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POLYPHENOLS AND ALKALOIDS FROM *PIPER* SPECIES

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Key Word Index—*P. khasiana*; *P. manii*; *P. pedicellosum*; *P. thomsoni*; Piperaceae; 3-(3,4-dimethoxyphenyl)propanoylpyrrole; 14-benzo[1,3]dioxol-5-yl-tetradecan-2-ol; 2-acetoxy-1,3-dimethoxy-5-(2-propenyl)benzene; 2,6-dimethoxy-4-(2-propenyl)phenol; amides; flavones; lignans; β-sitosteryl palmitate; (+)-asarinin; X-ray structure

Abstract—Thirty eight compounds of different types have been isolated from twelve *Piper* species. The ether extract of the leaves of *P. aduncum* yielded eleven compounds, out of which 2,6-dimethoxy-4-(2-propenyl)phenol was isolated for the first time from the genus *Piper* and 2-acetoxy-1,3-dimethoxy-5-(2-propenyl)benzene is a new compound. The petrol extract of the stems and leaves of *P. attenuatum* furnished a novel long chain alcohol, 14-benzo[1,3]dioxol-5-yl-tetradecan-2-ol. From *P. betle*, β-sitosteryl palmitate was isolated for the first time from the genus *Piper*. A novel amide, 3-(3,4-dimethoxyphenyl)propanoyl pyrrole has been obtained from *P. brachystachyum*. Nerolidol was isolated for the first time from *P. falconeri*. From the methanol extract of the stems and leaves of *P. khasiana*, piperlonguminine, piperine, apigenin dimethyl ether and β-sitosterol were obtained. Retrofractamide A was obtained for the first time from *P. longum*; the structure of (+)-asarinin, isolated from *P. longum*, was confirmed by X-ray crystallographic studies. Retrofractamide A, apigenin dimethyl ether, tetratriacontanol and tectochrysin were isolated from *P. manii*. *P. pedicellosum* furnished β-sitosterol, pellitorine, piperlonguminine, cepharadione A and furacridone, the last compound being isolated for the first time from the genus *Piper*.

INTRODUCTION

Piper species, widely distributed in the tropical and subtropical regions of the world are used medicinally in various manners [1, 2]. In continuation of our previous investigations on various Indian *Piper* species, we undertook the phytochemical examination of *P. khasiana*, *P. manii*, *P. pedicellosum* and *P. thomsoni* which have not earlier been investigated phytochemically along with *P. acutisleginum*, *P. aduncum*, *P. attenuatum*, *P. betle*, *P. brachystachyum*, *P. falconeri*, *P. longum* and *P. peepuloides*. This is the second report on the phytochemical investigation of *P. acutisleginum* [3]. Thirty eight compounds were isolated, out of which 2,6-dimethoxy-4-(2-propenyl)benzene (**10**), β-sitosteryl palmitate (**18**) and furacridone (**29**) are being reported for the first time from the genus *Piper* and 2-acetoxy-1,3-dimethoxy-5-(2-propenyl)benzene (**13**), 14-benzo[1,3]dioxol-5-yl-tetradecan-2-ol (**14**) and 3-(3,4-dimethoxyphenyl)-propanoylpyrrole (**21**) are new compounds.

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RESULTS AND DISCUSSION

Thirty eight compounds were isolated in all from twelve *Piper* species, these are listed in a comprehensive manner in Table 1. Compound **13** was isolated as an oil from *P. aduncum*. Its ^{1}H NMR spectrum revealed the presence of an allyl group (δ 3.35, 5.0–5.10 and 5.90–6.01) and an acetoxy group (δ 2.32). A singlet at δ 3.80 indicated two identical methoxy groups and a singlet at δ 6.44 indicated two identical aromatic protons stemming from a symmetrically tetrasubstituted benzenoid compound. On biogenetic grounds, *i.e.* the presence of other compounds with similar structures in the *Piper* genus [4], the structure **13** for this compound was considered the best candidate. This was confirmed by comparing the

Table 1. Phytochemicals from twelve *Piper* species

Species	Plant part (dried wt.) Extract (wt.)	Compounds isolated (amount)	Comments
P. acutisleginum	Stems + leaves (1.5 kg) Petrol extract (30 g)	β-Sitosterol (20 mg)	New from this species
	Dichloromethane extract (35.6 g)	Piperlonguminine (1) (15 mg)	,,
		Piperine(2) (20 mg)	,,
	Methanol extract (45 g)	Cepharadione A(3) (20 mg)	,,
P. aduncum	Leaves (700 g)	Dillapiole(4) (72 mg)	
	Steam distillate (400 mg)	Myristicin(5) (12 mg)	
		5-Methoxy-6-(2-propenyl)-1,3-benzodioxol(6)(53 mg)	
		Safrole (7) (12 mg)	New from this species
		Piperitone(8)	Confirmed by GCMS
	Leaves (700 g)	1,2,3-Trimethoxy-5-(2-propenyl)-benzene(9) (50 mg)	New from this species
	Petrol extract (34.21 g)	2,6-Dimethoxy-4-(2-propenyl)-phenol(10) (15 mg)	New from the genus *Piper*
		3,5-Bis(3-methyl-2-butenyl)-4-methoxybenzoic acid(11) (14 mg)	
		2′,6′-Dihydroxy-4′-methoxydihydrochalcone (12) (40 mg)	
		β-Sitosterol (8 mg)	
		Dillapiole(4) (100 mg)	
		Myristicin(5) (20 mg)	
		5-Methoxy-6-(2-propenyl)-1,3-benzodioxol(6) (60 mg)	
		Safrole(7) (47 mg)	
		2-Acetoxy-1,3-dimethoxy-5-(2-propenyl)benzene(13) (30 mg)	New compound
P. attenuatum	Stems + Leaves (2 kg)	β-Sitosterol (50 mg)	New Compound
	Petrol extract (65 g)	14-Benzo[1,3]dioxol-5-yl-tetradecan-2-ol(14) (50 mg)	
		Kadsurin A (15) (60 mg)	New from this species
		Kadsurin B (16) (70 mg)	,,
		(+)-Crotepoxide (17) (40 mg)	
P. betle	Leaves (820 g)	β-Sitosterol (12 mg)	
	Petrol extract (16.4 g)		
		Dotriacontanoic acid (15 mg)	New from this species
		Tritriacontane (10 mg)	,,
		Stearic acid (15 mg)	,,
		Cepharadione A(3) (20 mg)	
	Stems (1.32 kg)	Piperine(2) (20 mg)	New from this species
	Petrol + Dichloromethane extract (34 g)	Piperlonguminine(1) (15 mg)	,,
		β-Sitosterol (20 mg)	
	Roots (500 g)	β-Sitosterol (10 mg)	
	Petrol + Dichloromethane extract (16.2 g)	β-Sitosteryl palmitate (18) (8 mg)	New from family Piperaceae
P. brachystachyum	Stems + leaves (2 kg)	Sesamin(19) (20 mg)	
	Petrol extract (38 g)	(+)-Asarinin(20) (10 mg)	
		β-Sitosterol (10 mg)	
		Elemicin(9) (12 mg)	New from this species
	Dichloromethane-methanol extract (20 g)	β-Sitosterol (10 mg)	
		3-(3,4-Dimethoxyphenyl)-propanoylpyrrole(21) (200 mg)	New Compound
	Fruits (670 g)	β-Sitosterol (15 mg)	
	Petrol extract (10 g)	Parsley apiole(22) (14 mg)	

