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**N'Tamon Amon Diane Marina**
Département de Chimie Analytique, Minérale et Générale, Technologie Alimentaire, UFR Sciences Pharmaceutiques et Biologiques, Université Félix Houphouët-Boigny, 06 B. P. 2256 Abidjan 06, Côte d'Ivoire

**Konan Dibi Jacques**
Laboratoire de Chimie Bio-Organique et de Substances Naturelles (LCBOSN), UFR-SFA, Université NANGUI ABROGOUA, 02 BP 801 Abidjan 02, Côte d'Ivoire

**Kablan Richmond Jean-Francois**
Laboratoire de COVACHIM-M2E EA 3592, Campus de Fouillole, UFR SEN, Département de Chimie, B.P. 250, 97157 Pointe-à-Pitre Cedex

**Kablan Ahmont Landry Claude**
1. Département de Mathématiques-Physique-Chimie, UPR de Chimie organique, UFR des Sciences Biologiques, Université Peleforo GON COULIBALY, BP 1328 Korhogo, Côte d'Ivoire
2. Laboratoire de Constitution et Réaction de la matière, UFR Sciences des Structures de la Matière et Technologie, Université Félix HOUPHOUËT-BOIGNY, 22 BP 582 Abidjan 22, Côte d'Ivoire

**Kabran Aka Faustin**
Laboratoire de Constitution et Réaction de la matière, UFR Sciences des Structures de la Matière et Technologie, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire

**Attioua Koffi Barthélemy**
Laboratoire de Constitution et Réaction de la matière, UFR Sciences des Structures de la Matière et Technologie, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire

**Mamyrbékova-Békro Janat Akhanovna**
Laboratoire de Chimie Bio-Organique et de Substances Naturelles (LCBOSN), UFR-SFA, Université Nangui Abrogoua, 02 BP 801 Abidjan 02, Côte d'Ivoire

**Békro Yves-Alain**
Laboratoire de Chimie Bio-Organique et de Substances Naturelles (LCBOSN), UFR-SFA, Université NANGUI ABROGOUA, 02 BP 801 Abidjan 02, Côte d'Ivoire

**Corresponding Author:**
**Kablan Ahmont Landry Claude**
1. Département de Mathématiques-Physique-Chimie, UPR de Chimie organique, UFR des Sciences Biologiques, Université Peleforo Gon Coulibaly, BP 1328 Korhogo, Côte d'Ivoire
2. Laboratoire de Constitution et Réaction de la matière, UFR Sciences des Structures de la Matière et Technologie, Université Félix Houphouët-Boigny, 22 BP 582 Abidjan 22, Côte d'Ivoire

# Five amide-functional cassans isolated from the root bark of *Erythrophleum ivorense* A. Chev. (Fabaceae)

**N'Tamon Amon Diane Marina, Konan Dibi Jacques, Kablan Richmond Jean-Francois, Kablan Ahmont Landry Claude, Kabran Aka Faustin, Attioua Koffi Barthélemy, Mamyrbékova-Békro Janat Akhanovna and Békro Yves-Alain**

**Abstract**
The phytochemical study of *Erythrophleum ivorense*'s root barks extract resulted in five cassane-type diterpenoids (1-5). The structures of these compounds, which were isolated for the first time from this species, were established on the basis of their NMR and HR-ESIMS analyses. The particularity of isolated cassanes is the presence of an amide function; moreover, this study confirms that Erythropheum species are rich in cassan-type diterpenoids.

