Bull. Pharm. Sci., Assiut University
Vol. 12, Part 2, PP. 266-272 (1989).

FURTHER NEW ALKALOIDS FROM CASSIA SIAMEA LAM. LEAVES

S.M. El-Sayyad, H.M. Sayed and S.A. Ross
Pharmacognosy Department, Faculty of Pharmacy, Assiut University.

ABSTRACT

Two new isoquinolone alkaloids were isolated from the leaves of Cassia siamea Lam. and their structures were designated as 8-acetyl siamine and 3,8-dimethyl-6,7-methylene dioxy isoquinolone.

INTRODUCTION

In a previous publication, the authors isolated three isoquinolone alkaloids, siamine, siaminine A and siaminine B from Cassia siamea Lam. Leaves[1].

Siamine, an isoquinolone alkaloid, was obtained by Ahn and Zymalkowski from the seeds of the same plant[2]. However, piperidenol and monoterpene alkaloids have been isolated from several Cassia species[3-9].

The leaves of C.siamea were subjected to further phytochemical investigation with the aim of isolating and characterizing other new alkaloids.

EXPERIMENTAL

General Experimental Procedure :

Melting points were determined with a Kofler hot Stage apparatus and uncorrected. UV spectra were recorded in MeOH using Unicam SP1750 Spectrometer. IR spectra were determined in KBr discs using Unicam SP1025 Spectrometer. ^{1}H-and ^{13}C-NMR were recorded on Jeol FI models FX-60 and FX-90 Q

Spectrometers in DMSO-d_6 using TMS as internal standard. Mass spectra were determined on a Finnegan Quadrupol 4023 instrument. TLC on silica gel G (Merck) plates, developers : $CHCl_3$-MeOH (45:5) (syst. I) and $CHCl_3$-MeOH (4:1)(syst.II). Spots were sprayed with modified Dragendorff's reagent.

Plant Material :

The plant was collected during flowering in April 1986, from the Experimental Station of Ornamental Plants (Zohria Gardens), Cairo. It was identified by the late Prof. F.Y. Amin, Prof. of Floriculture and Horticulture, Faculty of Agriculture, Assiut University.

Extraction and Fractionation :

The powdered defatted leaves (2 kg) were extracted with ethyl alcohol (70%) at room temperature. The concentrated extract was fractionated with chloroform. The chloroform residue (7 g) was chromatographed on silica gel column with chloroform and chloroform-methanol gradient. The concentrated fractions giving positive response with Dragendorff's reagent were purified by preparative TLC and the eluted compounds were recrystallised from MeOH.

Compound I: Colourless fine needles(MeOH),m.p. 216-18°C,$[\alpha]_D^{22}$-0.93(C, 0.75,EtOH),UV λ_{max}^{MeOH} nm.(log ε): 226(3.3),242(3.36),250(3.8),292(3.24) +$AlCl_3$:- ;+NaOH: 224 (3.24). 256(3.42), 330(3.16); IR(KBr) ν cm^{-1} : 3300-3100, 1720, 1645(lactam), 1570, 1500,1440,1320,1160,890; ^{1}H-NMR (DMSO-d_6) δ ppm:2.19(3H,S, C_3-Me),2.28(3H,S,CH_3-C(=O)-), 5.98 (1H,S,H_4), 6.58(1H,d, J=2.4Hz,H_5), 6.72(1H,d, J=2.4Hz,H_7), 8.35(1H,br.S,NH); ^{13}C-NMR (DMSO-d_6) δ ppm: C_1(177.6), C_3(138.1), C_4(101.2), C_5(110.2), C_6(164.2), C_7(113.2), C_8 (161.1), C_9(158.9), C_{10}(118.1), C_{11}(19.3), C_{12}(204.2), C_{13}(29.6) , MS m/z(rel.int.): 234(1.4) (M^++1), 233(8.9)(M^+), 232(14.7) (M^+ -H), 215 (7.2)(M^+-18), 191(12.3)(M^+-42), 190(71.4)(M^+-43), 189(25.1)(M^+-44),163 (2.8), 162(21), 161 (20.4), 105(5.6), 91(5.3), 77(13.3), 43(100).

Further New Alkaloids From Cassia Siamea Lam. Leaves.