Table 1—*continued*.

Species	Plant part (dried wt.) Extract (wt.)	Compounds isolated (amount)	Comments
P. falconeri	Leaves (1 kg) Petrol extract (34 g)	Nerolidol(23) (54 mg)	New from this species
P. khasiana	Stems and leaves (130 g)	β-Sitosterol (25 mg)	
	Methanol extract (11.4 g)	Apigenin dimethyl ether(24) (6 mg)	Phytochemically investigated for the first time
		Piperlonguminine(1) (20 mg)	
		Piperine(2) (60 mg)	
P. longum	Stems + leaves (1.74 g)	(+)-Asarinin(20) (4.5 mg)	X-Ray studies
	Petrol extract (25 g)	Guineensine(25) (7 mg)	
		Retrofractamide A (26) (8 mg)	New from this species
P. manii	Stems (970 g)	Retrofractamide A(26)	First phytochemical
	Petrol extract (12 g)	(15 mg)	investigation
		Apigenin dimethyl ether(24) (40 mg)	
		Tectochrysin(27) (70 mg)	
	Fruits (700 g)	Tetratriacontanol(10 mg)	
	Petrol extract (20 g)		
P. pedicellosum	Stems and leaves (1.27 kg)		First
	Petrol extract (7.82 g)	Pellitorine(28) (30 mg)	phytochemical
		β-Sitosterol (25 mg)	investigation
		Piperlonguminine(1) (8 mg)	
	Dichloromethane extract (5.43 g)	Cepharadione A(3) (23 mg)	
	Methanol extract (12.6 g)	Furacridone(29) (7 mg)	New from genus *Piper*
P. peepuloides	Fruits (1.80 kg)	β-Sitosterol (20 mg)	
	Ethanol extract (170 g)	Apigenin dimethyl ether(24) (20 mg)	
		Luteolin 3′,4′,7-trimethyl ether(30) (40 mg)	
		(+)-Diaeudesmin(31) (43 mg)	
P. thomsoni	Stems + leaves (1.98 kg)	Dotriacontanol (20 mg)	First phytochemical
	Petrol extract (51.6 g)	Dotriacontanoic acid (30 mg)	investigation
		(−)-Galbelgin(32) (15 mg)	
		β-Sitosterol (10 mg)	
	Dichloromethane-methanol extract(cold) (32.6 g)	Piperine(2) (20 mg)	
		Cepharadione A(3) (10 mg)	

^{1}H NMR and ^{13}C NMR spectra of compound **13** with those of **10** [5], the deacetylated derivative of **13**. Thus we propose the structure of **13** to be 2-acetoxy-1,3-dimethoxy-5-(2-propenyl)benzene, a compound which has neither been isolated from any natural source nor synthesised.

Compound **14** was obtained as a white crystalline solid from *P. attenuatum*. In its ^{1}H NMR spectrum, a double-doublet at δ 6.60(1H, $J = 7.9$ and 1.6 Hz), two doublets at δ 6.66 (1H, $J = 1.6$ Hz) and δ 6.71 (1H, $J = 7.9$ Hz) and a singlet at δ 5.90(2H) indicated the presence of a piperonyl moiety. A multiplet at δ 3.79 (1H) along with a peak at 3450 cm^{-1} in its IR spectrum revealed the presence of -CH- OH unit. A doublet at δ 1.18(3H) indicated the presence of CH_3CH- group. In its EIMS, peaks at m/z 290 ($[M]^+ - 45$) and m/z 45 indicated the alcohol to be a secondary alcohol, *i.e.* having the CH_3CHOH moiety. A symmetrical multiplet for one proton at δ 3.79 further extended this to $CH_3CHOHCH_2$-. A long saturated carbon chain was evident from a broad multiplet in the region δ 1.2–1.4. A peak at m/z 135 in its EIMS indicated the piperonyl moiety attached to a methylene group. Thus the presence of a 3,4-methylenedioxy benzyl group ($=135$ units), a $CH_3CHOHCH_2$ moiety ($=59$ units) and a long saturated carbon chain were confirmed. Subtraction of molecular mass of these moieties (194 units) from M^+ (334 units) gives us the remaining unaccounted 140 units, which suitably fits for ten methylene units. The DEPT spectrum in the region δ 25.77 to 39.4 indicated the presence of 12-CH_2 groups. On the basis of above spectral data, **14** was identified as 14-benzo[1,3] dioxol-5-yl-tetradecan-2-ol. The structure is fully compatible with ^{13}C NMR spectrum

