The second problem is the intensity of the IT band. The IT band of Complex III in acetone appears at $\nu_{max}=13.5$ kK with $\varepsilon_{max}=303$ M^{-1} cm^{-1} as a shoulder on a strong absorption occurring at a higher frequency.[4] The IT band is the totality of transitions, $\nu'\rightarrow\nu$. But the major contribution originates in the transitions from the $\nu'=0$ vibrational levels, the relative population of which is over 98% even at 306 K. Associating a Gaussian lineshape (half width, 2000 cm^{-1}) with each transition $0\rightarrow\nu$, we get an IT band with $\nu_{max}=13.5$ kK and $\varepsilon_{max}=526$ M^{-1} cm^{-1}. The calculated ε_{max} is much larger than the measured value, considering the IT band overlaps with another absorption. This means that the PKS parameters determined from the IT band alone can be quite different from our values. The discrepancy may be attributed to Eq. (1), which is an approximation for the transition probability. In order to check how good this equation is, we need to study mixed-valence systems for which both the transition probabilities and the IT band contour can be measured accurately.

In summary, we have determined the ground vibronic manifold of Complex III using the PKS model, and have shown that the intramolecular electron transfer in this system at 261-306 K is a tunneling process occurring mostly at the lowest three pairs of vibrational levels below the top of the energy barrier. More work on related systems is needed to clarify the solvent effects and the validity of Eq. (1).

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Piperoctadecalidine, a New Piperidine Alkaloid from *Piper retrofractum* Fruits

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A chemical investigation of the fruits of *Piper retrofractum* (Piperaceae) has led to the isolation and characterization of a novel piperidine alkaloid, piperoctadecalidine together with three known alkaloids piperine, pipernonaline and guineensine. The structure of the new compound was detemined to be (2E,4E,14Z)-N-(2,4,14-Octadecatrienoyl) piperidine by spectral and synthetic methods.

Introduction

The fruits of Piperaceae plants have been recently received much attention because they have many physiologically active principles, and a number of studies on the chemical constituents of the fruits have been conducted.[1,2] Among these components, unsaturated amides constitute a major group of secondary metabolites. In continuing our studies on the chemical components of Piper fruits, we have isolated a new piperidide named piperoctadecalidine (1) from *P. retrofractum*, together with three known alkaloids, piperine (2), pipernonaline (3) and guineensine (4). This paper describes the structural elucidation of the new compound.

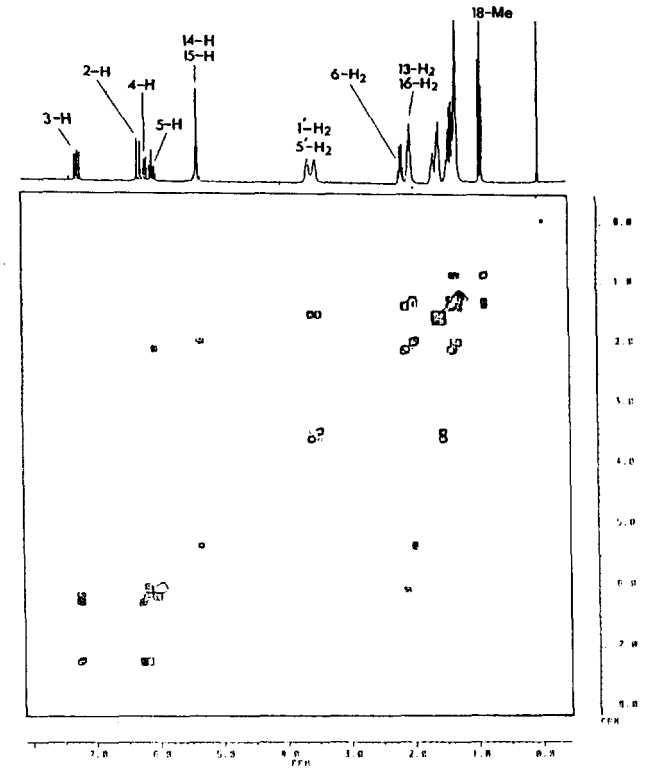


Figure 1. ^{1}H-^{1}H COSY spectrum of piperoctadecalidine (1).

Results and Discussion

The hexane extract of the fruits of *P. retrofractum* was fractionated by a combination of column chromatography (CC) on silica gel and a Lobar column and finally purified by Recycling Preparative HPLC to afford compound **1**.

