Malaysian Journal of Science 22: 87-93 (2003)

Alkaloids and flavones from *Desmos dumosus*, Roxb. Saff. (Annonaceae)

Mazdida Sulaiman[1], **A. Hamid A. Hadi**[2] and **Khalijah Awang**[2]

[1]Centre of Fundamental Studies, University Malaya, 50603 Kuala Lumpur, Malaysia
[2]Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

ABSTRACT Eleven isoquinoline alkaloids and two flavones were isolated from the leaves and stem-barks of *Desmos dumosus*. The alkaloids identified were *o*-methylmoschatoline, lysicamine, *O*-methylisopiline, discretamine, stepharine, pronuciferine, asimilobine, norlirioferine, nornuciferine, 3-hydroxynornuciferine and liriodenine. The two flavones isolated were 5-hydroxy-6,7-dimethoxyflavone and 5-hydroxy-7,8-dimethoxyflavone. The structures were determined by the usual spectroscopic technique.

ABSTRAK. Sebelas alkaloid isokuinolina dan dua sebatian flavon telah dipisahkan dari daun dan batang kayu *Desmos dumosus*. Alkaloid tersebut adalah *o*-methylmoschatolina, lisikamina, *o*-metilisopilina, diskretamina, stefarina, pronusiferina, asimilobina, norlirioferina, nornuciferina, 3-hidroksinornuciferina dan liriodenina. Manakala dua sebatian flavon yang dijumpai adalah 5-hidroksi-6,7-dimetoksiflavon dan 5-hidroksi-7,8-dimetoksiflavon. Elusidasi struktur telah dibuat melalui teknik spektroskopi.

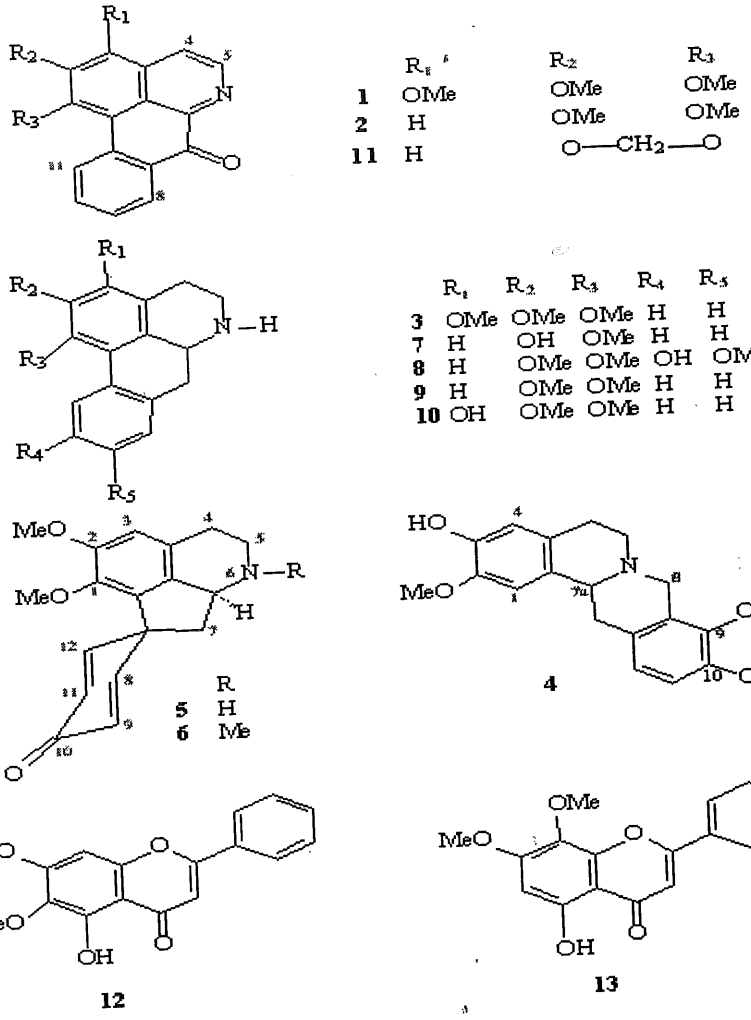
(*Desmos dumosus*, isoquinoline, alkaloids, flavones, NMR.)