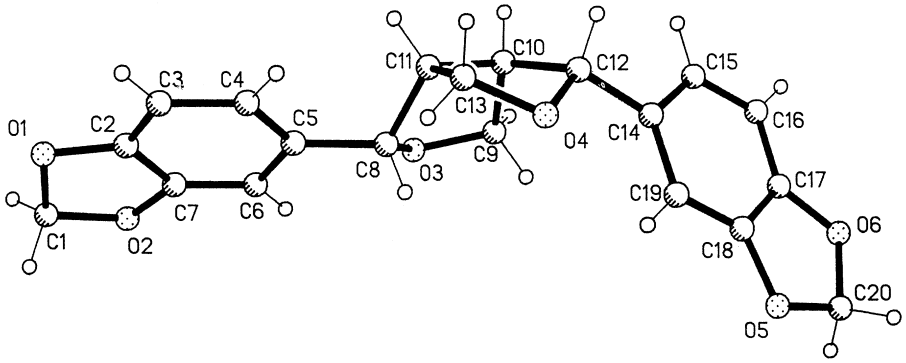


Fig. 1. X-ray crystal structure of (+)-asarinin (**20**).

of **14**, this compound is a hitherto unknown compound.

Compound **18**, suspected to be β-sitosteryl palmitate, was obtained as a white solid (from *P. betle*), mp 85–86°. The ion at m/z 652 in the mass spectrum was compatible with a molecular formula of $C_{45}H_{80}O_2$. The base peak at m/z 396 could stem from elimination of palmitic acid, leading to a conjugated diene system in the sterol moiety. The IR absorption maximum at 1740 cm^{-1} together with ^1H NMR and ^{13}C NMR spectral data of **18** indicated it to be a steroidal ester. The ^1H NMR spectrum showed a multiplet between δ 0.64 and 2.1 from which a number of methyl groups emerged. A triplet at δ 2.26 corresponding to the CH_2COO moiety was overlayed with another multiplet, but still discernible. Multiplets at δ 4.61 and 5.37 originated from H-3 and H-6, respectively. The ^{13}C NMR spectrum had the following characteristic ranges and signals, assignment having been aided by a DEPT spectrum: **a)** 11.8 to 19.8 (7 methyl groups), **b)** 21.0 to 56.7 (7 CH and 20 plus discernible CH_2 groups from the alcohol and acid moieties, **c)** 73.66 (-COO-CH<), **d)** 122.56 and 139.73 (>C=C<) and **e)** 173.32 (C=O). To confirm the structure, a synthetic sample was prepared [6]. All ^{13}C NMR spectral chemical shifts for the natural and synthetic samples agreed within 0.02 ppm. Also the ^1H NMR spectra and the mass spectral fragmentation pattern as well as TLC R_f-values agreed well for the two samples. On these grounds, **18** is considered to be β-sitosteryl palmitate. Although β-sitosteryl palmitate has been isolated [7] and synthesised [6, 7] earlier, this is the first report of its isolation from the Piperaceae and also of its NMR and mass spectral data.

The structure of (+)-asarinin was confirmed as **20** on the basis of its ^1H NMR, EIMS and ^{13}C NMR spectra [8]. Owing to its pharmacological potential, *i.e.* insecticidal [9], antituberculostatic and antifungal [10] activities, it was decided to examine the relative stereochemistry by X-ray analysis [Fig. 1] which confirmed its structure.

Compound **21** was obtained as a white crystalline solid from *P. brachystachyum*. The molecular formula was determined by HR-EIMS to be $C_{15}H_{17}NO_3$, compatible with hydrogen and carbon counts based on the ^1H and ^{13}C NMR spectra. Two singlets at δ 3.83 and 3.84, each for 3H, revealed the presence of two methoxy groups on a phenyl ring. A multiplet between δ 3.03 and 3.10 integrating for 4H indicated the presence of two -CH_2 groups which was confirmed by the DEPT spectrum. The aromatic region of the ^{13}C NMR spectrum above 100 ppm showed evidence of ten aromatic carbons out of which only three are unprotonated. A multiplet between δ 6.76 and 6.78 (3H) was assigned to the C-2′, C-5′ and C-6′ protons. A doublet at δ 6.27 (2H) and a singlet at δ 7.29 (2H) indicated the presence of a pyrrole ring. The peak at 1700 cm^{-1} in the IR spectrum and a signal at δ 169.59 in the ^{13}C NMR spectrum were compatible with a tertiary amide group. On basis of the above spectral data, the compound was assigned the structure 3-(3,4-dimethoxyphenyl)propanoylpyrrole and X-ray diffraction studies confirmed this [11]. This amide is a hitherto unknown compound.

EXPERIMENTAL

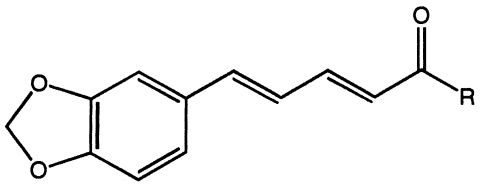
General

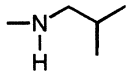
Mps were determined in a bath and are uncorrected. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer, chemical shifts are relative to TMS. Mass spectra were determined at 70 eV on a Jeol AX505 W or a Varian MAT 311A mass spectrometer. Silica gel (60–80 mesh) was used for column chromatography and silica gel G for TLC.