**Keywords:** Fabaceae, *Erythrophleum ivorense*, isolation, Cassane diterpenoid, amide

## 1. Introduction
*Erythrophleum* alkaloids or cassain alkaloids are diterpenoid cassains of amide or amine type, are the main metabolites present in the genus *Erythrophleum* [1, 2, 3, 4, 5].
These metabolites are known for their biological properties, in particular on the heart [6], but also a cytotoxicity towards certain tumor cell lines [7]. The particularity of these compounds is the presence of amide or amine functions in their basic structures [8, 9, 10, 11]. The species of the genus Erythrophleum are known for their numerous uses in traditional African medicine [12]. It is reported in the literature that species of the genus Erythrophleum have a high content of cassane-type terpenoids [13, 14, 15]. It is also reported that the extracts as well as the secondary metabolites from species of the genus Erythrophleum have interesting biological properties such as antioxidant properties such as antioxidant [13], antibacterial [16], anti-inflammatory, anticancer [17], anti-angiogenesis [18], cytotoxic [19], and cardiac [10] activity. *Erythrophleum ivorense* is commonly used as a traditional remedy in many countries in west Africa [20]. Thus, the seeds are used as analgesic [21], emetic [21] and as antimicrobial [22]; the stem bark against smallpox and convulsions [23, 24]. The seeds and bark are toxic if ingested [25]. Although *Erythrophleum ivorense* is widely used in traditional medicine in Côte d'Ivoire, its chemical constituents are little known. This work is a contribution to a better knowledge of the chemical constituents synthesized by *E. ivoriense*. Thus, the fractionation of the methanolic extract of the root barks led five known cassane diterpenoids. The exploitation and interpretation of NMR and ESIMS spectral data led to their structural identification.

## 2-Material and Methods
### 2.1. General Experimental Procedures
An Agilent LC-MS system was used for samples analysis. The system was composed of Agilent 1260 Infinity HPLC coupled to an Agilent 6530 QTOF-MS equipped with an ESI source operating with positive polarity. A C18 column was used for preparative HPLC analysis. For flash chromatography 120 g and 24 g silica Grace cartridges were used using an Armen Instrument flash liquid chromatography spot apparatus. Chemical solvents were purchased from Sigma-Aldrich. A Polar 32 polarimeter was used to measure optical rotations at 25 °C. IR spectra were recorded with a Bruker Vector 22. NMR spectra were recorded on a Bruker AM-400 NMR spectrometer (400 MHz), using CD3OD as solvent.

### 2.2. Plant Material

The plant matter was collected in Agboville region - Côte d'Ivoire (December 2014), identified and authenticated at the National Flower Center of Félix HOUPHOUËT-BOIGNY University (Côte d'Ivoire). A voucher specimen **(**n°8 DIBI EI-2014) was deposited in the herbarium.

### 2.3. Extraction and purification of the compounds

The dried and powdered root barks of *E. ivorense* (500 g) was extracted with methanol (5L) to give 32.3 g of methanolic crude extract. This extract was dissolved in MeOH (100 mL), then alkalized with a few drops of $NH_4OH$ (25%), and then supplemented with $CH_2C1_2$ (100 mL). To the obtained solution, 1% sulfuric acid was added and then it was counter-extracted with $CH_2C1_2$ (100 ml x 4) to give, after evaporation under reduced pressure, the dichloromethane extract (DME). The supernatant phase was first alkalized with $NH_4OH$ at (pH = 10), then counter-extracted with distilled AcOEt (100 ml x 4) to give, after evaporation with a rotary evaporator, the ethyl acetate extract (ESA). ESA was successively fractionated and purified by column chromatography of sillica gel, Sephadex® LH-20 and semi-prep HPLC methods.

The elution schedule of the semi prep HPLC purification is as follows: flow rate 250 µL/min, linear gradient from 5% B (A: H2O + 0.1% formic acid, B: ACN) to 100% B over 30 min. Thus, nine compounds were collected on the basis of their retention time: 1 (rt 9.41 min, 6.7 mg), 2 (rt 9.46 min, 2.0 mg), 3 (rt 14.18 min, 6.0 mg), 4 (rt 18.34 min, 5.0 mg), 5 (rt 19.70 min, 5.4 mg) (Figure 1).