INTRODUCTION

The Malayan flora is considered as one of the richest in the world. It possesses an estimated 8000 species of Angiosperms but very little chemical studies have been carried out. In view of this, a chemical study on the leaves and bark of *Desmos dumosus* (Annonaceae) was initiated. Preliminary screening of this plant have shown that it is rich in alkaloids. The genus *Desmos* is of particular interest since some of its species are reportedly to be used by the native tribes as post partum medicine and also to treat dysentry or vertigo. Infact the leaves of some *Desmos* species are given to women after childbirth to increase the secretion of milk [1].

Locally, *Desmos dumosus* is known as *pisang pisang padi* and it is a large climber [2]. The studied sample was collected at Hutan Simpan Air Hitam, Selangor (KL 3715). Stem-barks and leaves were extracted with dichloromethane and the alkaloids were extracted by conventional acid-base extraction. The crude alkaloidal extract were subjected to extensive TLC and column chromatography. The bark afforded two oxoaporphines; *o*-methylmoschatoline **1** and lysicamine 2, one aporphine; *o*-methylisopiline 3, and one protoberberine named discretamine 4. The leaves yielded two proaporphines namely stepharine **5** and pronuciferine **6**, four aporphines; asimilobine **7**, norlirioferine **8**, nornuciferine **9** and 3-hydroxynornuciferine **10** and three oxoaporphines *i.e.* *O*-methylmoschatoline 1, lysicamine 2, liriodenine **11**. All these alkaloids belong to the isoquinoline type.

The neutral portion of the dichloromethane extract yielded two flavones; 5-hydroxy-6, 7-dimethoxyflavone **12** and 5-hydroxy-7,8-dimethoxyflavone **13**. Structural elucidation was performed by means of spectroscopic methods such as MS, UV, IR and ^{1}H NMR.



EXPERIMENTAL

General Experimental Procedures. Spectra were recorded on the following instruments: UV (MeOH) Shimadzu UV-160 UV-VIS spectrophotometer; IR ($CHCl_3$), Perkin Elmer 2000 FT-IR spectrometer; NMR ($CDCl_3$), Jeol JNM-400; EIMS, Shimadzu GCMS-QP2000A spectrometer; APCI, Perkin Elmer PESCIEX spectrometer. Column chromatography was performed using Si gel Merck H 60. Column chromatography analysis were performed using Merck kieselgel 60 (230-400 mesh) and Merck kieselgel 60_{254} was used for preparative thin layer chromatography.

Plant material. Bark and leaves of *Desmos dumosus* (Roxb.) Safford. were collected at Hutan Simpan Air Hitam, Selangor. Identification was made by Mr. Teo Leong Eng, (University Malaya). Voucher specimens (KL 3715) were deposited at the Laboratoire de Phanerogamie, Museum National d'Historie Naturelle in Paris, at the Herbarium of Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia and at the Herbarium of

the Forest Research Institute of Malaysia, Kepong, Malaysia.

Extraction and isolation of the alkaloid. Dried and milled stem-bark/leaves of (1kg) were defatted with petroleum-ether. Then the sample was dried and moistened with 20% ammonia solution followed by extraction with dichloromethane. The alkaloids were extracted by the classical method. The crude alkaloids (2.0g) from the bark (1kg) were purified by column chromatography with CH_2Cl_2 containing increasing amounts of MeOH followed by prep. TLC to yield *o*-methylmoschatoline (1) (50mg) CH_2Cl_2-MeOH, 99:1, lysicamine(2) (20mg) CH_2Cl_2-MeOH, 98:2, *o*-methylisopiline 3 (5mg) CH_2Cl_2-MeOH, 97:3 and discretamine 4 (8mg) CH_2Cl_2-MeOH, 98:2. Two flavones were obtained from the neural part of the extract; 5-hydroxy-6,7-dimethoxyflavone 12 (16mg) and 5-hydroxy-7,8-dimethoxyflavone 13 (6mg). The eluting solvent system was 100% CH_2Cl_2.