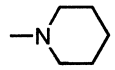
Isolation procedure

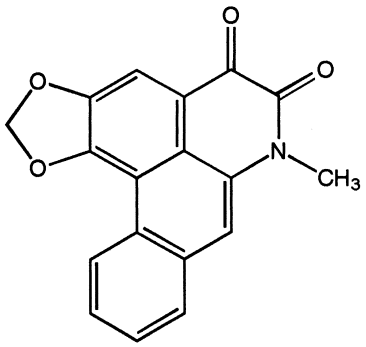
All the plant materials, except for *P. aduncum*, *P. attenuatum* and *P. longum*, were collected from the forests around Botanical Survey of India(BSI, Eastern Circle, Shillong) and identified by Dr. B. M. Wadhwa (Deputy Director, BSI, Shillong); specimens were submitted to the Herbarium of this Institute.

The stems and leaves of *P. longum* and *P. attenuatum* (submitted at the National Research Centre for Spices, NRCS, Calicut, Kerala) were collected from



1 R= 

2 R= 



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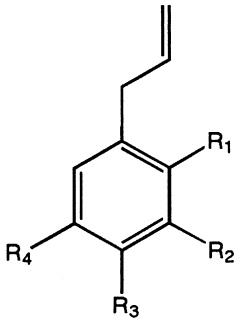

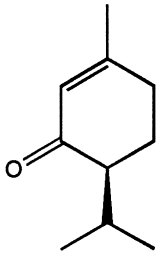

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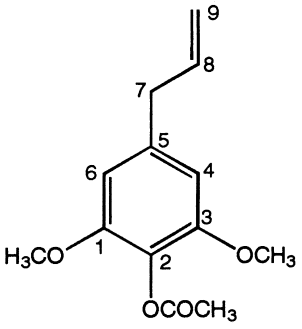
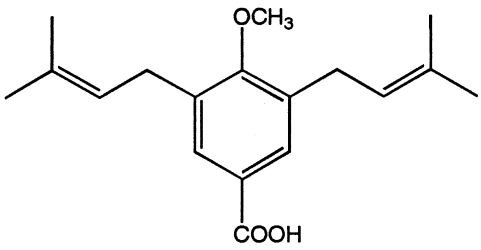


13

4 $R_1=R_2=OCH_3$, $R_3+R_4=OCH_2O$
5 $R_1=H$, $R_2=OCH_3$, $R_3+R_4=OCH_2O$
6 $R_1=OCH_3$, $R_2=H$, $R_3+R_4=OCH_2O$
7 $R_1=R_2=H$, $R_3+R_4=OCH_2O$
9 $R_1=H$, $R_2=R_3=R_4=OCH_3$
10 $R_1=H$, $R_2=R_4=OCH_3$, $R_3=OH$
22 $R_1=R_4=OCH_3$, $R_2+R_3=OCH_2O$



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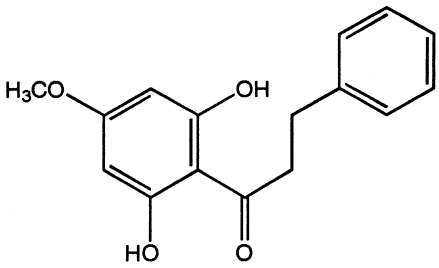

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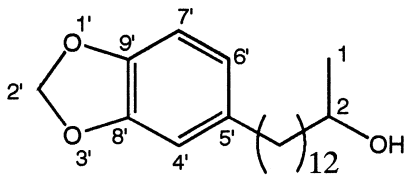
the forests of Ooty, Kotagiri and Avalanchi and identified by Dr. P. N. Ravindran, NRCS, Calicut. The leaves of *P. aduncum*, collected in Ecuador were obtained from Professor Dr Kurt Torssell (Department of Chemistry, Aarhus University, Denmark).

P. acutisleginum—The dried stems and leaves were extracted in succession with petrol, CH_2Cl_2 and MeOH. The dried petrol extract on column chromatography yielded β-sitosterol, while the CH_2Cl_2 and MeOH extracts on a similar work up yielded **1**, **2** and **3**, respectively. *P. aduncum*—The dried leaves were steam extracted, and the oily residue obtained was subjected to prep. TLC in petrol:EtOAc (49:1). Four compounds, **4–7**, were isolated in the pure state; the presence of piperitone (**8**) was confirmed by GCMS. The dried leaves were also extracted with petrol and



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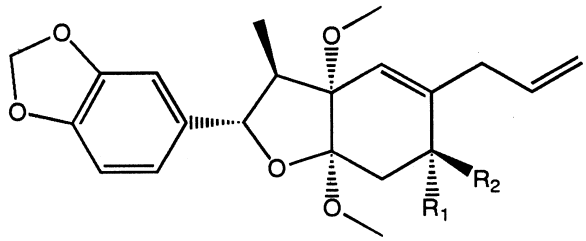
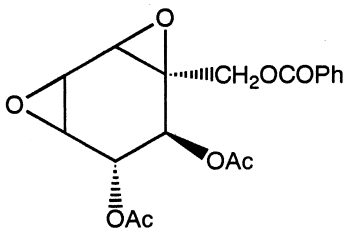


15 R_1,R_2=O
16 R_1=H, R_2=OH



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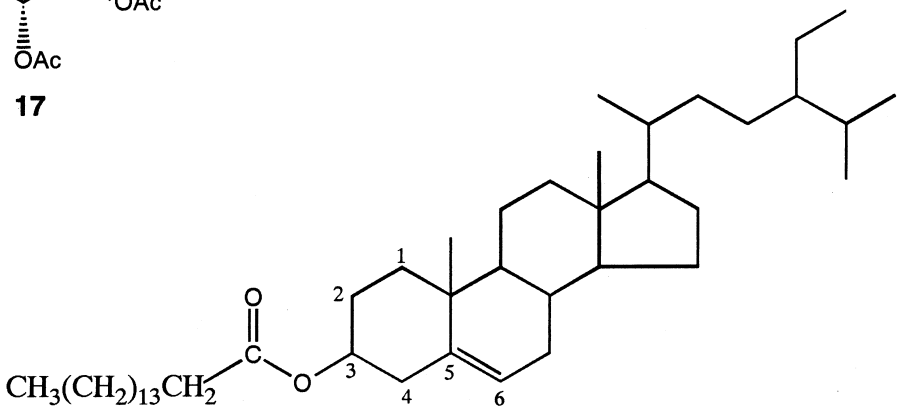