Compound **1** had the molecular formular $C_{23}H_{29}NO$(m/z 345.3014) indicating 5 degrees of unsaturation. The alkaloid nature of the compound was indicated by a positive Dragendorff reaction. The absorption bands at 1651 (conjugated carbonyl group), 1624 (conjugated double bond) and 999 (*trans* double bond) cm^{-1} in FT-IR spectrum and λ_{max} at 265 nm in the UV spectrum suggested the presence of a conjugated system related to 2E,4E-dienamide as observed in those of 5.[3] ^{1}H- and ^{13}C-NMR spectra indicated signals due to one methyl [δ 0.90 (3H, t)], three allylic methylenes [δ 2.14 (2H, m), 2.00 (4H, m)], a conjugated diene [δ 7.24 (1H, dd, J= 14.8, 10.6 Hz), 6.27 (1H, d, J=14.8 Hz), 6.16 (1H, dd, J= 15.1, 10.6 Hz), 6.04 (1H, m)], an isolated double bond [δ 5.35 (2H, m)], an amide carbonyl group (δ 165.3) and characteristic of a piperidine ring moiety.[4]

In the ^{1}H-NMR spectrum (300.13 MHz), a doublet at δ 6.27 (H-2) and a double doublet at δ 7.24 (H-3) were assigned to *trans* α- and β-olefinic proton, respectively, conjugated to the amide carbonyl group. The multiplet centered at δ 5.35 (2H) was assigned to the protons on the isolated *cis*-double bond. The geometry of this double bond was based on the coupling constants of these olefinic protons ($W_{1/2}$~9 Hz). The location of this double bond in the molecule was deduced by detailed analysis of its 2D ^{1}H-^{1}H COSY (Figure 1) and ^{13}C-^{1}H hetero correlation. The *cis*-olefinic protons at δ 5.35 (2H, m), which showed correlation peaks with the carbon signals

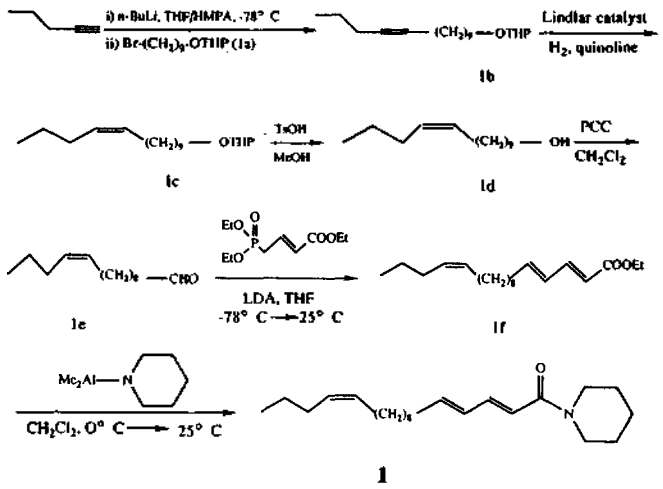


Figure 2. Synthetic scheme of piperoctadecalidine (1).

of δ 129.7 and 129.3 in the ^{13}C-^{1}H hetero correlated spectrum, were coupled to the two allylic methylene protons centered at δ 2.00 (4H, m). This latter signal was also correlated with the poorly resolved methylene proton around δ 1.28 (H_2-17) which was coupled with the methyl proton at δ 0.90 (Me-18). In addition, another allylic methylene proton at δ 2.14 (H_2-6) was coupled with a *trans*-olefinic proton at δ 6.04 (H-5).

On the basis of the above spectral data and 2D COSY experiments, the structure of 1 was established to be (2E,4E, 14Z)-N-(2,4,14-Octadecatrienoyl) piperidine, and confirmed by the following synthesis (Figure 2).

1-Pentyne was reacted with *n*-BuLi in THF and then treated with 9-bromo-1-nonanol THP ether (**1a**) in the presence of hexamethylphosphoramide (HMPA) as a cosolvent to afford **1b**. The triple bond in **1b** was selectively hydrogenated to *cis*-olefin (**1c**) with Lindlar catalyst (Pd-C on $CaCO_3$). Depyranylation[5] of **1c** followed by oxidation and Wadsworth-Emmons reaction[6] with triethyl phosphonocrotonate gave a triene ester **1f**. Finally, treatment of **1f** with dimethylaluminum piperidide[7] in CH_2Cl_2 gave (2E,4E,14Z)-N-(2,4,14-Octadecatrienoyl)piperidine (1) which was identical with natural product (chromatographic behavior and spectral data).