A total of 2.0g of crude alkaloids (leaves) were similarly subjected to column chromatography on silica gel followed by extensive prep. TLC. The alkaloids obtained were *o*-methylmoschatoline 1 (10mg) CH_2Cl_2-MeOH, 99:1, lysicamine 2 (20mg) CH_2Cl_2-MeOH, 98:2, liriodenine 11 (50mg) CH_2Cl_2-MeOH, 98:2, asimilobine 7 (16mg) CH_2Cl_2-MeOH, 97:3, norlirioferine 8 (40mg) CH_2Cl_2-MeOH, 97:3, nornuciferine 9 (20mg) CH_2Cl_2-MeOH, 97:3, 3-hydroxynornuciferine 10 (20mg) CH_2Cl_2-MeOH, 97:3, stepharine (5mg) CH_2Cl_2-MeOH, 95:5 and pronuciferine (10mg) CH_2Cl_2-MeOH, 95:5. The neutral portion of the extract afforded 5-hydroxy-6,7-dimethoxyflavone (20mg) and 5-hydroxy-7,8-dimethoxyflavone (16mg). Both were eluted with 100% CH_2Cl_2.

O-methylmoschatoline (1): m.p. 182-184°C; $UV\lambda_{max}$ (MeOH), nm: 274(log ε4.34), 315(log ε3.67), 436(log ε 3.50); $IR\nu_{max}$ ($CHCl_3$), 1662cm^{-1} (conjugated C=O), 1480, 1400, 1350, 1260 and 950cm^{-1}; MS m/z (rel. int.): 322$[M+1]^+$, 293, 235, 149, 89; ^{1}HNMR ($CDCl_3$) δ8.91 (1H, d, J=5.40Hz, H-5), 8.16 (1H, d, J=5.40Hz, H-4), 9.10 (1H, dd, J=8.30Hz, J'=1.20Hz, H-11), 8.52(1H, dd, J=7.80Hz, J'=1.80Hz, H-8) 7.54 (2H, m, H-9, H-10), 4.08 (3H, s, OCH_3-1), 4.10 (3H, s, OCH_3-2), 4.19 (3H, s, OCH_3-3); ^{13}CNMR ($CDCl_3$) δ61.10 (OCH_3-1), 61.57 (OCH_3-2), 61.91 (OCH_3-3), 119.27 (C-4), 144.66 (C-5), 182.75 (C-7), 127.76 (C-11), 128.28 (C-8),129.04 (C-9),134.48 (C-10), 134.65 (C-11a).

Lysicamine (2): $UV\lambda_{max}$ (MeOH), nm: 236(log ε 3.77), 267(log ε 3.69), 310(log ε 3.23), 395(log ε 3.04); $IR\nu_{max}$ ($CHCl_3$), 1665cm^{-1}, 1490cm^{-1}, 1416cm^{-1}, 1355cm^{-1}, 1257, 1125, 1040 and 955cm^{-1}; MS m/z (rel. int.): 292$[M+1]^+$, 276, 184, 122, 87; ^{1}HNMR ($CDCl_3$) δ7.24 (1H, s, H-3), 4.02 (3H, s, OCH3-1), 4.11 (3H, s, OCH_3-2), 7.80(1H,d, J=5.30Hz, H-4) 8.80 (1H, d, J=5.2Hz, H-5), 9.17 (1H, dd, J=8.50Hz, J'=1.10Hz, H-11), 8.60(1H, dd, J=7.80Hz, J'=1.10Hz, H-8), 7.78 (1H, m, H-9), 7.58(1H, m, H-10).

O-methylisopiline (3): $UV\lambda_{max}$ (MeOH), nm: 213 (log ε 3.97), 272(log ε 3.76); $IR\nu_{max}$ ($CHCl_3$), 2940, 2830, 1605, 1585, 1000, 960 and 890cm^{-1}; MSm/z (rel. int.): 312$[M+1]^+$, 210, 156, 74; ^{1}HNMR ($CDCl_3$) δ3.71 (3H, s, OCH_3-1), 3.92 (3H, s, OCH_3-2), 3.89 (3H, s, OCH_3-3), 7.14-7.28(3H, m, H-8, H-9, H-10), 8.25 (1H, d, J=7.80Hz, H-11).

Discretamine (4): m.p. 209-211°C $UV\lambda_{max}$ (MeOH), nm: 207(log ε 3.49), 273(log ε 3.44); $IR\nu_{max}$ ($CHCl_3$), 3246, 3000, 2850, 2960, 2920, 1455, 1340, 1240, 1190, 1125, and 1025cm^{-1}; MS m/z (rel. int.): 328$[M+1]^+$, 256, 148, 87; ^{1}HNMR ($CDCl_3$) δ6.68 (1H, s, H-1), 6.71 (1H, s, H-4), 6.82 (1H, d, J=8.79Hz, H-12), 6.81(1H, d, J=8.79Hz, H-11), 3.82 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 4.18(1H, d, J=16.00Hz, H-8).