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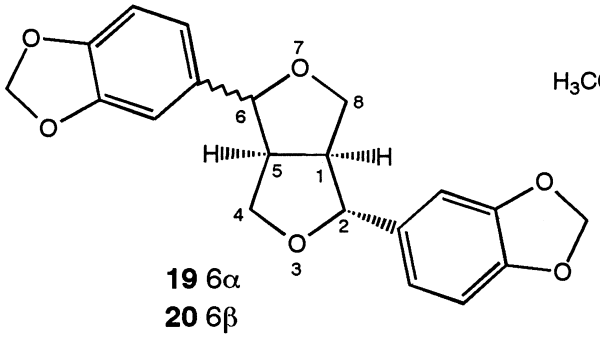
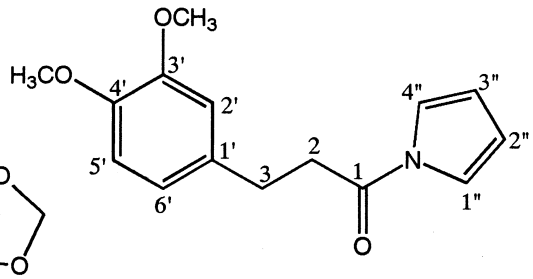


19 6α
20 6β



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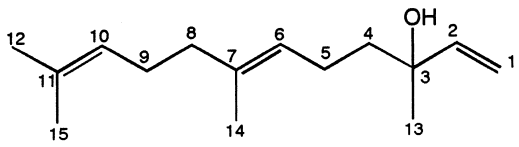
the dried extract column chromatographed on silica gel, elution with petrol and petrol-EtOAc in increasing polarities yielded ten compounds, *i.e.* β-sitosterol, compounds **4–7** and **9–13**. *P. attenuatum*—The dried petrol extract of the stems and leaves on column chromatography gave β-sitosterol and compounds **14–17**. *P. betle*—The leaves, stems and roots were dried and extracted with petrol, CH_2Cl_2 and MeOH in succession. The dried petrol extract of leaves on column chromatography gave β-sitosterol, dotriacontanoic acid, tritriacontane, stearic acid and **3**. The petrol and CH_2Cl_2 extracts of the stems were



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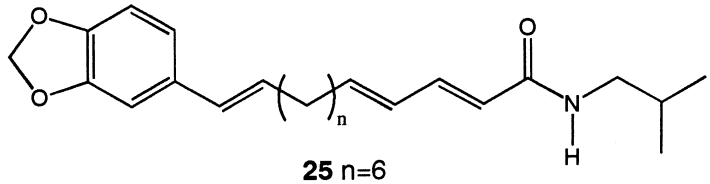
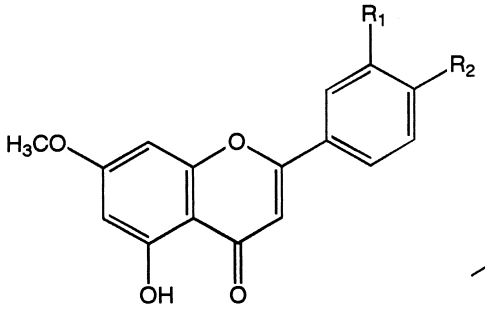
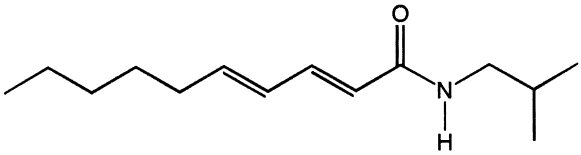


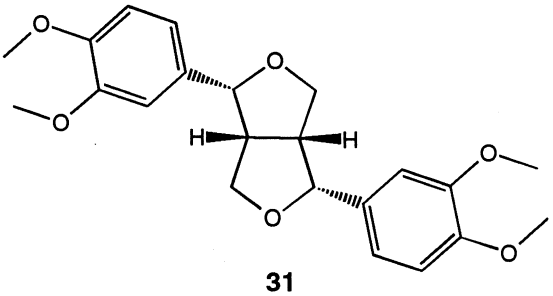
25 n=6
26 n=2



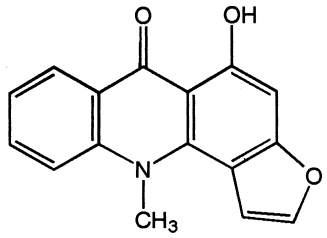
24 R_1=H, R_2=OCH_3
27 R_1=R_2=H
30 R_1=R_2=OCH_3



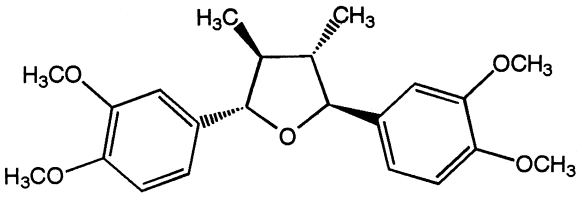
28



31



29



32

combined and solvent evaporated. The residue on column chromatography afforded **1**, **2** and β-sitosterol, while the combined petrol and CH_2Cl_2 extracts of the roots yielded β-sitosterol and **18**. *P. brachystachyum*—Its stems and leaves were dried and extracted with CH_2Cl_2 = MeOH (1:1, cold). The dried extract on column chromatography gave β-sitosterol and **21**. Stems and leaves were also extracted with hot petrol and from that extract, β-sitosterol, **9**, **19** and **20** were isolated. Dried fruits were extracted with petrol and the dried petrol extract on column chromatography yielded β-sitosterol and **22**. *P. falconeri*—The dried

