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THE STRUCTURE OF (-)-THALIMONINE

MARIA P. VELCHEVA,* RUMIANA R. PETROVA,

Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

SELENGHE DANGHAAGHIIN, and ZHAMYANSAN YANSANGHIIN

Institute of Chemistry, Mongolian Academy of Sciences, 51 Ulan Bator, Mongolia

ABSTRACT.—Thalimonine [**2**] was isolated from Mongolian *Thalictrum simplex*. The structure has been elucidated as (-)-3,4-methylenedioxy-2,8,9-trimethoxypavinane by spectral studies including ^1H , ^{13}C , and nOe nmr and mass spectrometry.

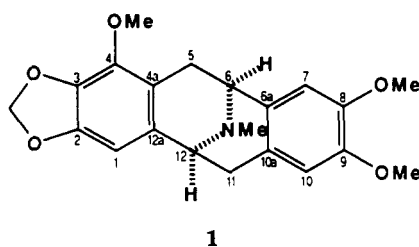
The alkaloid (-)-2,3-methylenedioxy-4,8,9-trimethoxypavinane [(-)-2,3,7-trimethoxy-8,9-methylenedioxy-pavinane] [**1**] has been isolated from *Thalictrum strictum* Ledeb (Ranunculaceae) (1). For a review on pavines and isopavines see Gözler *et al.* (2).

As a part of ongoing studies of the alkaloids of Mongolian *Thalictrum* species (3), we investigated *Thalictrum simplex* L. An alkaloid with physical data (uv, eims and ^1H nmr) similar to those of **1** has been isolated. A partial ^1H -nmr nOe experiment was carried out in order to establish the positions of the substituents in the isolated alkaloid. Irradiation of the 2-OMe (δ 3.86) or H-1 (δ 6.31) signals produced a strong nOe between the two. On the other hand, ir-

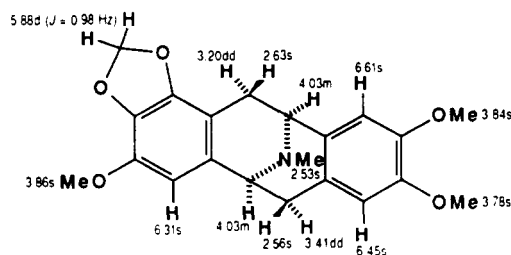
radiation of the other aromatic singlet at δ 6.45 effected enhancement of the 9-OMe group (δ 3.78). The 8-OMe (δ 3.84) was determined by the effect of its signal on H-7 (δ 6.61).

Another partial nmr nOe experiment was performed to verify the substitution on ring A and to assign the chemical shift of the MeO group. Irradiation of H-6 and H-12 (m) (δ 4.03) effected aromatic singlets at H-1 (δ 6.31) and H-7 (δ 6.61).

Finally, irradiation of the H-7 (δ 6.61) aromatic singlet affected the 8-OMe singlet (δ 3.84) and the triplet-like multiplet at δ 4.03 (H-6 and H-12). Conversely, irradiation of the aromatic singlet at δ 6.31 resulted in an increase of the multiplet at δ 4.03 (H-6 and H-



1



2

12 positions) and showed strong reversible nOe with the meta-coupled protons of 2-OMe (δ 3.86) on ring A.

Uv, eims, and ^1H data of the isolated alkaloid are similar to those published for the alkaloid (–)-2,3-methylenedioxy-4,8,9-trimethoxypavinane (**1**), whenever the partial nOe analyses showed that the MeO substituent on ring A is located at C-2 while the methylenedioxy group is at C-3 and C-4. Unfortunately, as an authentic sample of alkaloid **1** was not available, we are not sure whether our isolated alkaloid is new or whether we are now presenting a corrected structure for alkaloid **1**. Our alkaloid (–)-3,4-methylenedioxy-2,8,9-trimethoxypavinane [**2**] has been named (–)-thalimonine.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Uv and ir spectra were recorded on a Bruker IFS-113 V Spectrophotometer. Optical rotation was determined on a Perkin Elmer 241 polarimeter. The cd spectrum was measured on a Dichrographe III Jobin Yvon in MeOH, cells (cm) 0.2, 0.05 and 0.01. ^1H - and ^{13}C -nmr spectra were recorded on a Bruker WM-250 spectrometer in CDCl_3 solution with TMS as an internal standard. Eims data were obtained on a Jeol JMS-D 300 mass spectrometer by direct inlet to the probe at 70 eV.

PLANT MATERIAL.—The aerial parts of *T. simplex* were collected in August 1987, near Ulan Bator during full flowering. The plant was identified by Prof. Ch. Sanchill and Prof. E. Ganbold (Institute of Botany, Mongolian Academy of Sciences). A voucher specimen has been deposited in the Herbarium of the Institute of Botany, Mongolian Academy of Sciences, Ulan Bator.

EXTRACTION AND ISOLATION.—The dried and ground plant material (3 kg) was extracted with EtOH at room temperature. The solvent was evaporated in vacuo. The residue was suspended in 10% HCl and extracted with CHCl_3 . The

acidic layer was alkalinized with 25% NH_4OH (pH 9–10) and extracted with petroleum ether. The petroleum ether extract was dried over anhydrous Na_2SO_4 , and after concentration in vacuo it yielded 3.2 g crude alkaloids. Cc was performed using neutral alumina with a hexane/ Et_2O gradient. Final purification of the fraction eluted with 25% hexane in Et_2O was performed on Si gel GF₂₅₄ tlc plates using petroleum ether- CHCl_3 - Me_2CO -MeOH (4:4:1:1), affording 46 mg of pure product.

(–)-**THALIMONINE** [**2**].— $\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}$; (–)-3,4-methylenedioxy-2,8,9-trimethoxypavinane; $[\alpha]^{22}_{\text{D}} -118^\circ$ ($c=0.20$, MeOH); uv λ max (EtOH) 287 nm ($\log \epsilon$ 3.84); ir ν max (CHCl_3) 3009, 2962, 2872, 1600, 1517, 1465, 1450, 1373, 1172 cm^{-1} ; cd (MeOH) $\Delta\epsilon$ (nm) +0.16 (294), –0.46 (287), +1.94 (274), +0.47 (247), +8.10 (220), –43.16 (206); eims m/z (%) $[\text{M}]^+$ 369 (67), 368 (23), 204 (100), 218 (63); relative nmr nOe H-1 to 2-OMe (10%), 2-OMe to H-1 (4%), H-7 to 8-OMe (13%), 8-OMe to H-7 (6%), H-10 to 9-OMe (11%), 9-OMe to H-10 (6%), H-6 and H-12 to H-1 (4%), H-1 to H-6 and H-12 (7%), H-5 to H-6 and H-12 (15%), H-6 and H-12 to H-5 (2%), H-11 to H-10 (3%), H-11 to H-6 and H-12 (17%), H-6 and H-12 to H-11 (2%), H-7 to H-6 (8%), H-6 to H-7 (5%); ^{13}C nmr (CDCl_3) δ 106.3 (C-1), 146.3 (C-2), 142.3 (C-3 and C-4), 132.5 (C-4a), 27.6 (C-5), 56.4 (C-6), 129.8 (C-6a and C-12a), 110.4 (C-7), 147.8 (C-8), 148.2 (C-9), 111.3 (C-10), 123.9 (C-10a), 34.2 (C-11), 56.7 (C-12), 55.9 (2-OMe), 55.4 (8-OMe), 55.7 (9-OMe), 101.3 (3,4- OCH_2O), 40.8 (NMe).

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