Stepharine (5): Brown amorphous, $UV\lambda_{max}$ (MeOH),nm: 230(log ε 4.44), 277(log ε 3.45); $IR\nu_{max}$ ($CHCl_3$), 3500, 2820, 1665, 1500, 1450, 1433, 1368, 1253, 1105, 1000 and 850 cm^{-1}; MS m/z (rel. int.): 297$[M^+]$ (100), 296(53), 268(67.6), 253(14.9), 238(10.8), 225(14.2), 209 (9.4), 195 (3.4), 165(10.8); ^{1} H NMR ($CDCl_3$) δ6.29 (1H, dd, J=10.00, 1.80Hz, H-9), δ6.42 (1H, dd, J=10.00, 1.80Hz, H-11), δ6.87 (1H, dd, J=10.00, 1.80Hz,H-8), δ7.01 (1H, dd, J=10.00, 1.80Hz,H-12) , 6.64 (1H, s, H-3), 3.60 (3H, s, C-1 OCH_3), 3.81(3H, s, C-2 OCH_3).

Pronuciferine (6): m.p. 157-159°C; $UV\lambda_{max}$ (MeOH),nm: 230(log ε 4.44), 280(log ε 3.47); $IR\nu_{max}$ ($CHCl_3$), 3445, 2850, 1662, 1488, 1438, 1375, 1295, 1265, 1000 and 850cm^{-1}; MS m/z (rel. int.): 311$[M^+]$ (100), 310(53), 294(2.6), 282(56), 268(36), 253(13), 225(15.6), 209 (9),195(3.8), 165(11.6); ^{1} H NMR ($CDCl_3$) δ6.57

(1H, dd, J=10.00, 1.80Hz, H-9), δ6.58 (1H, dd, J=10.00, 1.80Hz,H-11), δ6.73 (1H, dd, J=10.00, 1.80Hz, H-8), δ6.75 (1H, dd, J=10.00, 1.80Hz, H-12), 6.21 (1H, s, H-3), 3.98 (3H, s, C-1 OCH_3), 3.99 (3H, s, C-2 OCH_3), 2.04 (3H,s,N-CH_3).

Asimilobine (7): UVλ_{max} (MeOH), nm: 274(log ε4.08), 229(log ε4.08); IRν_{max} ($CHCl_3$), 3521, 2940, 2830, 1600, 1580, 1360, 1105, 1080, 950, 920 and 890cm^{-1}; MS m/z (rel. int.): 267 [M^+] (58.7), 266(100), 251(30.7), 236(17.3), 223(7.3), 206(8.0), 194(8.0) 194(6.7), 178 (16.0), 165 (14.7); ^{1}HNMR ($CDCl_3$) δ6.71 (1H, s, H-3), 7.16-7.30 (3H, m, H-8, H-9, H-10), 8.29 (1H, d, J=8.30Hz, H-11), 3.58(3H, s, OCH_3).

Norlirioferine (8): m.p.94-96°C; UVλ_{max} (MeOH), nm: 226(log ε4.30), 281(log ε3.83) 310 (log ε 3.98); IRν_{max} ($CHCl_3$), 3617, 2950, 2820, 1603, 1150, 1000, 960, 925, 890cm^{-1}; MS m/z (rel. int.): 327 [M^+] (68.40), 326(100), 312 (19.70), 310(6.49), 298 (5.19), 295 (9.09), 283 (13.00), 281(15.60), 267 (15.60); ^{1}HNMR ($CDCl_3$) δ8.08 (1H, s, H-11), 6.80 (1H, s, H-8), 6.56 (1H, s, H-3), 3.89(3H, s, OCH_3-9), 3.88 (3H, s, OCH_3-2), 3.66 (3H, s, OCH_3-1, 2.04 (1H, s, NH); ^{13}C NMR ($CDCl_3$) δ144 (C-1), 152.11 (C-2), 110.85 (C-3), 29.20 (C-4), 43.17 (C-5), 55.76 (C-6a), 36.70 (C-7), 129.91 (C-7a), 111.3 (C-8), 145.25(C-9), 144.87(C-10), 113.83(C-11), 124.07(C-11a), 60.19(C-1, OCH_3), 55.86(C-2, OCH_3), 56.06 (C-9, OCH_3).

