Malaysian Journal of Science **18**: 35-40 (1999)

Chemical constituents of three Malaysian Annonaceae

O. Rozana, S. Mazdida, U. Shasya, K. Awang and **A. Hamid A. Hadi**

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Abstract. Three Malaysian Annonaceous climbers plants, *Cyathostemma viridiflorum* Griff., *Desmos dumosus* and *Fissistigma manubriatum*, have been studied for their studied for their chemical constituents. The plants afforded seven alkaloids and one chalcone. *Cythostemma viridiflorum* yielded three oxoaporphine which are liriodenine, lanuginosine and atherospermidine, and an aporphine, anonaine. *Desmos dumosus* gave three alkaloids of which two are of the oxoaporphine type; *o*-methylmoschatoline and lysicamine, and a tetrahydroprotoberberine, discretamine. *Fissistigma manubriatum* afforded three oxoaporphines: lanuginosine, lysicamine and liriodenine. The chalcone isolated was α,2'-dihydroxy-3',4',5'-trimethoxychalcone. Structural elucidation were carried out by UV, IR, MS and ^{1}HNMR.

Abstrak. Kandungan kimia bagi tiga jenis pokok pemanjat Annonaceae Malaysia, *Cyathostemma viridiflorum* Griff., *Desmos dumosus* dan *Fissistigma manubriatum*, telah dikaji. Pokok-pokok ini menghasilkan tujuh alkaloid dan satu calkon. *Cyathostemma viridiflorum* menghasilkan tiga oksoaporfina, iaitu liriodenina, lanuginosina dan atherospermidina dan satu aporfina, iaitu anonaina. *Desmos dumosus* memberi tiga alkaloid dimana dua adalah dari jenis oksoaporfina; *o*-metilmoskatolina dan lisikamina, dan satu tetrahidroprotoberberina; diskritamina. *Fissistigma manubriatum* pula menghasilkan tiga oksoaporfina, lanuginosina, lisikamina dan liriodenina. Calkona yang didapati adalah α,2'-dihidroksi-3',4',5'- trimetoksicalkona. Penentuan struktur dilakukan melalui kaedah UV, IR, MS dan ^{1}HNMR.

Introduction

The family of Annonaceae, locally known as "Mempisang", is an important source of edible fruit, edible oil and soap (from the seeds), alcohol (from the wood), and perfume (from the flowers), and is alos used in folk remedy for ailments [1]. Three Malaysian Annonaceous plants have been studied for their chemical constituents. They were collected by the phytochemical group of the Chemistry Department, University of Malaya, under a collaborative programme with the Institut de Chimie des Substances Naturelles of France.

Cyathostemma viridiflorum Griff., also known locally as Akar Pisang-Pisang or Akar Mempisang, is a small genus of large climbers with big woody lianas [2]. The stems of *Cyathostemma viridiflorum* Griff. were collected at Hutan Simpan Bukit Bauk, Dungun, Terengganu. *Desmos dumosus* is a large climber or straggling shrub. The barks of this plant were collected at Hutan Simpan Air Hitam, Puchong, Selangor. *Fissistigma manubriatum* is also a climber and usually found all down the western side of Peninsula Malaysia. The barks of this plant were obtained at Gunung Jerai, Kedah. The species of this particular genus is taken by the Malay mothers after childbirth and for treatment against stomach-ache and malaria [3].

Experimental

All solvents, except those used for bulk extractions, were AR grade. Aluminium supported silica gel 60 F_{254} plates were used for thin layer chromatography. The plates were degreased with hexane and dried at 75°C for one hour and stored in a dessicator until required. Silica gel 60 F_{254} (230-400 Mesh ATM) was used in preparative thin layer chromatography on 20 x 20 cm plates on layer thickness of 0.25to 1mm depending on the quantity of the sample. UV light (254nm and 365nm) was used to examine the thin layer chromatography (tlc)

spots or bands after the plates were sprayed with the staining reagents. Dragendorff's reagent was used to identify alkaloids. Melting points were measured on a Fischer John melting point apparatus and were uncorrected. UV absorption spectra were recorded on a UV-Visible spectrophotometer (model Shimadzu UV-160A); the samples were dissolved in methanol as solvent. IR spectra were obtained with $CHC1_3$ as solvent on a Perkin Elmer 16000 series FT spectrometer. ^{1}HNMR and ^{13}CNMR analyses were carried out on a JEOL GXX 200 MHz spectrometer in deuterochloroform ($CDC1_3$) with TMS (tetramethylsilane) as internal reference. Chemical shifts are reported in ppm and the coupling constants are given in Hz. Mass spectra were obtained on a Kratos MS30 instrument.