Compound II: Light yellow crystals (MeOH), m.p. 222-225°C; UV λ_{max}^{MeOH} nm(log ε): 228(3.65), 254(3.7), 315 (3.16), 330(3.1), 366(3.15). IR (KBr) ν cm^{-1}: 3100-3000, 1660(lactam), 1580, 1440, 950(O-CH_2-O); ^{1}H-NMR (DMSO d_6) δ ppm: 2.18(3H, S, C_3-Me), 2.32(3H, S, C_8-Me), 6.06(1H, S, H_4), 6.46(2H, br.S, O-CH_2-O), 6.83(1H, S, H_5), 8.32(1H, br, S, NH); ^{13}C-NMR (DMSO-d_6) δ ppm: C_1(160.4), C_3(137.9), C_4(100.4), C_5(105.6), C_6(158.5), C_7(154.8), C_8(112.2), C_9(152.9), C_{10}(120.5), C_{11}(19.2), C_{12}(98.6), C_{13}(23.7); MS. m/z(rel.int.) 215(3)(M^+-2), 213(100), 185(7.1), 170(4.3), 156(5.4), 141(3.8), 128(5.4), 115(7.5), 106(11.4), 77(11.2), 63(14.7), 51(14.4), 43(28.4).

Alkaline hydrolysis of I : 10 mg was dissolved in 5 ml MeOH to which 5 ml of 5% methanolic KOH was added. The mixture was stirred at room temperature for 18 hours. MeOH was distilled and 10 ml water was added. The solution was extracted with (4 x 10 ml) $CHCl_3$. The extract was dried over anhydrous Na_2SO_4 and solvent was distilled under reduced pressure to give light yellow residue. The latter was chromatographed using system I and the major zone was scraped and extracted with $CHCl_3$.

RESULTS AND DISCUSSION

The chloroform fraction of the defatted alcoholic extract of Cassia siamea Lam. leaves was found to show, at least, six Dragendorff's-positive and fluorescing spots on silica gel chromatograms.

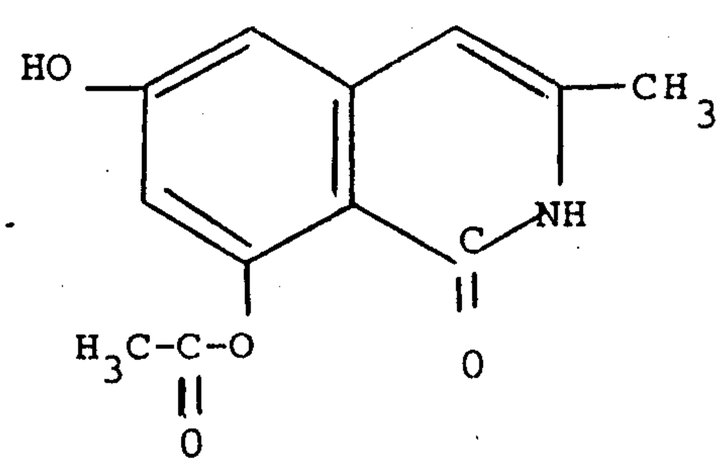
Fractionation of this fraction on a silica gel column and purification of the subsequent fractions by preparative TLC afforded two pure compounds (I and II). Both compounds gave orange colour with Dragendorff's reagent, fluoresced under UV light and failed to give hydrochloride salts.

Compounds I & II showed UV absorption maxima between 230-370 nm indicating a highly conjugated chromophore. Their IR spectra exhibited intense peaks at 3000-3100 cm^{-1} assignable to N-H stretching vibration of lactam, while peaks at 1660 , 1645 cm^{-1} were consistent with the presence of a β-lactam carbonyl[10]. IR spectrum of I showed another band at 3300 cm^{-1} for OH which is supported by a bathochromic shift in UV upon addition of N NaOH and formation of green colour with $FeCl_3$.

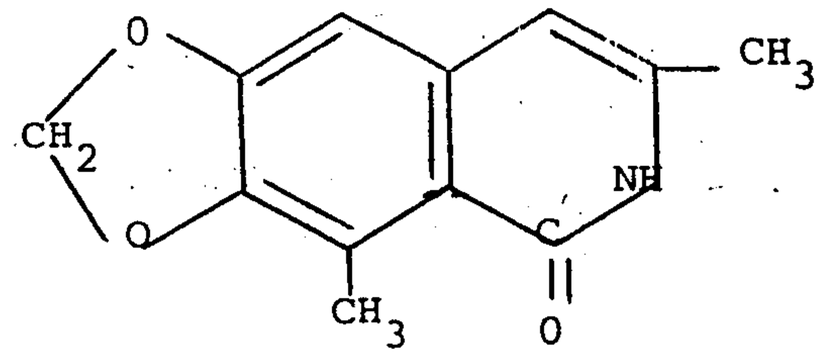
Mass spectrum of I revealed a molecular ion peak at m/z 233, in addition to a peak at m/z 190 (M-43) for the cleavage of a lactam group. Its ^{1}H-NMR showed three aromatic protons, two of them appeared as doublets with meta coupling for H_5 and H_7 at δ 6.58 and 6.72 ppm respectively, while, the third appeared as a singlet at δ 5.98 ppm for C_4-H. A singlet for 3H at δ 2.19 assignable to C_3-Me which appeared in ^{13}C-NMR at δ 19.3 ppm (characteristic for C_3-Me)[11]. An acetoxy group could be deduced by the appearance of a singlet for 3H at δ 2.28 ppm in ^{1}H-NMR which is supported by an intense band at 1720 cm^{-1} in the IR spectrum and mass fragment (100%) at m/z 43 in addition to a signal at δ 204 ppm for $\overset{O}{\overset{\|}{C}}$ (^{13}C-NMR spectrum). A broad singlet assignable to one proton of NH at δ 8.35 ppm was also observed. Trials to obtain a chelate complex with $AlCl_3$ were unsuccessfull indicating that the acetoxy group must be at C-8 while OH is at C-6. On these bases, compound I might be 8-acetyl siamine. This assumption was confirmed by the appearance of 12 signals in ^{13}C-NMR, comparable with similar compounds[11]. Alkaline hydrolysis produced a compound identical with siamine (m.m.p and CO-TLC).