Nornuciferine (9): m.p. 245-246°C; UVλ_{max} (MeOH), nm: 216(log ε4.69), 272(logε3,70); IRν_{max}($CHCl_3$), 3688, 2895, 1596, 1460, 1370, 1190, 1150, 1105, 1000, 965, 920, 850 and 815cm^{-1}; MS m/z (rel. int.): 218 [M^+] (61.8), 280 (100), 266(22.3), 250(27.6), 236(9.2), 224(19.7), 165(19.7) 152(6.6); ^{1}HNMR ($CDCl_3$) δ6.58 (1H, s, H-3), 8.30(1H, d, J=8.90Hz, H-11), 7.20 (3H, m, H-9, H-10), 3.60(3H, s, OCH_3-1), 3.67 (3H, s, OCH_3-2).

3-Hydroxynornuciferine (10): m.p. 163-164°C; UVλ_{max} (MeOH), nm: 219(log ε 4.39),.240(log ε3.90), 280(log ε 4.14), 292(log ε 4.04); IRν_{max} ($CHCl_3$), 3521, 2942, 2800, 1480, 1360, 1040, 940, 925 and 850cm^{-1}; MS m/z (rel. int.): 297 [M^+] (84.6), 296(100), 280(30.7); ^{1} H NMR ($CDCl_3$) δ7.16-7.30(3H, m, H-8, H-9, H-10), 8.28(1H, dd, J=7.80Hz, H-11), 3.72(3H,s, OCH_3-1, 3.98 (3H, s, OCH_3-2).

Liriodinine (11): UVλ_{max} (MeOH), nm: 273 (log ε4.10), 270(log ε3.80), 313(log ε 3.41), 410(log ε 3.42); IRν_{max} ($CHCl_3$), 1662, 1420, 1357, 1255, 1120, 969 and 958cm^{-1}; MS m/z (rel. int.): 276[M+1]$^+$ (100), 248(5), 247(18), 246(10); ^{1}HNMR($CDCl_3$) δ7.24(1H, s, H-3), 6.40(2H, s, OCH_2O), 7.82 (1H, d, J=5.10,H-4), 8.92(1Hd, J=4.90Hz, H-5) 7.61 (1H, m, H-10), 7.79 (1H, m, H-9), 8.62 (1H, dd, J=7.80Hz, J'=1.10Hz, H-8), 8.72 (1H, dd, J=8.70Hz, J=1.80Hz, H-11).

5-hydroxy-6,7-dimethoxyflavone (12): m.p. 205-207°C; UVλ_{max} (MeOH),nm: 221(log ε 4.33), 274(log ε 4.47), 313(log ε 4.27); IRν_{max} ($CHCl_3$), 3160, 1665, 1585, 1515, 1355, 1255, 1250, 1230, 1170, 1075, 830 and 820cm^{-1}; MS m/z (rel. int.): 299 [M^+], 292, 276, 241, 187, 135, 87; ^{1} H NMR ($CDCl_3$) δ6.50 (1H, s, H-8), 6.65 (1H, s, H-3), 12.61 (1H, s, OH), 3.90 (3H, s, OCH_3-6), 3.86 (3H, s, OCH_3-7), 7.48 (3H, m, H-3', H-4', H-5'), 7.83 (2H, m, H-2', H-6').

5-hydroxy-7,8-dimethoxyflavone (13): m.p. 210-212°C; UVλ_{max} (MeOH), nm: 216(log ε 4.18), 273(log ε 4.18), 320(log ε 3.91); IRν_{max} ($CHCl_3$), 3140, 1665, 1610, 1585, 1510, 1360, 1295, 1220, 1180, 1075, 830 and 820cm^{-1}; MS m/z (rel. int.): 299 [M^+], 292, 276, 241, 187; ^{1} H NMR ($CDCl_3$) δ6.42 (1H, s, H-6), 6.60 (1H, s, H-3), 12.09 (1H, s, OH), 3.93 (3H, s, OCH_3-7), 3.93 (3H, s, OCH_3-8), 7.52 (3H, m, H-3', H-4', H-5'), 7.88 (2H, m, H-2', H-6'); ^{13} C NMR ($CDCl_3$) δ 56.34(C-7, OCH_3), 61.67(C-8, OCH_3), 95.85(C-6), 105.35(C-3), 126.32(C-4'), 129.14(C-3'), 131.92 (C-5'), 131.35(C-2), 157.58(C-2'), 158.74(C-6'), 163.94(C-OH), 182.73(C=O).