Experimental

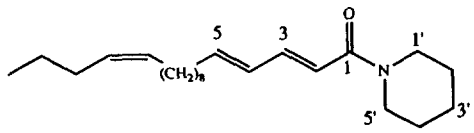
General. Recycling Preparative HPLC (JAI, LC-20) was used for separation of mixture. The column employed was JAIGEL GS-320 column (20 mm i.d×500 mm). Medium pressure liquid chromatography (MPLC) was carried out on silica gel (Merck No. 9390). NMR spectra were recorded on Bruker AM-300. Chemical shifts were reported versus TMS. All two-dimensional and DEPT spectra were recorded by using pulse programs supplied by Bruker. The fruits were collected in Jawa, Indonesia in March 1989.

Extraction and Isolation. The ripe fruits (450 g) were extracted with *n*-hexane to give 20 g of crude extract. A part of the extract (8 g) was fractionated by CC using a EtOAc-CH_2Cl_2 solvent system to give four fractions, I (EtOAc-CH_2Cl_2, 0 : 1): 5.2 g, II (EtOAc-CH_2Cl_2, 1 : 9): 1.5 g, III (EtOAc-CH_2Cl_2, 1 : 4): 0.2 g, IV(EtOAc-CH_2Cl_2, 1 : 0): 0.1 g. Separation of fraction II by MPLC (silica gel; EtOAc-*n*-

Table 1. ^{13}C and ^{1}H-NMR for Compound 1 ($CDCl_3$, TMS as int. standard)

C	^{13}C*	^{1}H**
1	165.3 s	–
2	118.3 d	6.27 d (14.8)‡
3	142.5 d	7.24 dd (14.8, 10.6)
4	128.6 d	6.16 dd (15.1, 10.6)
5	142.1 d	6.04 m
6	32.7 t	2.14 m
7-12	28.9-29.5 t	1.42-1.28
13	26.9 t[a]	2.00 m
14	129.7 d[b]	5.35 m
15	129.3 d[b]	5.35 m
16	28.6 t[a]	2.00 m
17	22.6 t	1.28 overlap
18	15.5 q	0.90 t (7.3)
1′	46.5 t[c]	3.61 br s[c]
2′	26.4 t[d]	1.65-1.56
3′	24.4 t	1.65-1.56
4′	25.4 t[d]	1.65-1.56
5′	42.9 t[c]	3.49 br s[c]

*Multiplicities established by DEPT pulse sequence. **Assigned by 2D-hetero correlated spectrum ‡J in Hz in parenthesis [a-c]These assignments may be reversed in each column.



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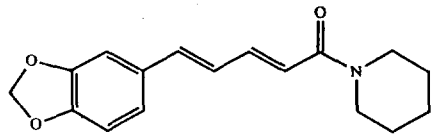

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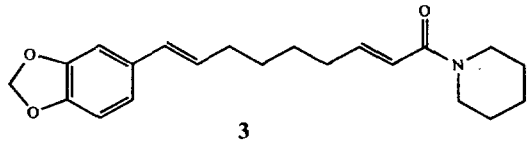

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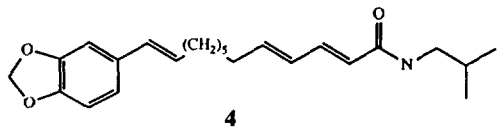

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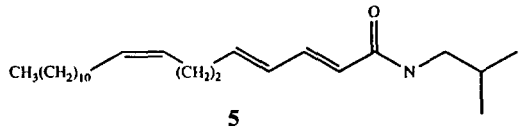

5

hexane, 1 : 4), prep. TLC (silica gel; Acetone-*n*-hexane, 1 : 4) and finally by Recycling Preparative HPLC with MeOH gave 1 (45 mg). Rechromatography of fraction III by prep. TLC (silica gel; 30% EtOAc in *n*-hexane) gave piperine (2) (R_f 0.32, 60 mg) and pipernonaline (3) (R_f 0.40, 120 mg). Fraction IV was crystallized from EtOAc to afford guineensine (4) (21 mg). These known compounds were identified by direct comparison of their spectroscopic properties with literature values.[8,9]

Piperoctadecalidine (1). Colorless oil; IR ν_{max}^{KBr} cm^{-1}: 1651, 1624, 1435, 1257, 1134, 999; UV λ_{max}^{MeOH} nm (ε): 265 (28700); EIMS (70 eV) m/z (% rel.int.): 345$[M]^+$ (100), 316 $[M-C_2H_5]^+$ (20), 302 (15), 248 (18), 192 (63), 178 (27), 164 (61), 138 (65), 112$[C_6H_{10}NO]^+$ (33), 84$[C_5H_{10}N]$ (84); HRMS: observed 345.3014, $C_{23}H_{39}NO$ requires 345.3032.