## 3. Results and Discussion

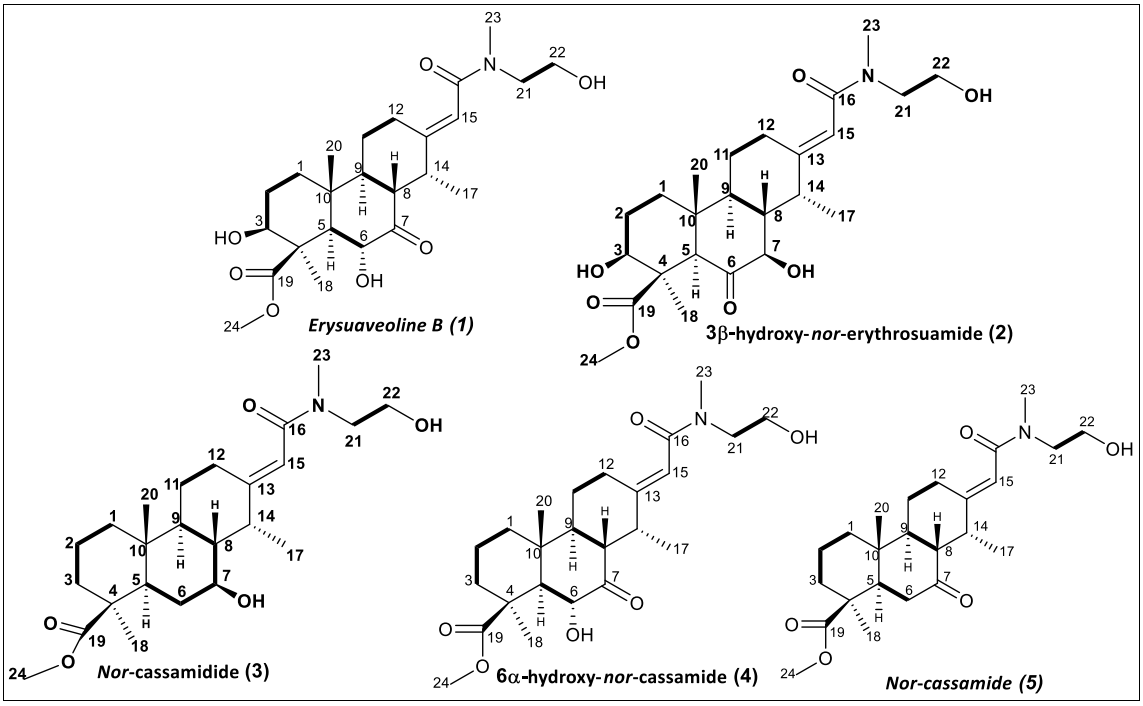


**Fig 1:** Structures of cassane diterpenoids amide isolated from *E. ivorense*

**Compound 1:** (Fig. 1), $[\alpha]_D^{24}$ -28.1 appears as a yellowish oil, soluble in methanol. The molecular formula ($C_{24}H_{37}NO_7$) matches the fragment at m/z 452.2631 $[M+H]^+$ on its HRESIMS spectrum. Concerning the IR spectrum, It gave three bands at υmax 1696; 1651; 1602 cm-1 which correspond to carbonyl function absorptions. The first being that of an ester □□□□unsaturated (R-C=C-C=O-OR), then the second indicates the presence of a ketone function (R-C=O-R) and the last the presence of an amide function (R-C=O-NH-R). In addition to these functions, this spectrum reveals an absorption band at υmax 3422 $cm^{-1}$ and 3267 $cm^{-1}$; characteristic of the hydroxyl group. Methyl ($CH_3$) and methylene ($CH_2$) groups are also observed at υmax 2962; 2937 and 2852 $cm^{-1}$ [14].

The $^1H$ NMR spectral data of 1 (Table 1) gave caractéristic chemical shifts at $\delta_H$: 1.69 (H-18, s, $CH_3$), 0.88 (H- 20, s, $CH_3$), 3.74 (H-24, s, -$OCH_3$), 5.78 (H-15, s, =CH), and 3.05 (H-23, s, N-$CH_3$). The general appearance of this spectrum is reminiscent of a cassane; especially the singlet at $\delta_H$ 0.88; 1.69 and the doublet at $\delta_H$ 1.12 which are characteristic of chemical shifts of methyl groups of cassane-type diterpenoids [26]. The $^{13}C$ NMR spectral data allowed to make some interestin assignments. Thus the double bonds carbon-carbon (C=C) peaks were observed at □C 115.0 (C-15) and 156.1 (C-13). The signals at □C 169.5 (C-16) and 178.1 (C-19) are due to the carbonyls (C=O) of the ester functions. The first one at □C 169.5 corresponds to the amide function (C=C-CO-O-R) and the second one at □C 178.1 corresponds to the unsaturated ester □□□ (C=C-CO-O-R). The highly unshielded peak à□□C 210.2 (C-7) indicates the presence of a ketone function.