The dried stems or barks of the plants (1.0 kg) were degreased with petroleum ether (60-80°C) for 24 hours to remove the waxes. They were then dried at room temperature and wetted with 20% ammonia and left overnight. The plants were exhaustively reextracted with dichloromethane and methanol successively by using the Soxhlet extractor for about 17 hours. The supernatants obtained were concentrated under reduced pressure by using a rota-evaporator to a volume of about 500 mL, and were examined for their alkaloid content by using tlc and Dragendorff's reagent. The concentrated dichloromethane extracts (crude) were repeatedly extracted with 5% hydrochloric acid until Mayer's test was negative. The combined HC1 extracts were then basified with concentrated ammonia to *ca.* PH 11, then cooled to room temperature, and reextracted with dichloromethane. They were then washed with water, dried with anhydrous sodium sulphate, filtered and evaporated under reduced pressure to dryness to yield a dark gummy residue (5.34 g). The crude alkaloids were subjected to column chromatography over solica gel. The eluent system was dichloromethane with an increasing methanol gradient; CH_2C1_2 (100%), CH_2C1_2:MeOH (99:1, 98:2, 97:3, 95:5, 90:10); finally, pure methanol was used. The chromatographic fractions collected were monitored by thin layer chromatography and the fractions showing similar spots were grouped into together. Each series was then treated separately to isolate and purify its alkaloid content by extensive column chromatography or preparative thin layer chromatography. The purity of the alkaloids was determined by the use of single spot tlc by using several solvent systems. The petroleum-ether extract was chromatographed on a column of silica gel with 100% CH_2Cl_2 as eluting solvent. Further purification was performed by using silica gel precoated plates with 100% CH_2C1_2 as solvent. The flavonoid was detected by the deep purple colour under UV light. Only one flavonoid was isolated.

Liriodenine **1**: Yellow crystals, m.p. 270-272°C (decomposed). UV λ_{max} (log ε) in MeOH: 209 (4.26), 249 (4.24), 268 (4.15), 416 (3.80) nm. IR ν_{max} in $CHC1_3$: 1668, 1206, 910 cm^{-1}. ^{1}H-NMR in $CDC1_3$: 6.47 (2H,s, OCH_2O), 7.24 (1H, s, H-3), 7.63 - 7.85 (2H, m, H-9, 10), 7.83 (1H, d, *J* = 5.4 Hz, H-4), 8.65 - 8.69 (2H, m, H-8, 11), 8.9((1H, d, *J* = 5.4 Hz, H-5) : ppm. MS: m/z 27 (M^+, 100%), 247, 219, 189, 162.

Linuginosine **2**: Yellow needles, m.p. 302-305°((decomposed). UV λ_{max} (log ε) in MeOH: 24 (4.29), 272 (4.18), 384 (3.51) and 432 (3.59) nm IR ν_{max} in $CHCl_3$: 1660, 2927, 2855 cm ^{1}HNMR in $CDC1_3$: 3.99 (3H, s, OCH_3), 6.35(2H s, OCH_2O), 7.15 (1H, s, H-3), 7.29 (1H, dd, *J* 8.8 Hz, H-11), 8.88 (1H, d, *J* = 5.4 Hz, H-5 ppm. MS: m/z 305(M^+, 100%), 275, 247, 23 176.

Atherosperimidine **3**: Amorphous orange soli UV λ^{max} (log ε) in MeOH: 249 (4.1), 280 (4.5 315 (3.8) and 4,30 (3.4) nm. IR: ν_{max} in CHCl 1660, 745 cm^{-1}. ^{1}HNMR in $CDCl_3$: 4.27(3H, OCH3), 6.28(2H, s, OCH2O), 7.39-7.73 (2H, H-9, H-10), 8.12 (1H, d, *J* = 5.4 Hz, H-4), 8.3 8.58 (2H, m, H-8, H-11), 8.90(1H, d, *J* = 5.4 H H-5) ppm. MS: m/z 305 (M^+, 100%), 290, 26 234, 206, 176, 175, 149.