Compound II: IR was similar to compound I with an additional band for aromatic methylene dioxy at 940 cm^{-1}, supported by a broad singlet for 2-protons at δ 6.46 ppm in ^{1}H-NMR.

The latter revealed a broad singlet at δ 8.32 ppm for one proton of NH and two singlets each for 3H, one at δ 2.18 ppm (C_3-Me) and the other at δ 2.32 ppm (C_5- or C_8-Me). The singlet at δ 6.06 ppm was ascribed to C_4-H. Another singlet was observed at δ 6.83 ppm assignable either to C_5-or C_8 -H. Similar compounds[11] showed that C_5-H and C_8-H resonate at δ 6.57-6.9 and 7.58-7.87 ppm respectively. Therefore, the singlet at δ 6.83 ppm corresponds to the resonance of C_5 -H proton and a methyl group is, accordingly, attached to C-8. Compound II is suggested to be 3,8-dimethyl-6,7-methylene dioxy isoquinolone. ^{13}C-NMR showed 12 signals comparing favourably with related compounds[11].



I



II

ACKNOWLEDGEMENT

We thank Prof. Dr. S.W. Pelletier, Institute for Natural products Research and the School of Chemical Sciences, the University of Georgia, Athens, Georgia, USA for Carrying ^{1}H-, ^{13}C-NMR and Mass spectral analysis through a governmental mission of one of the authors.

REFERENCES

1. S.M.El-Sayyad, S.A.Ross and H.M.Sayed, J.Nat. Prod. 47 (4), 708(1984).
2. B.Z. Ahn and F. Zymalkowski, Tetrahedron Lett., 11, 821 (1976).
3. I. Christofidis, A. Welter and J. Jadot, Tetradedron 33, 977 (1977).
4. N.B. Mulchandani and S.A. Hassarajam, Planta Med. 32, 357(1977).
5. D. Lythgoe and M.J. Vernego. Tetrahedron Lett. 12,1133 (1967).
6. R.J. Highet, J. Org. Chem. 29, 471 (1964).
7. W.Y. Rice and J.L. Coke, J. Org. Chem. 31, 1010 (1966).
8. A.M. Mendez, Phytochemistry 10, 2255 (1971).
9. K. Wiesner, Z. Valenta, B.S. Hurlbert, F. Bicke ihaupat and L.R. Fowler, J.Am. Chem. Soc. 80, 1521 (1958).
10. R.M. Silverstein and G.C.Bassler, "Spectrometric Identification of Organic Compounds" 2nd. Ed., John Wiley and Sons, Inc. N.Y., London, Sydney (1968).
11. B.D. Krane and M. Shamma. J. Nat, Prod. 47 (4), 377 (1982).

قلوانيات اضافيه جديدة من أوراق الكاسيا سياميا الام

سامية محمد الصياد ـ هناء محمد سيد ـ سمير انيس روس

قسم العقاقير ـ كلية الصيدلة ـ جامعة أسيوط

تم من خلال هذه الدراسة فصل قلوانيين يتبعان مجموعة الايزوكينولون وقد استنبط التركيب الكيميائى لهما على اسس دراسه الخواص الفيزيائية والكيميائية الى جانب الطيفية والتى تشتمل على مطياف الكتله والرنين النووى المغناطيسى لانويه الكربون والهيدروجين وكذلك قياس اطيافها فى الاشعه تحت الحمراء وفوق البنفسحيه وقد توصل الباحثون الى أن هذه المركبات تحوى مجموعه اميد وتركيبها كالتالى :

١ ـ ٨ ـ اسيتيل سيامين ٠

٢ ـ ٣ ، ٨ ـ ثنائى ميثيل ـ ٦ ، ٧ ميثلين داى اوكس ايزوكينولون ٠

received in 10/6/1989 & accepted in 21/12/1989,