Based on above data, 1 was identified as Erysuaveoline B; which was previously isolated from the stem barks of *E. suaveolens* [27].

**Compound 2:** (Fig. 1), $[\alpha]_D^{24}$ -185.1, was isolated as colorless needles. Its HRESIMS spectrum gave one ion fragment at *m/z* 452.2653 $[M+H]^+$ which agrees the molecular formula $C_{24}H_{37}NO_7$ (Cald;451.257 g/mol). The IR spectrum gave absorption bands of hydroxyl groups at $\upsilon_{max}$ 3422 and 3267 $cm^{-1;}$ those of the carbonyl groups are observed at $\upsilon_{max}$1720; 1689 and 1650 $cm^{-1;}$ methyl ($CH_3$) and methylene ($CH_2$) groups are also observed at $\upsilon_{max}$ 2939; 2874 and 2852 $cm^{-1}$. The $^1H$ and $^{13}C$ NMR spectral data (Table 1) of **2** were almost similar to those of norerythrophlamide [27,28], because, they are supposable in certain points. One can thus say that

this compound has the same basic skeleton as 1. However, a major difference can be noted at the position of the second hydroxyl group at $\delta_C$ 77.2. This one was placed on C-7 according to the HMBC correlations between H-7 ($\delta_H$ 4.00) and C-5 ($\delta_C$ 65.3) and the up field shift of the carbon C-5.
This hydroxyl group was determined as □-OH, due to the NOESY correlation between H-5(□) and H-7. Thanks to these spectral data, 2 was identified as 3□-hydroxy-*nor*-erythrosuamide; a cassane-type diterpene with amide function. This compound has been previously isolated from the stem barks of *E. fordii* [28] and *E. suaveolens* [15].

**Compound 3:** (Fig. 1) appears as a shapeless solid, soluble in methanol. The ion fragment at *m/z* 422.2911 $[M+H]^+$ agrees with the raw formula $C_{24}H_{39}NO_5$ (Cald. 421.2828 g/mol). IR absorptions bands of hydroxyl groups is observed at $\upsilon_{max}$ 3485 $cm^{-1}$, those of carbonyl groups at $\upsilon_{max}$1722; 1652 and 1605 $cm^{-1;}$ finally the absorption bands of methyl ($CH_3$) and methylene ($CH_2$) are observed at $\upsilon_{max}$ 2958; 2925 $cm^{-1}$. The $^1H$ and $^{13}C$ NMR spectral data of 3 (Table 1) are similar to those of 2 in several points, with some minor differences. Indeed, on the $^{13}C$ NMR spectrum of 3, the signals ketone ($\delta_C$ 210.3, C=O) and that of hydroxyl group ($\delta_C$ 78.4, OH) previously osbserved on the $^{13}C$ NMR spectrum of 2 are absente. But, we observe the presence of a secondary alcohol at $\delta_C$ 72.2 (HC-OH). The HSQC spectrum indicates that the carbon at $\delta_C$ 72.2 carries the proton at $\delta_H$ 3.40. The HMBC correlations allowed to fixe the second hydroxyl group ($\delta_C$ 72.2) on the carbon chain. Indeed, the carbon at $\delta_C$ 72.2 (C-7, HC-OH) correlates in $^2J_{CH}$ with the protons at $\delta_H$ 1.72 (H-6β) ; 2,15 (H-6α) and $\delta_H$ 1.51(H-8), and in $^3J_{CH}$ with the proton at $\delta_H$ 1.16 (H-5). By comparing these spectral data with those of literature, 3 was identifed as nor-cassamidide; which has also been isolated by Loder *et al.* (1972)[29] from *E. chlorostachys*.