Anonaine **4**: White amorphous solid. UV λ_m (log ε) in MeOH: 234 (4.20), 272 (4.30) and 3 (3.55) nm. IR: ν_{max} in $CHCl_3$: 1406, 944 cm ^{1}HNMR in $CDCl_3$: 5.97 (1H, d, *J* = 1.5 H OCH_2O), 6.10(1H, d, *J* = 1.5 Hz, OCH_2O), 6. (1H, s, H-3), 7.20(3h, m, H-8, 9, 10), 8.10 (1 m, H-11) ppm. MS: EI m/z 265 (M+, 100%); M+-1 = 265.

o-Methylmoschatoline **5**. Orange needles, m 182-184°C. UV: λ_{max} (log ε) in MeOH: 27 (3.51), 207 (3.56), 220 (3.26) nm. IR: ν_{max}

$CHCl_3$: 1661 cm^{-1}. ^{1}HNMR in $CDCl_3$: 4.08 (3H, s, OCH_3), 4.10(3H, s, OCH_3), 4.19(3H, s, OCH3), 8.20(1H, d, H-4), 8.96(1H, d, H-5), 7.50 - 7,78 (2H, m, H-9 and H-10), 8.57(1H, dd, H-8), 9.10(1H, dd, H-11) ppm. MS: m/z 321 (M^+, 100%), 306, 278, 263, 235, 220, 192.

Lysicamine **6**. Yellow amorphous solid. UV: λ_{max} (log ε) in MeOH: 209 (3.79), 248 (3.68), 285 (3.59 nm. IR:ν_{max} in $CHCl_3$: 1665 cm^{-1}. ^{1}HNMR in $CDCl_3$: 4.11 (3H, s, OCH3), 4.03 (3H, s, OCH3), 7.43 (1H, s, H-3), 7.56 - 7.82 (2H, m, H-9, H-10), 8.61 (1H, dd, H-8), 8.9 (2H, d, H-4, H-5), 9.20 (1H, dd, H-11) ppm. MS: m/z 291 (M^+, 100%), 276, 248, 233, 205, 177.

Discretamine **7**: Brown amorphous solid that crystallized into greyish needles in MeOH, m.p. 204-207°C. UV: λ_{max} (log ε): 207.2 (3.49), 273 (3.44), 220 (3.25) in MeOH. IR: ν_{max} in $CHCl_3$: 3248.5 cm^{-1}. ^{1}HNMR in $CDCl_3$: 3.82 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 4.17 (1H, s, H-8), 4.23 (1H, s, H-8), 6.68 (1H, s, H-4), 6.70 (1H, s, H-1), 6.82 (2H, s, H-11, H-12); MS: m/z 327(M^+, 100%), 326, 178, 176, 150, 135.

α,2'-Dihydroxy-3',4',5'-trimethoxylchalcone **8**: UV: λ_{max} in MeOH: 315, 240 nm. IR: ν_{max} in $CHCl_3$: 3533, 1350, 1632 cm^{-1}. ^{1}HNMR in $CDCl_3$: 3.84 (3H, s, OCH3), 3.90 (3H, s, OCH_3), 4.14(3H, s, OCH_3), 5.41 (1H, s, OH-2'), 7.40-7.42 (3H, m, H-3, H-4, H-5), 7.62-7.65 (2H, m, H-2, H-6), 7.90(1H, s, H-6'), 7.90 (1H, s, H-β), 12.91 (1H, s, OH-α) ppm. MS : m/z 330(M^+, 100%), 253, 225, 211, 183, 131.

Results

The dried stem of *Cyathostemma viridiflorum* Griff. yielded liriodenine **1** (0.98% of the total alkaloid content), lanuginosine **2** (0.18%), atherospermidine **3** (0.16%) and anonaine **4** (0.09%). The dried and milled bark of *Desmos dumosus* yielded *o*-methylmoschatoline **5**, lysicamine **6** and discretamine **7**. The dried bark of *Fissistigma manubriatum* yielded lysicamaine 6 (0.58% of the total alkaloid content), liriodenine **1** (0.48%), lanuginosine **2** (0.65%) and α-2'-dihydroxy-3',4',5'-trimethoxychalcone **8** (11.07%).