petrol extract of leaves on column chromatography using petrol-$CHCl_3$ as eluent yielded **23**. *P. khasiana*—The dried stems and leaves were extracted with petrol (60–80°), CH_2Cl_2 and MeOH, successively. Column chromatography of the dried MeOH extract on silica gel and elution with petrol-$CHCl_3$ afforded *β*-sitosterol and compounds **1**, **2** and **24**. *P. longum*—The air-dried stems and leaves were extracted with petrol, $CHCl_2$ and MeOH in succession. The dried petrol extract after being subjected to fractionation on silica gel using petrol, petrol-$CHCl_3$ and $CHCl_3$ as eluents with increasing polarities led to the isolation of **20**, **25** and **26**. *P. manii*— Its stems and fruits were dried and each extracted with petrol separately. The dried petrol extract of stems on column chromatography using petrol, petrol-$CHCl_3$, $CHCl_3$ and $CHCl_3$-MeOH in increasing polarities as eluents yielded **24**, **26** and **27**, while the petrol extract of the fruits on similar treatment yielded tetratriacontanol. *P. pedicellosum*—The dried stems and leaves were extracted with petrol (60–80°), CH_2Cl_2 and MeOH, successively. The dried petrol extract on column chromatography with petrol-$CHCl_3$ as eluent yielded *β*-sitosterol, **1** and **28**. By similar treatment of the dichloromethane extract, **3** was isolated. The dried MeOH extract on column chromatography yielded the alkaloid **29** on elution with $CHCl_3$-MeOH. *P. peepuloides*—The dried fruits were extracted with EtOH; column chromatography of the dried extract using $CHCl_3$-MeOH as eluent yielded *β*-sitosterol, **24**, **30** and **31**. *P. thomsoni*—The stems and leaves were dried and extracted with petrol (60–80°); dotriacontanol, dotriacontanoic acid and **32** were obtained by column chromatography of the dried extract using petrol, petrol-$CHCl_3$, $CHCl_3$ and $CHCl_3$-MeOH, in increasing polarities as eluents. The CH_2Cl_2:MeOH (1:1) extract on similar work up yielded *β*-sitosterol, **2** and **3**.

Piperlonguminine (**1**). Yellow solid, mp164° (lit [12, 13] mp 166–168°). Its UV, IR, ^{1}H NMR and EI mass spectra were comparable with those in the literature [12, 13]. *Piperine* (**2**). Pale yellow crystalline solid, mp 130° (lit [14] mp 129°). Its spectral data (^{1}H NMR, ^{13}C NMR and EIMS) were as reported in literature [15]. *Cepharadione A* (**3**). Mp > 340° (lit. [16, 17] mp > 350°). Its IR, UV, ^{1}H NMR spectra and EIMS data were as previously reported [16]. 4,5-*Dimethoxy*-6-(2-*propenyl*)-1,3-*benzodioxol* (*dillapiole*, **4**). Identified by comparing its spectral data with those reported in literature [18]. 4-*Methoxy*-6-(2-*propenyl*)-1,3-*benzodioxol* (*myristicin*, **5**). Its ^{1}H NMR, ^{13}C NMR and EIMS tallied with the spectral data reported in literature [19]. 5-*Methoxy*-6-(2-*propenyl*)-1,3-*benzodioxol*(**6**). Its ^{1}H NMR and EIMS data tallied well with those reported in literature [19]. 5-(2-*Propenyl*)-1,3-*benzodioxol* (*safrole*, **7**). Identified by comparison with the commercially available sample of safrole. 1,2,3-*Trimethoxy*-5-(2-*propenyl*)*benzene* (*elemicin*, **9**). Its ^{1}H NMR and EIMS data were similar to the published data [20]. *β-Sitosterol*. White solid, mp 136–137° (lit [21] mp 136°). Identified by comparison with an authentic sample. 