**Compound 4: (**Fig. 1) was colorless solid. The ion fragment at *m/z* 436.2695 $[M+H]^+$ was observed on its HRESIMS spetrum; which made it possible to deduce the raw formula $C_{24}H_{37}NO_6$ (Cald. 435.2621g/mol). Absorption band of hydroxyl group are observed at υmax 3395 and 3285 $cm^{-1}$, and those of carbonyl groups at υmax 1723; 1702 and 1650 $cm^{-1}$. The methyl ($CH_3$) and methylene ($CH_2$) groups give absorption bands at υmax 2939; 2874 and 2852 $cm^{-1}$. According to $^1H$ NMR spectral data (Table 1), signals at $\delta_H$: 1.43 (H-18) and 0.91 (H- 20) are singulets, attribuable to three methyl groups; the other singulets at $\delta_H$: 3.70 (H-24), 5.91 (H-15) and 3.11 (H-23) are respectvely asigned to one methoxyl (-$OCH_3$), one olefinic proton (=CH) and one secondary amine (N-$CH_3$) protons. Concerning the $^{13}C$ NMR spectral data (Table 1), the chemical shifts at $\delta_C$: 171.2 (C-16), 179.1 (C-19), and 211.5 (C-7) were respectively assigned to carbonyl of aminde □□□□unsatured, carbonyl of ester□□□□-unsaturated, and carbonyl of ketone. The alkene carbons have chemical shifts at $\delta_C$ 155.6 (C-13) and 116.8 (C-15). These data allowed us to identify 4 as a known cassane-type diterpenoid named 6*α*-hydroxy-*nor*-cassamide. This compound was previously isolated to two Erythrophleum species; the first time *E. fordii* Oliv by Dade *et al.* (2015) [27] and the second time in *E. suaveolens by* Ahmont *et al.* (2020) [26].

**Compound 5:** (Fig. 1) was a colorless solid whose molecular formula has been established using its HR-ESI-MS data. Indeed, the ion $[M+H]^+$ at *m/z* 420.2763 agrees with the molecular formula $C_{24}H_{37}NO_5$ (Cald. 419.2672 g/mol). Its IR spectrum showed absorption bands of carbonyl groups at υmax 1720 and 1648 $cm^{-1}$, and those of methyl ($CH_3$) and methylene ($CH_2$) groups at υmax 2989, 2969 and 2901$cm^{-1}$. The $^1H$ NMR spectral data (Table 1) of compound 5 contains several chemical shifts of proton singlets at $\delta_H$: 1.42 (H-18, $CH_3$), 0.92 (H-20, $CH_3$), 3.70 (H-24, O-$CH_3$), 5.91 (H-15, C=CH) and 3.11 (H-23, N-$CH_3$ of N-methylamide). The $^{13}C$ NMR spectral data (Table 1) provide enough information to help establish the structure of 5. Indeed, peaks at $\delta_C$ 179.1 (C-19) was attributed to the carbonyl of ester group (-COO-), that at $\delta_C$ 212.5 (C-7) to cabonyl of ketone (C=O), and those at $\delta_C$: 155.9 and 116.6 to quaternary carbon (=C=; C-13) and sp2 carbon (=CH-, C-15) respectively. The methylic carbon carried by the nitrogen gave the signal at $\delta_C$ 33.7 (N-$CH_3$). These data reveal a strong structural similarity between both compounds 5 and 3. The difference here is the oxo group at position C7 (□C 210.3) in the carbon chain of 5; at the same position, at compound 3, there is a hydroxyl group ($\delta_C$ 72.2, C-OH). Through the spectroscopic and spectrometric analyses, the structure of 5 was established as that of *nor*-cassamide; previously descript of species of the genus Erythrophleum [26, 2].