9-Bromo-1-nonanol THP ether (1a). To a mixture of 9-bromononanol (4.3 g, 19.5 mmol) and *p*-toluenesulfonic acid monohydrate (370 mg, 1.9 mmol) in CH_2Cl_2 (20 m*l*) was added dropwise dihydropyran (2.5 g, 29.3 mmol) with stirring at 25℃ under N_2. Strring was continued for 3 hr. The mixture was then poured into saturated $NaHCO_3$ solution and extracted with Et_2O. The organic extract was washed with brine and dried over $MgSO_4$. The crude product obtained on removal of solvent was purified by CC on silica gel (EtOAc-*n*-hexane, 1 : 10) to give **1a** (5.5 g, 91%) as a colorless oil. IR (neat) ν_{max} cm^{-1}: 1432, 1340, 1244, 1195, 1026, 981, 901; ^{1}H NMR ($CDCl_3$): δ 4.58 (1H, m), 3.87 (1H, m), 3.72 (1H, m), 3.50 (1H, m), 3.42 (3H, m), 1.90-1.28 (20H, m).

10-Tetradecyn-1-ol THP ether (1b). To a stirred solution of 1-pentyne (691 mg, 10.1 mmol) in THF (3 m*l*) was added dropwise *n*-BuLi (6.3 m*l*), 10.1 mmol) at −78℃. The reaction mixture was allowed to warm to 0℃ and HMPA (3 m*l*) was added with stirring. After 10 min, the bromide **1a** (3.1 g, 10.1 mmol) was added into the mixture. Stirring was continued overnight at room temperature. The reaction mixture was extracted with Et_2O and washed. The Et_2O extract was concentrated and subjected to CC over silica gel (EtOAc-*n*-hexane, 1 : 20) to afford **1b** (2.8 g, 93%) as a colorless oil. IR (neat) ν_{max} cm^{-1}: 1427, 1337, 1194, 1153, 1026, 981, 901; ^{1}H-NMR ($CDCl_3$): δ 4.58 (1H, m), 3.87 (1H, m), 3.72 (1H, m), 3.50 (1H, m), 3.39 (1H, m), 2.13 (2H, m), 1.82-1.27 (24H, m), 0.96 (3H, t, J=7.3 Hz).

***Cis*-10-tetradecen-1-ol THP ether (1c).** The compound **1b** (2.8 g, 9.5 mmol) in *n*-hexane (5 m*l*) was hydrogenated under atmospheric pressure over Lindlar catalyst. After the uptake of H_2 was complete, the reaction mixture was filtered and washed with 0.1 N HCl. The crude product was purified by flash column chromatography (EtOAc-*n*-hexane, 1 : 40) to give *cis*-olefin **1c** (2.6 g, 93%) as a colorless oil. IR (neat) ν_{max} cm^{-1}: 1453, 1357, 1195, 1130, 1020, 982; ^{1}H-NMR ($CDCl_3$): δ 5.35 (2H, m), 4.58 (1H, m), 3.87 (1H, m), 3.74 (1H, m), 3.50 (1H, m), 3.38 (1H, m), 2.00 (4H, m), 1.84-1.29 (22H, m), 0.90 (3H, t, J=7.3 Hz).

***Cis*-10-tetradecen-1-ol (1d).** A mixture of the THP ether **1c** (2.6 g, 8.9 mmol) and *p*-toluenesulfonic acid monohydrate (168 mg, 0.9 mmol) in MeOH was stirred for 2 hr at room temperature. The reaction mixture was concentrated *in vacuo* and subjected to CC on silica gel (EtOAc-*n*-hexane, 1 : 6) to give alcohol **1d** (1.5 g, 77%) as a colorless oil. IR (neat) ν_{max} cm^{-1}: 3302, 1443, 1051; ^{1}H NMR ($CDCl_3$): δ 5.36 (2H, m), 3.62 (2H, t, J=6.7 Hz), 2.01 (5H, m), 1.55 (2H, m), 1.43-1.29 (14H, m), 0.90 (3H, t, J=7.3 Hz).