Liriodenina **1** was obtained as yellow crystal with melting point of 270-272°C. The oxoaporphinic nature for this major alkaloid was based on its intense yellow colour and deep red colouration it produced in trifluoroacetic acid. Its mass spectrum showed a molecular ion peak at m/z 275 (100%; base peak), which gave the possibility of the molecular formula as $C_{17}H_9O_3N$ [4]. The UV spectrum revealed absorption bands at 209 nm (log ε 4.26), 249 (4.24), 268 (4.15) and 416 (3.80), which indicate a highly unsaturated chromophore which is typical of an oxoaporphine. The IR spectrum showed a strong peak due to C=O stretching at 1668 cm^{-1}. The data signified the presence of a highly conjugated chromophore with a ketone group in the system. Furthermore, a peak at 910 cm^{-1} is the result of a C-H out-of-plane deformation of a single isolated aromatic proton, which is attributable to H-3 [5]. In addition, a peak at 1206 cm^{-1} was also observed which is characteristic of a methylenedioxy unit [6,7]. The ^{1}HNMR spectrum of alkaloid **1** further supported the hypothesis that C-3 was not substituted. It showed a singlet corresponding to one proton at δ 7.24ppm. A singlet representing two protons was observed at δ 6.47 ppm that is attributed to the methylenedioxy protons located on C-1 and C-2 in ring A. The aromatic protons of ring D showed two sets of multiplet at δ 7.63 - 7.85 and 8.65 - 8.69 ppm, for which each set corresponded to two protons. The former was assigned to H-9 and H-10 and the latter to H-8 and H-11 since these two protons normally resonate at lower field in oxoaporphines. H-5 resonated as a doublet at δ 8.96ppm (1H, d, J_5 = 5.4 Hz), whereas the doublet of H-4 appeared at δ 7.83ppm (1H, d, J_4 = 5.4Hz).

Lanuginosine **2** was obtained as yellow needle crystal with melting point of 302 –305°C. The presence of oxoaporphinic skeleton of this alkaloid can be deduced from the UV spectrum at 248 nm (log ε 4.29), 272 (4.18), 384 (3.51) and 432 (3.59), the absorptions indicating a highly unsaturated system which is typical of an oxoaporphine. The IR spectrum showed a conjugated ketone peak at 1735 cm^{-1}. The mass spectrum of alkaloid **2** showed a molecular ion peak at m/z 305 (100%, base peak), which suggests a molecular formula of $C_{18}H_{11}O_4N$. A singlet in the NMR spectrum corresponding to two protons at δ 6.35 ppm belonged to a methylenedioxy group. An aromatic singlet at δ 3.99 ppm represents the three protons of a

methoxy group. Six aromatic protons were revealed signals in the δ 7.16 – 8.88 ppm region. The aromatic region of the spectrum showed signals of two highly deshielded protons centered at δ 8.88 and 8.88 ppm. The former was assigned to represented H-5 (1H, d, J_5 = 5.4 Hz), which was highly deshielded by the adjacent nitrogen. The latter was attributed to H-11 (1H, d, J_{11} = 8.8 Hz). The appearance of a doublet at δ 7.77 ppm (1H, d, J_4 = 5.4Hz) was indicative of H-4; H-8 resonated at δ 8.02 ppm (1H, d, J_8 = 2.4 Hz). In addition, H-10 resonated at δ7.29 ppm to give rise to a doublet of doublet (dd, 1H, J = 8.8Hz, J' = 2.9Hz). The singlet at δ 7.15 ppm corresponded to H-3. The C-3 atom in alkaloid **2** was also unsubstitued.

Atherospermidine **3** was isolated as an amorphous orange solid. The mass spectrum revealed a molecular ion peak which was also the base peak at m/z 305, which allowed the possibility of the molecular formula to be $C_{18}H_{11}O_4N$. The UV spectrum gave maxima at 249 nm (log ε 4.1), 280 (4.5), 315 (3.8) and 430 (3.4) indicated the existence of a highly unsaturated chromophore. The free base showed an IR absorption at 1660 cm^{-1} attributable to a highly conjugated ketone function. The ^{1}HNMR spectrum exhibited a strong singlet at δ 4.27 ppm that indicated the presence of a methoxy group. Another singlet at δ 6.28ppm suggested the presence of a methylenedioxy at C-1,2. The four aromatic protons of ring D resonated at δ 8.39 – 8.58 (2H, multiplet, H-8, H-11) and 7.39 – 7.73 ppm (multiplet, 2H, H-9, H-10). H-11 was the most deshielded proton compared with the other three aromatic protons owing to the deshielding effect of ring A. The absence of a singlet at about δ 7.2 ppm suggested that C-3 was substituted. A pair of doublets (AB system, J = 5.4Hz) was observed at δ 8.90 and 8.12 ppm, which signify H-5 and H-4, respectively [8].