RESULTS AND DISCUSSION

Desmosine, an artefact alkaloid [3] and new desmosdumotin A, B and C [4] were previously isolated from *Desmos dumosus* (Roxb.) Saff.. Desmosdumotin C showed significant and selective *in vitro* cytotoxicity against HOS bone cancer, MCF-7 breast cancer and 1A9 ovarian cancer cell lines.

The alkaloid *O*-methylmoschatoline 1 [5,6] was isolated as orange needles from chloroform with m.p. 182-184°C. The APCI mass spectrum showed an [M+1]$^+$ peak at m/z 322 thus suggesting a molecular formula of $C_{19}H_{15}NO_4$. The UV spectrum revealed absorptions at λ_{max} 274, 315 and 436 nm (log ε 4.34, 3.67 and 3.50) indicative of a 7-oxodibenzoquinoline skeleton.

A strong absorption band reminiscent of the highly conjugated oxoaporphinic carbonyl group was observed at 1662cm^{-1}.

The oxoaporphinic nature of 1 was further confirmed by the presence of a pair of doublets at δ8.16 and δ8. 91 with a small coupling constant of 5Hz in the ^{1}H NMR spectrum. These are the signals of H-4 and H-5 respectively. The small coupling constant is due to the presence of the adjacent nitrogen. H-11 appeared as a dd at δ9.10 (J=8.3 Hz, J'=1.8 Hz). Signals of H-10 and H-9 were seen as dt (J=8.3 Hz, J'=1.2 Hz) at δ7.54 and 7.75. A dd 10 (J=8.3 Hz, J'=1.8 Hz) attributable to H-8 was observed at δ8.52. The protons of the three methoxyls resonated as three singlets between δ4.1 and 4.25. The ^{13}C NMR showed a signal of a carbonyl at δ182.8. The methoxyl carbons gave peaks at δ61.1, 61.5 and 61.9.

Lysicamine 2 [7] was isolated as yellow amorphous solid. The APCI mass spectrum revealed an $[M+1]^+$ peak at m/z 292 giving possibility to a molecular formula of $C_{18}H_{13}NO_3$. Its UV and IR spectrum are similar to those of 1 thus indicating the oxoaporphinic nature of 2. However, the ^{1}H NMR showed a slight difference by showing a singlet corresponding to H-1 hence suggesting that C-1 is not substituted. In addition only two methoxyl peaks appeared at δ4.02 and 4.11.

O-methylisopiline 3 [8,9] was afforded as white amorphous solid and its APCI mass spectrum gave an $[M+1]^+$ peak at m/z 312, which matched a molecular formula of $C_{19}H_{21}NO_3$. The UV spectrum showed absorptions at λ_{max} 213 and 272 nm (log ε 3.97 and 3.76). The IR spectrum lacked the usual carbonyl absorption of an oxoaporphine. The ^{1}H NMR spectrum showed multiplets corresponding to the four aliphatic protons attached to C-4 and C-7. The methylene protons on C-5 resonated at lower field (δ3.43 and 3.74) due to the deshielding effect of the neighbouring nitrogen. The aromatic H-11 of ring D gave a dd at δ8.25 (J= 7.8 Hz, J'= 1.8 Hz). The signals of the other three protons (H-8, H-9, H-10) were overlapped and were observed as multiplets between between δ7.14-7.28.

The protoberberine discretamine 4 [10] was obtained as white crystals ($CHCl_3$) with m.p. 209-211°C. The APCI mass spectrum exhibited an [M+1] peak at m/z 328 which corresponded to a molecular formula of $C_{19}H_{21}NO_4$. The UV spectrum showed two maxima at λ_{max} 207 and 273 nm (log ε 3.49 and 3.44). The IR spectrum showed a broad absorption band at 3246cm^{-1} indicating the presence of hydroxyl group/s. The ^{1}H NMR spectrum showed that it is tetrasubstituted since only four aromatic proton signals were present. H-1 and H-4 appeared as singlets at δ6.68 and 6.71 respectively while H-11 and H-12 present an AB system dd at δ6.82 and 6.81 (J= 8.8 Hz). Protons of the two methoxyls resonated at δ3.82 and 3.90. An AB dd of H-8 and H-8' was observed at δ4.21 and 3.59 (J=16 Hz) respectively. The large coupling of 16 Hz was indicative of a C-9 and C-10 substituted system.