**Table 1:** $^1H$ and $^{13}C$ NMR spectral data for compounds **1-5** (in $CD_3OD$).

| | **1** | | **2** | | **3** | | **4** | | **5** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **$\delta^1H$ *m; J*, Hz** | **$\delta^{13}C$ (ppm)** | **$\delta^1H$. *m; J*, Hz** | **$\delta^{13}C$ (ppm)** | **$\delta^1H$. *m; J*, Hz** | **$\delta^{13}C$ (ppm)** | **$\delta^1H$ *m; J*, Hz** | **$\delta^{13}C$ (ppm)** | **$\delta^1H$ *m; J*, Hz** | **$\delta^{13}C$ (ppm)** |
| 1 | 1.21*m*<br>1.87*m* | 38.1 | 1.40 *m*<br>1.79 *m* | 38.0 | 1.53 *m*<br>1.78 *m* | 40.2 | 1.61 *m*<br>1.87 *m* | 40.7 | 1.16 *m*<br>1.85*m* | 39.7 |
| 2 | 1.87 *m*<br>1.91 *m* | 28.0 | 1.64 *m*<br>2.19 *m* | 28.1 | 1.45 *m*<br>1.82*m* | 20.5 | 1.52 *m*<br>1.72*m* | 20.4 | 1.52*m*<br>1.84*m* | 20.4 |
| 3 | 3.10 *m* | 75.6 | 3.41 d*d*<br>(11.9; 4.3) | 78.4 | 1.07 *m*<br>2.19*m* | 38.1 | 2.08 *m*<br>2.22 *m* | 40.1 | 1.09 *m*<br>2.07*m* | 38.7 |
| 4 | - | 50.5 | - | 43.6 | - | 45.0 | - | 46.5 | - | 45.1 |
| 5 | 1. 34 *d*<br>(12.0) | 58.2 | 2.58*s* | 65.3 | 1.16 *m* | 54.0 | 1.46*d*<br>(12.3) | 59.7 | 1.57*dd*<br>(2.8; 13.8) | 60.3 |
| 6 | 4.57 *d*<br>(12.0) | 78.2 | - | 210.3 | 1.72 *m*<br>2.15 *m* | 34.0 | 4.75 *d*<br>(12.5) | 77.8 | 2.63 m<br>2.87 m | 40.5 |
| 7 | - | 210.2 | 4.00 *d*<br>(8.9) | 77.2 | 3.40 *dd*<br>(11.0;3.6) | 72.2 | - | 211.5 | - | 212.5 |
| 8 | 2.38 *m* | 51.2 | 1.82 *m* | 52.0 | 1.51 *dd*<br>(11.3; 4.4) | 48.8 | 2.50 *dd*<br>(12.6; 2.7) | 52.9 | 2.33 *dd*<br>(3.4; 12.6) | 54.7 |
| 9 | 1.63 *m* | 46.5 | 1.70 *m* | 47.5 | 1.23 *m* | 46.9 | 1.74 *m* | 48.0 | 1.70 *m* | 48.4 |
| 10 | - | 37.8 | - | 38.4 | - | 39.0 | - | 37.9 | - | 37.8 |
| 11 | 1.21*m* | 27.5 | 1.19 *m* | 27.3 | 1.19 *m* | 27.6 | 1.29*m* | 28.3 | 1.24 *m* | 28.1 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1.87*m* | | 1.86 *m* | | 1.83 *m* | | 1.98 *m* | | 1.96*m* | |
| 12 | 1.97 *m*<br>3.06*m* | 24.6 | 2.12 *m*<br>2.79 *m* | 26.0 | 2.00 *m*<br>2.73 *m* | 26.3 | 2.11*m*<br>2.75*m* | 26.1 | 2.07 *m*<br>2.75*m* | 26.3 |
| 13 | - | 156.1 | - | 156.5 | - | 158.1 | - | 155.6 | - | 155.9 |
| 14 | 2.96 *m* | 39.1 | 2.80 *m* | 40.7 | 2.85 *m* | 40.5 | 2.97 *m* | 33.9 | 3.09 *m* | 39.6 |
| 15 | 5.87 *s* | 115.0 | 5.90 *s* | 116.8 | 5.94 *s* | 115.5 | 5.91*s* | 116.8 | 5.88*s* | 116.6 |
| 16 | - | 169.9 | - | 171.3 | - | 171.3 | - | 171.2 | - | 171.4 |
| 17 | 1.12 d, (7.2) | 15.2 | 1.21 *d, (*6.8) | 14.0 | 1.08 *d,* (6.8) | 14.0 | 1.14 *d,* (6.8) | 15.3 | 1.07*d,* (6.8) | 15.2 |
| 18 | 1.69 *s* | 25.5 | 1.27*s* | 26.2 | 1.20*s* | 29.1 | 1.43*s* | 32.1 | 1.16 *s* | 28.6 |
| 19 | - | 178.1 | - | 175.6 | - | 179.3 | - | 179.1 | - | 178.6 |
| 20 | 0.88 *s* | 13.8 | 0.96 *s* | 15.0 | 0.65 *s* | 13.4 | 0.91*s* | 14.3 | 0.83*s* | 12.5 |
| 21 | 3.57 *m* | 51.1 | 3.52 *m* | 51.8 | 3.51 *m* | 50.9 | 3.52 *m* | 50.9 | 3.52 *m* | 50.9 |
| 22 | 3.78 t, (4.8) | 61.7 | 4.00 *m* | 60.3 | 3.68 *m* | 60. 4 | 3.61 *m* | 61.3 | 3.66 *m* | 60.6 |
| 23 | 3.05 *s* | 37.4 | 3.11 *s* | 37.8 | 3.11 *s* | 38.0 | 3.11 *s* | 38.9 | 2.97 *s* | 33.7 |
| 24 | 3.74 *s* | 51.9 | 3.66 *s* | 52.0 | 3.63 *s* | 51.8 | 3.70*s* | 52.1 | 3.66 *s* | 52.0 |