2,6-*Dimethoxy*-4-(2-*propenyl*)*phenol*(**10**). Its ^{1}H and ^{13}C NMR spectra were identical with those in literature [5]. 3,5-*Bis*(3-*methyl*-2-*butenyl*)-4-*methoxybenzoic acid*(**11**). It had identical spectral data (^{1}H NMR, ^{13}C NMR and EIMS) to those in the literature [22]. 2′,6′-*Dihydroxy*-4′-*methoxydihydrochalcone*(**12**). Colourless solid (40 mg), mp 164° (lit. [22] mp 164–65°). Spectroscopic data (^{1}H NMR, ^{13}C NMR and EIMS) were identical with the previously reported data [22]. 2-*Acetoxy*-1,3-*dimethoxy*-5-(2-*propenyl*)*benzene*(**13**). Obtained as a colourless oil. ^{1}H NMR ($CDCl_3$): δ 2.32(3H, *s*, -$OCOCH_3$), 3.35(2H, *d*, $J = 7$ Hz, -$CH_2CH=CH_2$), 3.80(6H, *s*, $2 \times OCH_3$), 5.0–5.1(2H, *m*, CH_2-$CH=CH_2$), 5.90–6.01(1H, *m*, -CH_2-$CH=CH_2$), 6.44(2H, *s*, H-4 and H-6). ^{13}C NMR($CDCl_3$): δ 20.41 (-$OCOCH_3$), 40.63(C-7), 56.09($2 \times OCH_3$), 105.21(C-4 and C-6), 116.23(C-9), 126.5(C-5), 136.89(C-8), 138.52(C-1 and C-3), 152.00(C-2), 168.84(>C = O). 14-*Benzo*[1,3]*dioxol*-5-*yl*-*tetradecan*-2-*ol*(**14**). White crystalline solid, mp 107°. UV (MeOH) nm: 287. IR (KBr) cm^{-1}: 3450, 2980, 2910, 1510, 1450, 1225, 1135, 935 and 807. ^{1}H NMR ($CDCl_3$): δ 1.18(3H, *d*, $J = 6.2$ Hz, H-1), 1.25(18H, *m*, $9 \times CH_2$), 1.40(4H, *m*, H-3 and H-4), 2.50(2H, *dd*, $J = 7.7$ and 7.7 Hz, H-14), 3.79(1H, *m*, H-2), 5.90(2H, *s*, OCH_2O), 6.60(1H, *dd*, $J = 7.9$ and 1.6 Hz, H-6′), 6.66(1H, *d*, $J = 1.6$ Hz, H-2′) and 6.71(1H, *d*, $J = 7.9$ Hz, H-5′). ^{13}C NMR($CDCl_3$): δ 23.50 (C-1), 25.77(C-4), 29.19(C-5), 29.49(C-12), 29.58(C-6, C-11), 29.63(C-7 to C-10), 31.75(C-13), 35.7(C-14), 39.4(C-3), 68.20(C-2), 100.66(C-2′), 108.00(C-4′), 108.86(C-6′), 121.01(C-7′), 136.70(C-5′), 145.20(C-8′), and 147.30(C-9′). EIMS *m*/*z* (rel. int.): 334 $[M]^+$ (59), 316(7), 290(4), 274(<1), 246(<1), 232(<1), 204(<1), 175(<1), 161(5), 149(4), 148(10), 136(19), 135(100), 105(5), 91(4), 77(8) and 45(20). *Kadsurin A* (**15**). Obtained as an oil. Its spectroscopic data (^{1}H NMR, ^{13}C NMR, UV, IR and EIMS) tallied well with those reported in literature [23]. *Kadsurin B*(**16**). Colourless crystalline solid, mp 100–101° (lit. [24] mp 101–102°). All the spectral data were completely in agreement with the published data [24]. (+)-*Crotepoxide* (**17**). Mp 150–151° (lit. [25] mp 150–151°). Its spectral data were as reported previously [25, 26]. *β-Sitosteryl palmitate* (**18**). Mp 85–86° (lit. [6] mp 85.5° and [7] 83.5°); IR ν_{max}(nujol) cm^{-1}: 1740. ^{1}H NMR ($CDCl_3$): δ 0.64–2.1 (*m*, $7 \times CH_3$, -CH_2- and -CH< protons of alcohol and acid moieties), 2.26(2H, *t*, -CH_2COO-), 4.61(1H, *m*, H-3), 5.37(1H, *d*, H-6). ^{13}C NMR ($CDCl_3$): δ 11.86, 11.99, 14.11, 18.78, 19.04, 19.32 and 19.81 (CH_3); 21.03, 22.69, 23.07, 24.29, 25.07, 26.10, 27.83, 28.24 and 29.11 (CH_2); 29.17(CH); 29.25, 29.37, 29.45, 29.58, 29.65 and 29.70 (CH_2); 31.88 (CH); 31.92, 33.95 and 34.73 (CH_2); 36.16(quat. C); 36.60(CH), 37.02, 38.17, and 39.73 (CH_2) and 42.31 (quat. C); 45.85, 50.03, 56.04 and 56.69(CH); 73.66(COO-CH<), 122.56 and 139.73(>C=C<), 173.32(>C=O). EIMS *m*/*z* (rel. int.): 652$[M]^+$ (<1), 638(<1), 534(<1), 508(<1), 480(<1), 452(<1), 396[M-palmitic acid]$^+$ (100), 338(32), 255 (6), 147(10),