***Cis*-10-tetradecen-1-yl aldehyde (1e).** To a stirred suspension of pyridinium chlorochromate (2.1 g, 9.9 mmol)[10] in CH_2Cl_2 was added a solution of the alcohol **1d** (1.4 g, 6.6 mmol) in CH_2Cl_2 and the mixture stirred for 1.5 hr at

room temperature. Et_2O was added and the supernatant liquid decanted off. The residue was washed with Et_2O (3× 10 m*l*). The combined organic extracts were filtered through a short pad of Florisil and the solvent was removed. The crude product obtained was purified by CC on silica gel (EtOAc-*n*-hexane, 1 : 15) to produce aldehyde **1e** (1.1 g, 88%) as a oil. IR (neat) ν_{max} cm^{-1}: 1719, 1453. ^1H-NMR ($CDCl_3$): δ 9.76 (1H, t, *J*=0.9 Hz), 5.36 (2H, m), 2.42 (2H, dt, *J*=7.3, 1.2 Hz), 2.01 (4H, m), 1.62 (2H, m), 1.43-1.30 (12H, m), 0.90 (3H, t, *J*=7.4 Hz).

(2E,4E,14Z)-2,4,14-Octadecatrienoic acid ethyl ester (1f). To a solution of lithium diisopropylamide (LDA) which prepared from diisopropylamine (622 mg, 6.2 mmol) and *n*-BuLi in THF was added triethyl phosphonocrotonate (1.4 g, 5.6 mmol) at −10℃. After strring for 10 min, the mixture was cooled to −78℃. The aldehyde 1e (980 mg, 4.7 mmol) was then added slowly, the mixture was stirred and allowed to warm to 25℃. This was then poured into saturated Na_2SO_4 solution (25 m*l*) and extracted with Et_2O. The Et_2O extract was dried and concentrated. The residue was purified by flash column chromatography (EtOAc-*n*-hexane, 1 : 15) to give trienoic acid ethyl ester **1f** (934 mg, 65%) as a colorless oil. IR (neat) ν_{max} cm^{-1}: 1714, 1612, 1441, 1361, 1290, 1252, 1170, 1030, 994; ^1H NMR ($CDCl_3$): δ 7.20 (1H, m), 6.15 (2H, m), 5.78 (1H, d, *J*=15.4 Hz), 5.35 (2H, m), 4.19 (2H, q, *J*=7.2 Hz), 2.17 (2H, m), 2.01 (4H, m), 1.44-1.26 (17H, m), 0.90 (3H, t, *J*=7.3 Hz).

(2E,4E,14Z)-N-(2,4,14-Octadecatrienoyl)piperidine (1). To a cooled solution of piperidine (744 mg, 8.7 mmol) in CH_2Cl_2 at −40℃ was added trimethyl aluminum and the mixture was allowed to warm to 0℃ during a period of 20 min. A solution of the ester **1f** (535 mg, 1.8 mmol) in CH_2Cl_2 was then added, the mixture was stirred overnight at room temperature. The reaction mixture was poured into saturated sodium potassium tartrate solution (10 m*l*) and extracted with CH_2Cl_2 (3×10 m*l*). The combined extracts were dried over $MgSO_4$ and filtered. The solvent was evaporated *in vacuo* and the crude product was purified by flash column chromatography (EtOAc-*n*-hexane, 1 : 4) to give the desired product **1** (332 mg, yield 55%) as a colorless oil, which was identical with the natural product.

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Carbonylation of Benzyl Alcohols and Benzyl Bromide to Phenylacetic Acids with Rhodium(I) and Iridium(I) Complexes

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Rhodium(I) and iridium(I) complexes, $M(ClO_4)(CO)(PPh_3)_2$ and $[M(CO)(PPh_3)_3]ClO_4$ (M=Rh, Ir), and $RhX(CO)(PPh_3)_2$ (X=Cl, Br, OH) catalyze the carbonylation of benzyl alcohols to produce phenylacetic acids under 6 atm of CO at 110℃ in deuterated chloroform. Benzyl alcohols initially undergo dehydration to give dibenzyl ethers which are then carbonylated to benzyl phenylacetates, and the hydrolysis of benzyl phenylacetate produces phenylacetic acids and benzyl alcohols. The carbonylation is accompanied with dehydrogenation followed by hydrogenolysis of benzyl alcohols giving benzaldehydes and methylbenzenes which are also produced by CO_2 elimination of phenylacetic acids. Phenylacetic acid is also produced in the reactions of benzyl bromide with CO catalytically in the presence of $Rh(ClO_4)(CO)(PPh_3)_2$ and H_2O, and stoichiometrically with $Rh(OH)(CO)(PPh_3)_2$ in the absence of H_2O.

Introduction

Catalytic carbonylation of alcohols to produce acids has been studied with several metal complex catalysts but mostly in the presence of iodide as a promoter in aqueous solution[1] while metal-catalyzed carbonylation of allyl alcohols has been