## Conclusion

The chemical study of *E. ivorense* root bark extract revealed five compounds which are diterpenoid amides of cassane type (1-5). These compounds, which all have an amide function, have never been reported or described in *E. ivorense*. The results of this study first confirm that Erythrophleum species are rich in cassane-type diterpenoids, and then show that they synthesize them with a variety of functions including amides.

## Declaration of compétent interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

1. Dalma G. The Erythrophleum alkaloids, in: Alkaloids Chem. Physiol., Elsevier; c1954. p. 265-273.
2. McCawley EL. Cardioactive alkaloids, in: Alkaloids Chem. Physiol., Elsevier; c1955. p. 79-107.
3. Bonting SL, Hawkins NM, Canady MR. Studies of sodium-potassium activated adenosine triphosphatase: VII-inhibition by erythrophleum alkaloids, Biochem. Pharmacol. M.R. 1964;13:13-22.
4. Gupta RS. Mutants of HeLa cells resistant to ouabain and cassaine: Genetic evidence for the common site of action of cardiac glycosides and erythrophleum alkaloids, Biochem. Pharmacol. 1981;30:3039-3044.
5. Maurya R, Ravi M, Singh S, Yadav PP. A review on cassane and norcassane diterpenes and their pharmacological studies, Fitoterapia. 2012;83:272-280.
6. Loder JW, Culvenor CCJ, Nearn RH, Russell GB, Stanton DW. Tumour inhibitory plants. New alkaloids from the bark of *Erythrophleum chlorostachys* (Leguminosae). Aust. J Chem.1974;27:179-185.
7. Du D, J Qu JM, Wang SS, Yu XG, Chen S, Xu SGl *et al*. Fang, Cytotoxic cassaine diterpenoid-diterpenoid amide dimers and diterpenoid amides from the leaves of *Erythrophleum fordii*, Phytochemistry. 2010;71:1749-1755.
8. Cronlund A. Two new alkaloids from the bark of Erythrophleum ivoirense. Acta Pharm. Suec. 1973a;10:507-514.
9. Cronlund A. New alkaloids from Erythrophleum species. Planta Med. 1973b;24:371-374.
10. Verotta L, Aburjai T, Rogers CB, Dorigo P, Maragno I, Fraccarollo D, *et al*. Chemical and pharmacological characterization of *Erythrophleum lasianthum* alkaloids. Planta Med. 1995;61:271-274.
11. Tsutui M, Tsutsup EA. Cassane and norcassane. Chem. Rev. 1959;59:1030-1075.
12. Anaïs-Pasiphaé G, Adeline F, Jean-Louis D, Écologie et gestion des espèces multi-usages du genre Erythrophleum (Fabaceae-Caesalpinioideae) en Afrique (synthèse bibliographique). Biotechnol. Agron. Soc. Environ. 2015;19(4):415-429.
13. Tsao CC, Shen YC, Su CR, Li CY, Liou MJ, Dung NX, *et al*. New diterpenoids and the bioactivity of *Erythrophleum fordii*. Bioorg. Med. Chem. 2008;16:9867-9870.
14. Kablan LA, Dade JME, Say M, Okpekon TA, Yapo KD, Ouffoue SK, *et al*. Four new cassane diterpenoid amides from *Erythrophleum suaveolens* [(Guill. et Perr.), Brenan]. Phytochem. Lett. 2014;10:60-64.
15. Konan JD, Attioua BK, Kablan CLA, Kabran FA, Koffi PA, Any-Grah SA, *et al*. New cassane diterpenoids from the root bark of *Erythrophleum suaveolens*. Phytochem. Lett. 2019b;31:166-169.
16. Ngounou FN, Manfouo RN, Tapondjou LA, Lontsi D, Kuete V, Pénal V, *et al*. Antimicrobial diterpenoid alkaloids from *Erythrophleum suaveolens* (Guill&Perr.) Brenan. Bull. Chem. Soc. Ethiop. 2005;2:221-226.
17. Miyagawa T, Ohtsuki T, Koyano T, Kowithayakorn T, Ishibashi M. Cassaine diterpenoid dimers isolated from *Erythrophleum succirubrum* with TRAIL-resistance overcoming activity. Tetrahedrom Lett. 2009;50(32):4658-4662.
18. Tran MH, To Dao C, Jeong AK, Nara T, Jeong HL, Byung SM. Cassaine diterpene alkaloids from *Erythrophleum fordii* and their anti-angiogenic effect. Bioorg. Med. Chem. Lett. 2013;24:168-172.
19. Du D, Qu J, Yu S, Ma S, Haining LV, Liu J, *et al*. Oleanane-type triterpene saponins and cassaine-type diterpenoids from *Erythrophleum fordii*. Planta. Med. 2011;77:1631-1638.
20. Armah FA, Annan K, Mensah AY, Amponsah IK, Tocher DA, Habtemariam S. Erythroivorensin: A novel anti-inflammatory diterpene from the root-bark of *Erythrophleum ivorense* (A Chev). Fitoterapia. 2015;105:37-42.
21. Loder JW, Culvenor CCJ, Nearn RH, Russell GB, Stanton DW. Tumour inhibitory plants. New alkaloids from the bark of *Erythrophleum chlorostachys* (Leguminosae). Aust. J Chem. 1974;27:179-185.