107(8), 95(11), 81(15), 71(15), 57(25), 43(24). *Sesamin*(**19**). White solid, mp. 120–22° (lit. [8] mp 122–24°). Its spectroscopic data were completely in agreement with the reported data [8, 27]. (+)-*Asarinin*(**20**). Mp 119° (lit. [8] mp 120°), $[\alpha]_D^{22}+124.5°$ ($CHCl_3$, *c* 0.38) (lit. [8] $[\alpha]_D^{22}+124.4°$, $CHCl_3$). Its structure was confirmed by its X-Ray crystallographic analysis Fig. 1. *Crystal data*. $C_{20}H_{18}O_6$, $Mr=354.34$, Monoclinic, Space group P2(1), $a=9.552(5)$, $b=5.535(5)$, $c=15.572(10)$ Å, $\alpha=\gamma=90°$, $\beta=103.87(5)°$, $V=799.3(10)$ Å^3, $Z=2$, D_{calc} 1.472 Mg/m^3, $F(000)=372$, $\lambda(MoK\alpha)=0.71073$ Å, μ ($MoK\alpha$) $=0.109$ mm^{-1}.

Data were collected using a crystal size, *ca* $0.70\times0.16\times0.07$ mm on a Siemens P3R3 four-circle diffractometer in a w-Ze mode. A total of 1677 reflections were measured for $2.20<\Theta<25.05°$ and $0<h<11$, $0<k<6$, $-18<l<18$. No absorption correction was applied. The compound is essentially non-planar. The methylenedioxyphenyl ring and the hydrogen atom attached to the same carbon atom are *trans* with respect to each other. The methylenedioxyphenyl ring at C-2 is in *cis* position with respect to C-1H, whereas the methylenedioxyphenyl group at C-6 is in *trans* position with respect to C-5H. Both methylenedioxyphenyl rings are in *trans* position with respect to each other while the tetrahydrofuran rings are *cis* fused *via* C_1-C_5. The final *R* indices were $R_1>=0.0468$, $wR_2>=0.0982$ and *R* indices (all data) were $R_1>=0.0828$, $wR_2>=0.1158$. The tables of crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. 3-(3,4-*Dimethoxyphenyl*) *propanoylpyrrole* (**21**). White crystalline solid, mp 108°. UV (MeOH) nm: 285. IR (Nujol) cm^{-1}: 3150, 3100, 1700, 1610, 1600, 1520, 1325, 1300, 1260, 1220, 1155, 1020, 920, 850, 810, 795, 750. ^{1}H NMR ($CDCl_3$): δ 3.03–3.10 (4 H, *m*, H-2 and H-3), 3.83 (3H, *s*, -OCH_3), 3.84 (3H, s, -OCH_3), 6.27 (2H, *d*, $J=2.4$ Hz, H-2″ and H-3″), 6.76–6.78 (3H, *m*, H-2′, H-5′ and H-6′), 7.29(2H, broad *s*, H-1″ and H-4″). ^{13}C NMR ($CDCl_3$):δ 169.59 (>C=O), 148.90 (C-3′), 147.56 (C-4′), 132.70 (C-1′), 120.09 (C-6′), 118.79 (C-1″ and C-4″), 112.97 (C-2″ and C-3″), 111.74 (C-5′), 111.37 (C-2′), 55.78 (OCH_3), 55.71 (OCH_3) 36.47 (C-2), 29.91(C-3). EIMS *m*/*z* (rel.int.): 259[M]$^+$ (70), 192(32), 177(7), 164(30), 151(100), 135(4), 121(5), 107(10), 91(8), 77(9) and 67(13). *Parsley apiole* (**22**). Colourless oil (12 mg). It was identified by comparison of its spectral data (^{1}H NMR, ^{13}C NMR and EIMS) with the reported data [23, 28]. *Nerolidol*(**23**). Yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.3(3H, *s*, H-14), 1.6 (8H, *m*, H-9, H-12 and H-15), 1.65(3H, *s*, H-13), 2.0–2.1(6H, *m*, H-4, H-5 and H-8), 5.0–5.05(2H, *m*, H-6 and H-10), 5.1(2H, *m*, H-1), 5.95–6.0(1H, *m*, H-2). ^{13}C NMR ($CDCl_3$): δ 15.95(C-15), 17.61(C-12), 22.66(C-9), 25.62(C-14), 26.59(C-8), 27.79(C-13), 39.64(C-5), 42.01(C-4), 73.40(C-3), 111.59(C-1), 124.18(C-6, C-10), 131.31 (C-11), 135.45(C-7) and 145.02(C-2). EIMS tallied well with that reported in the literature [29]. *Apigenin dimethyl ether* (**24**). Yellow solid, mp 163–164° (lit. [30] mp 165°). It was identified by comparison with an authentic sample. *Guineensine* (**25**). Mp 116° (lit. [31] mp 116°). All the spectral data were in agreement with the reported data [31].

Retrofractamide A (**26**). Mp 132° (lit. [32] mp 120°). Its spectral data (^{1}H NMR, ^{13}C NMR and EIMS) were as reported in literature [32]. *Tectochrysin* (**27**). Mp 164° (lit. [33] mp 165°). Identified by comparison with an authentic sample. *Pellitorine* (**28**). Mp 88–90° (lit. [34] mp 60–68°). All the spectral data (^{1}H NMR, ^{13}C NMR and EIMS) were as reported earlier [34]. *Furacridone* (**29**). Mp 230° (lit. [35] mp 223–225°). Its ^{1}H NMR and EIMS tallied well with the data reported in the literature [35]. *Luteolin 3′,4′,7-trimethyl ether*(**30**). Mp 162–163° (lit. [36] mp 163°). All the spectral data (^{1}H NMR, ^{13}C NMR and EIMS) corresponded well with those reported in literature [36]. (+)-*Diaeudesmin*(**31**). Mp 160–162°, $[\alpha]_D^{22}+338.36°$ ($CHCl_3$, *c* 0.645) (lit. [37] mp 157–158°, $[\alpha]_D^{27}+316°$, $CHCl_3$). Its spectroscopic data were completely in agreement with the published data [37]. (−)-*Galbelgin*(**32**). Mp 142° (lit. [38] mp 141–142°), $[\alpha]_D^{22}-85.1°$ ($CHCl_3$, *c* 0.047) (lit. [38] $[\alpha]_D^{22}-140.5°$ ($CHCl_3$, *c* 0.31)). Its ^{1}H NMR, ^{13}C NMR and EIMS data were in agreement with the reported data [38]. *Dotriacontanoic acid*. White solid, mp 95° (lit. [39] mp 96°). ^{1}H NMR ($CDCl_3$): δ 0.9(3H, *t*, CH_3), 1.2–1.4(56H, *m*, $28\times CH_2$), 1.6–1.7(2H, *m*, C$H_2$$CH_2$COOH), 2.35(2H, *t*, -C$H_2$COOH). ^{13}C NMR ($CDCl_3$): δ 13.99(C-32), 22.59 to 29.60 (C-4 to C-31), 31.83(C-3), 33.79(C-2), 179.06(>C=O). EIMS *m*/*z* (rel. int.): 480 ([M$^+$], 20), 452(M-C_2H_4]$^+$, 30), 396(0.5), 353(0.5), 294(0.5), 241(0.5), 185(0.5), 57(100). It could be a mixture of lower and higher homologues of dotriacontanoic acid. *Tritriacontane*. Mp 73° (lit. [40] mp 71.8°). *Stearic acid*. Mp 64–65° (lit. [41] mp 69°). *Tetratriacontanol*. Mp 80° (lit. [42] mp 81°). All the spectral data (^{1}H NMR, ^{13}C NMR and EIMS) were in agreement with the reported data [42]. *Dotriacontanol*. White solid, mp 87° (lit. [43] mp 89°). ^{1}H NMR ($CDCl_3$): δ 0.85(3H, *t*, CH_3), 1.2–1.4(60H, *m*, $30\times CH_2$), 3.55(2H,*t*, -CH_2OH). ^{13}C NMR ($CDCl_3$): δ 14.02(C-32), 22.61(C-31), 25.66(C-30), 29.28 to 29.62(C-29 to C-4), 31.84(C-3), 32.79(C-2), 63.02(C-1). EIMS *m*/*z* (rel. int.): 448([M$^+$-H_2O], 4), 420([M$^+$-H_2O-C_2H_4], 10), 392(10), 364(20), 336(10), 111(8), 97(24), 83(40), 69(48), 57(78), 43(100). It could be a mixture of lower and higher homologues of dotriacontanol.

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