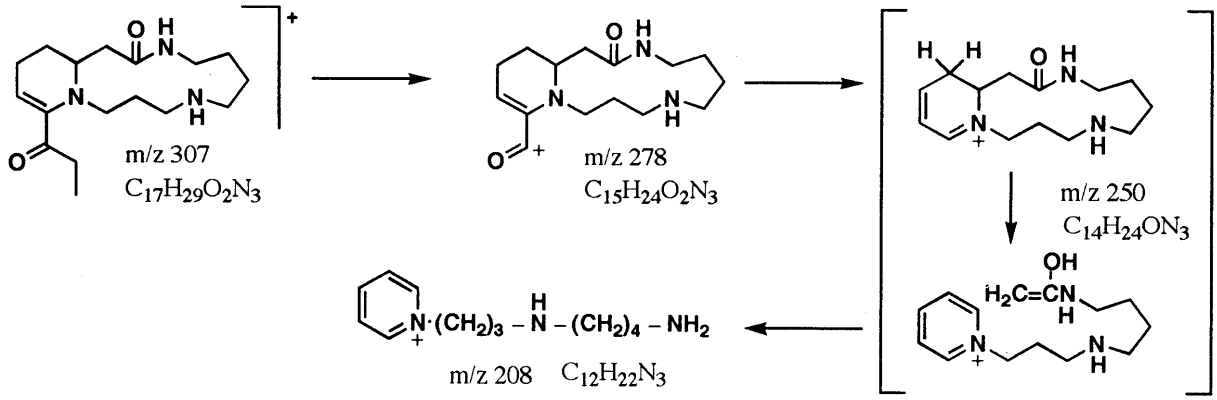

Chart 1. MS Fragmentation of Compound **1**

support for this was obtained from the UV (λ_{max} 237nm) and the IR spectrum (ν_{max} 1682 cm^{-1}) of **1**, indicating the presence of α,β-unsaturated ketone. Consequently, **1** was characterized as 17-(1-oxopropyl)-1,5,10-triazabicyclo [11.4.0]heptadec-16-en-11-one, and it was named albizzine A.

This is the first report of macrocyclic spermidine type alkaloids from Leguminosae plants. Several related spermidine alkaloids are known in Nature, such as palustrine and palustridine which were found in *Equistum* species (family Equisetaceae), and cannabissativine[6] and annhydrocannabisativine which were found in *Cannabis sativa* (family Moraceae). It is remarkable that these families are taxonomically quite different.

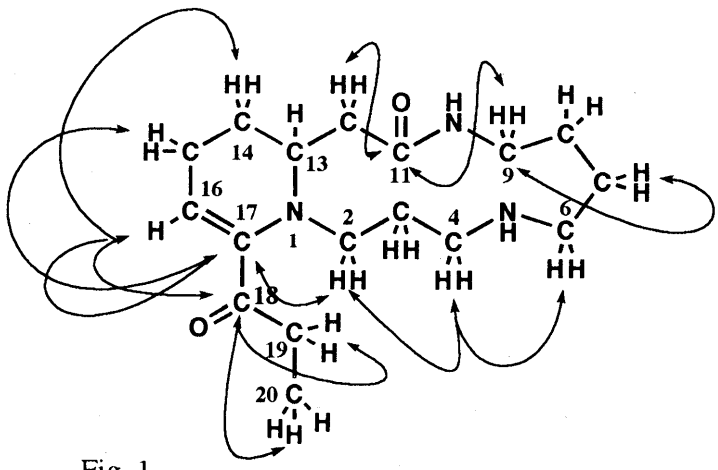

Fig. 1.
Diagnostically Important HMBC Correlation of **1**

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5) ^{13}C NMR (CD_3OD, 100MHz) δ 205.1 (*s* , C-18), 175.7 (*s* , C-11), 145.6 (*s* , C-17), 130.1 (*d*, C-16), 54.4 (*t* , C-2), 52.7 (*d* , C-13), 50.5 (*t* , C-4), 49.5 (*t* , C-6), 39.2 (*t* , C-9), 38.3 (*t* ,C-12), 31.7 (*t* , C-19), 25.3 (*t* , C-8), 24.3 (*t* , C-3), 23.8 (*t* , C-7), 21.3 (*t* , C-15), 19.7 (*t* , C-14), 9.0 (*q* , C-20); ^1H NMR (CD_3OD, 400MHz) δ 6.78 (1H, *dd*, *J* = 4.0, 3.7 Hz, H -16), 3.76 (1H, *ddd*, *J* = 13.0, 9.7, 4.2 Hz, H-9), 3.67 (1H, *m*, H-13), 3.26 (2H, *m*, H-4), 3.22 (1H, *m*, H-6), 3.10 (1H, *ddd*, *J* = 13.0, 4.2, 3.9 Hz, H-6), 2.87 (1H, *dq*, *J* = 14.5, 7.2 Hz, H-19), 2.83 (1H, *m*, H-9), 2.82 (1H, *m*, H-2), 2.76 (1H, *dq*, *J* = 14.5, 7.2 Hz, H-19), 2.60 (1H, *ddd*, *J* =12.0, 2.0, 1.7 Hz, H-2), 2.28 (2H, *m*, H-15), 2.25 (1H, *dd*, *J* = 14.0, 12.1 Hz, H-12), 2.07 (1H, *m*, H-3), 2.04 (1H, *dd*, *J* = 14.0, 2.6 Hz, H-12), 1.95–1.84 (3H, overlapped, H-7, 8, 14), 1.76– 1.65 (2H, overlapped, H-7,8), 1.58 (1H *m*, H-3), 1.54 (1H, *m*, H-14), 1.10 (3H, *t*, *J* = 7.2 Hz, H-20)
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