Alkaloid 5 was the proaporphine stepharine [11,12]. It was isolated as white amorphous solid. Its EIMS spectrum revealed a molecular ion peak at m/z 297 thus suggesting a molecular formula of $C_{18}H_{19}NO_3$. The UV spectrum gave two maxima at λ_{max} 230 and 280 nm (log ε 4.45 and 3.46). The IR spectrum showed a strong absorption band of a conjugated ketone at 1665 cm^{-1}. The ^{1}H NMR spectrum showed four sets of overlapping doublets corresponding to the olefinic protons α, α', β and β' at δ6.57, 6.58, 6.73 and 6.75. respectively. H-3 resonated as a singlet at δ6.21. Two methoxyl singlets appeared at δ3.60 and 3.81 assigned for C-1 and C-2 methoxyl group, respectively.

Pronuciferine 6 [13], another proaporphine, was afforded as white crystals, m.p. 127-129°C. Its EIMS mass spectrum showed an $[M]^+$ peak at m/z 311 which indicated a molecular formula of $C_{19}H_{21}NO_3$. It has an additional 14 mu as compared to stepharine thus suggesting that it has an extra methyl group. Infact its UV, IR and ^{1}H NMR spectra resemble that of stepharine and in incidently the NMR spectrum showed a singlet representing three protons at δ2.04 which is reminiscent of an N-methyl resonance.

The base asimilobine 7 [14, 15] was obtained as white amorphous solid. The EI mass spectrum showed an $[M]^+$ peak at m/z 267 thus corresponding to the molecular formula of $C_{18}H_{19}NO_3$. The base peak at m/z 266 $[M-1]^+$ was typical of an aporphine type skeleton. Infact, its UV and IR spectra resembles those of *o*-methylisopiline 3. The apparent difference in the ^{1}H NMR spectrum is the presence of only one

methoxyl singlet (δ3.58) and also the singlet of H-3 (δ6.71).

The alkaloids norlirioferine 8 [16], nornuciferine 9 [17], and 3-hydroxynornuciferine 10 [14] were also of the aporphinic type. Thus their UV, IR and ^{1}H NMR spectrum were similar. They only differ in their mass values (EIMS); m/z 327, 281 and 297 respectively. They possess a molecular formula of $C_{19}H_{21}NO_4$, $C_{18}H_{19}NO_2$ and $C_{18}H_{19}NO_3$ respectively.

Liriodenine 11 [18] was obtained as yellow amorphous solid. The UV spectrum showed maxima typical of an oxoaporhine; λ_{max} 270, 313 and 410 nm (log ε 3.8, 3.41 and 3.42). Moreover, a strong absorption band was observed in its IR spectrum at 1660 cm^{-1} indicative of the highly conjugated C-7 carbonyl group. The ^{1}H NMR spectrum showed the characteristic AB dd of H-4 and H-5 at δ7.82 and 8.92 (J=5Hz) respectively. A methylenedioxy singlet was also present at δ6.40 and another singlet belonging to H-3 appeared at δ7.23. The aromatic region also exhibited a set of multiplets attributable to H-9 and H-10 between δ7.61 - 7.79. In addition, two sets of dd corresponding to H-8 and H-11 were observed at δ8.62 (J=7.8, J'= 1.8) and 8.72 (J=8.7, J'= 1.8) respectively.

Besides the alkaloids, two flavones were also obtained; 5-hydroxy-6,7-dimethoxyflavone and 5-hydroxy-7,8-dimethoxyflavone.

5-hydroxy-6,7-dimethoxyflavone 12 [19,20] was obtained as yellow crystals from chloroform, m.p. 205-207°C. The mass spectrum showed an $M+1)^+$ peak at m/z 299 (APCI) thus corresponding to a molecular formula of $C_{17}H_{14}O_5$. The IR spectrum revealed a sharp peak at 1665cm^{-1}, indicative of a highly conjugated carbonyl group. The UV spectrum gave three maxima at λ_{max} 221nm, 274 nm and 313 nm (log ε 4.33, 4.74 and 4.27 respectively).