Anonaine **4** was isolated as an amorphous white solid. The mass spectrum (EI and CI) showed a molecular ion peak at m/z 265 and 266 (M+1), which correlated with the molecular formula of $C_{17}H_{15}O_2N$. The UV spectrum showed maxima at 234 nm (log ε 4.20), 272 (4.30) and 312 (3.55), typical of a 1,2 substituted aporphine and aporphine lacking substitution in ring D [9]. In the IR spectrum, two peaks were observed at 1406 and 944 cm^{-1}. The former could be assigned to the C-O stretching vibrations of methoxy or methylenedioxy group; the latter is characteristic of the methylenedioxy group. The ^{1}HNMR showed a pair of doublets at δ 5.97 and 6.10 ppm (J = 1.5 Hz), which are indicative of a methylenedioxy resonance in a twisted aporphine skeleton. A singlet could be observed at δ 6.60 ppm assignable to H-3. A lowfield chemical shift was observed for H-11 at δ 8.10 ppm and this was caused by the deshielding effect of the aromatic ring A. A set of multiplets centered at 8 7.20 ppm could be assigned to the other three aromatic hydrogens attached to ring D (H-8, H-9, H-10).

o-Methylmoschatoline **5** was isolated as orange needles, m.p. 182-184°C. The mass spectrum showed a molecular ion peak at m/z 321 which corresponded to the molecular formula of $C_{19}H_{15}NO_4$. The IR spectrum showed an absorption at 1661 cm^{-1} which indicated the presence of a conjugated carbonyl group. The UV spectrum gave maxima at 273.4 nm (log ε 3.51), 207 (3.56) and a shoulder at 220 nm which indicated the presence of conjugated system. The ^{1}HNMR spectrum displayed three methoxy singlets at δ 4.08, 4.10 and 4.19 ppm [10]. A pair of AB doublet aromatic protons was observed at δ 8.20 (1H, J = 5.1 Hz, H-4) and 8.96 (1H, J = 5.1 Hz, H-5) ppm. The small coupling constant value (7 – 8 Hz) may be caused by the neighbouring nitrogen atom. A doublet of triplets was observed at δ 7.50 - 7.78 ppm. This is characteristic for the H-9 and H-10 protons in the unsubstituted ring D. H-8 resonated as doublet-doublet at δ 8.57 ppm (J = 7.3, 1.5Hz). A doublet-doublet at δ 9.10 ppm was assigned to H-11 (J = 8 Hz).

Lysicamine 6 was isolated as a yellow amorphous solid. The mass spectra showed a molecular ion peak at m/z 291 which correlated to the molecular formula of $C_{18}H_{13}O_3N$. The UV spectrum showed maxima at 208.6 (log ε 3.79), 248 nm (3.68) and 285 (3.59)nm, which indicated a highly conjugated ketone. The ^{1}HNMR spectrum showed a singlet at δ 7.28 ppm that is typical of the H-3 signal of an oxoaporphine with C-2 and C-1 being substituted. Two singlets corresponding to two methoxyl groups were observed, which suggests that these were substituents on C-2 and C-1.

Two sets of triplets corresponding to two aromatic protons of ring D were revealed at δ 7.56 - 7.82 ppm that were attributable to H-9 and H-10. A doublet-doublet observed at δ 8.61 ppm (J = 7.8 Hz, J = 1Hz) was assigned to H-8 which experiences a deshielding effect from the neighbouring C-7 carbonyl group. A downfield doublet of doublet signal (J = 8 Hz) belonging to H-11 was also observed at δ 9.20 ppm.

Discretamine **7** was isolated as brown amorphous solid which crystallized as grey needles from MeOH, m.p. 204-207°C. The mass spectrum revealed the base peak as the molecular ion peak at m/z 327, which corresponded to the molecular formula of $C_{19}H_{21}NO_4$. The UV spectrum showed a maxima at 207.2 (log ε 3.49) and 273 (3.44) nm. The IR spectrum showed a peak at 3245.8 cm^{-1} which corresponded to an OH vibration. The ^{1}HNMR spectrum revealed two methoxy singlets (δ 3.82 and 3.90 ppm) [11,12]. An AB doublet pair was observed at δ 4.17 and 4.23 ppm (J = 16 Hz) for the protons at C-8. This indicated a 9,10 substituted tetrahydroprotoberberine entity. A two-proton singlet was observed at δ 6.82 ppm thath can be attributed to H-11 and H-12. Two singlets corresponding to one proton each appeared at δ 6.70 and 6.68 ppm that were assigned to H-1 and H-4.