22. Adu-Amoah CL, Agyare EK, Ayande PG, Mensah KB. Toxicity assessment of *Erythrophleum ivorense* and *Parquetina nigrescens*. Toxicology Reports. 2014;1:411-420.
23. Ogboru RG, Akideno LO, Owoeye EA. Chemical composition and medicinal potentials of the bark of *Erythrophleum ivorense* A. Chev. J Biosci. Biotechnol. Discov. 2017;2:1520.
24. Wakeel OK, Umukoro S, Kolawole OT, Awe EO, Ademowo OG. Anticonvulsant and sedative activities of extracts of *Erythrophleum ivorense* stem bark in mice. Asian J Biomed. Pharmaceut. Sci. 2014;4(28):43-47.
25. Chudnoff M. Tropical Timbers of the World. Ag. Handbook No. 607. USDA Forest Service, Wisconsin; c1984.
26. Kablan ACL, Konanb JD, Komlaga G, Kabran FA, Daouda A, N'Tamon AD, *et al*. Five new cassane diterpenes from the seeds and bark of *Erythrophleum suaveolens*. Fitoterapia. 2020;146:104700.
27. Dade JM, Kablan LA, Say M, Okpekon TA, Yapo Kicho D, *et al*. Cassane diterpenoids stem bark of *Erythrophleum suaveolens* [(Guill. et Perr.) Brenan]. Phytochem. Lett. 2015;12:224-231.
28. Qu J, Hu YC, Yu SS, Chen XG, Li Y. New cassaïne diterpenoid amides with cytotoxic activities from the bark of *Erythrophleum fordii*. Planta Med. 2006;72:442-449.
29. Loder JW, Culvenor CCJ, Nearn RH, Russell GB, Stanton DW. Isolation of nor-cassamide and authentic nor-cassamidine from *Erythrophleum chlorostachys*. Structural revision of the nor-cassamidine, nor-cassamine, nor-cassamine, nor-erythrosuamine and deshydro-nor-erythrosuamine. Tetrahedron Lett. 1972;50:5069-5072.