The ^{1}H NMR spectrum exhibited a very downfield peak at δ12.61 reminiscent of a hydroxyl proton involved in intramolecular hydrogen bonding, usually between the hydroxyl on C-5 and the C-4 carbonyl of a flavone. In addition, a one proton singlet (6.50) and two sets of multiplets corresponding to 5 protons were also observed (δ7.48, 7.78-7.83). The former belong to H-8 while the latter were the signals of the ring B protons. The two methoxyls protons resonated as two singlets at δ3.86 and δ3.90 respectively.

5-Hydroxy-7,8-dimethoxyflavone 13 [19,20,21] was obtained as yellow crystals ($CHCl_3$). The mass spectrum showed an $M+1)^+$ peak at m/z 299 (APCI), suggesting a molecular formula of $C_{17}H_{14}O_5$ which is the same as that of 12. The similarity were also observed in other spectrums (UV, IR and NMR). The mark difference between these compounds was significant in the H-6 singlet which appeared at δ6.42. The signal was more shielded compared to H-8 in 12, since H-6 was flanked by two strong electron donating group; methoxyl and hydroxyl. The H-3 was located at δ6.60.

In conclusion, thirteen compounds were isolated from *Desmos dumosus*. The isoquinoline alkaloids were all related to one another biogenetically and the occurrences of this type of alkaloids and flavones are common in the genus *Desmos*.

REFERENCES

1. Burkill, I.I. (1935). *A Dictionary of Economic Products of the Malay Peninsula*; Oxford Press. 757.
2. Sinclair, J.M. (1955). *The Garden's Bulletin; Revision of the Malayan Annonaceae* (Singapore). **14**: 41.
3. Mazdida Sulaiman, Marie-Therese Martin, Mary Pais, A. Hamid A. Hadi and Khalijah Awang (1998). Desmosine, an artifact alkaloid from *Desmos dumosus*, *Phytochemistry*. **49**(7): 2191-2192.
4. Jiu-Hong Wu, Andrew T. McPhail, Kenneth F. Bastow, Hiroaki Shiraki, Junko Ito and Kuo-Hsiung Lee (2002). Desmosdumotin C, a novel cytotoxic principle from *Desmos dumosus*, *Tetrahedron letters*. **43**: 1391-1393.
5. Mahmood, K., Chan, K.C., Park, M.H., Han Y.N. and Han B.H. (1986). *Phytochemistry*. **25**:1509.
6. Bick, I.R.C., Douglas, G.K. (1965). *Tetrahedron Letters*. **35**: 4655.
7. Dabrah, T.T., Sneyden, A.T. (1983). *J. Nat. Prod.*. **46**: 436.
8. Chen, C-L., Chang, H-M (1978). *Phytochemistry*. **17**: 779.

9. Leboef, M., Cortes, D., Hocquemiller, R. and Cave, A. (1983). *Journal of Medicinal Plant Research.* **48**: 234.
10. Leboef, M., Cave, A. and El Tohami, M. (1982). *J. Nat. Prod.*, **45**: 761.
11. Baldwin, M., London, A.G., Maccoll, A., Haynes, L.J. and Stuart, K.L (1967). *J. Chem Soc. (C)*. 154.
12. Fang-Rong Chang, Chung-Yi Chen, Tian-Jye Hsieh, Chun-Ping Che and Yang-Chang Wu (2000), *Journal of the Chinese Chemical Society*. **47**: 913-920.
13. Kametani, T. and Yagi, H. (1967). *J. Chem. Soc. (C)*. 2182.
14. Chen, C-L. and Chang, H-M. (1976). *Phytochemistry.* **15**: 547.
15. Gellert, E. and Rudzats, R. (1972). *Aust. J. of Chem.*. **25**: 2477.
16. Castro, O.C., Lopez, J.V., Vergara, A.G., (1985). *Phytochemistry*. **17**: 203
17. Guinaudeau, H., Leboef, M., Cave, A. (1983). *Journal of Natural Products*. **46**: 761-835.
18. Cava, M.P., Nomura, K., Schlessinger, R.H., Buch, K.T., Douglas, B., Raffauf, R.F. and Weisback, J. (1964). *Chem and Ind.*. 282.
19. Waterman, P.G. and Pootakahm, K. (1979) *Planta Medica*. **35**: 366.
20. Waterman, P.G. and Pootakahm, K. (1979) *Planta Medica*, **37**: 247
21. Gupta, K.K., Taneja, S.C., Dhar, K.L. and Atal, C.K (1983). Phytochemistry. **22**(1): 314-315.