α,2'-Dihydroxy-3',4',5'-trimethoxychalcone **8** was identified as a chalone because it turned red upon contact with alkali. The UV spectrum showed maxima at 315 and 240 nm, which are the charateristic of the chalcone skeleton. The IR spectrum showed a peak at 3533 cm^{-1}, which is typical of an intramolecular hydrogen bonded hydroxyl group. A peak was observed at 1350 cm^{-1} arising from the in plane OH bend. A strong peak appeared at 1632cm^{-1}, a characteristic of a conjugated ketone. The EI mass spectrum showed a molecular ion peak at m/z 330, which suggesting the molecular formula to be $C_{18}H_{18}O_6$. The ^{1}HNMR spectrum showed three methoxyl peaks at δ 3.84, 3.90 and 4.14 ppm, which are the H-3', H-4' and H-5' proton signals. Multiplets corresponding to five aromatic protons of ring B were revealed at δ 7.40 - 7.65 ppm. The H-2 and H-6 had higher chemical shifts compared with the other three aromatic protons because of the deshielding effect caused by the neighbouring olefinic group. The signal at δ 7.90ppm may be attributed to H-6'[13]. A broad singlet observed at δ 12.91 ppm belonged to the hydroxyl group. The downfield value ressulted from the intramolecular hydrogen bonding with the adjacent carbonyl group.

References

1 Lebeouf, M.L., Cave, A., Bhaumik, P.K., Mukherjee, B. and Mukherjee, R. (1982). *Phytochemistry* **21**: 00.

2 Ridley, H.N. (1922). *The Flora of the Malay Peninsula* **1**: 27-28.

3 Burkhill, I.I. (1935). *Economic Products of the Malay Peninsula.* Oxford University Press.

4 Bick, I.R.C., Bowie, J.H. and Douglas, G.K. (1967). *Aust. J. Chem.* **20**: 1403.

5 Torsell, K.B.G. (1983). *Natural Product Chemistry* – A mechanistic and biosynthetic approach to secondary metabolism. pp. 264-265.

6 Williams, D.H. and Fleming, I. (1989). *Spectroscopic methods in organic chemistry.* McGraw-Hill Book Co., pp. 29-62.

7 Briggs, L.H., Colebrook, L.D., Fales, H.M. and Wildman, W.C. (1957). *Analyt. Chem.* **29**: 904.

8 Chan, K.C., Kamaliah M., A. Hamid, A.H., and Kozirah S. (1987). *Malays. J. Sci.* **9**: 77.

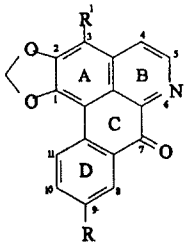
9 Bhakuni, D.S., Tewari S. and Dhar, M.M. (1972). *Phytochemistry* **11**: 1819.

10 Kamaliah, M., Kai, C.C., Myung, H.P., Yong, N.H. and Byung H.N. (1986). *Phytochemistry* **25**: 1509.

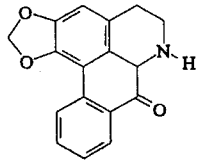
11 Ohiri, F.C.,Verpoort, R. and Baerheim Svendsen, A. (1983). *Planta Medica* **49**: 162.

12 Braochmann-Hanssen, H. and Nielsen, B. (1966). *Tetrahedron Lett.* **20**: 2261.

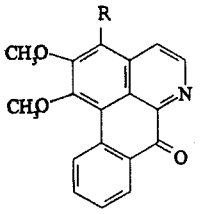
13 Mabry, T.J., Markham, K.R. and Thomas, M.B. (1970). *The systematic identification of flavonoids*, Springer Verlag, N.Y.



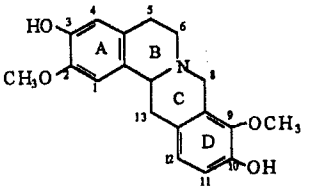
1 R=H, R^1=H
2 R=OCH_3, R^1=H
3 R=H, R^1=OCH_3



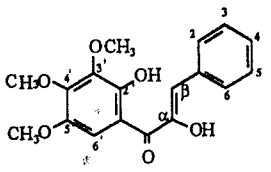
4



5 R=OCH_3
6 R=H



7



8