REFERENCES

1. Merxmuller, H., Leins, P. and Roesseler, H. (1977) in *The Biology and Chemistry of Compositae* (Heywood, J. B., Harborne, J. B. and Turner, B. L., eds). pp. 590. Academic Press, New York.
2. Leins, P. (1971) *Bot. Jahrb.* **91**, 91.
3. Pascual, Teresa, J., Barrero, A. F., San Feliciano, A., Grande, M., and Medarde, M. (1978) *Tetrahedron Letters* **43**, 4141.
4. Pascual Teresa, J., Barrero, A. F., San Feliciano, A. and Medarde, M. (1980) *Phytochemistry* **19**, 2155.
5. Ahmed, A. A., Jakupovic, J., Eid, F. and Ali, A. A. (1989) *Phytochemistry* (in press).
6. Tatum, J. H. and Berry, R. E. (1972) *Phytochemistry* **11**, 2283.
7. Row, L. R. and Sastry, G. (1963) *Indian J. Chem.* **1**, 207.
8. Joseph-Nathan, P., Abramo-Bruno and Torres Ma. M. (1981), *Phytochemistry* **20**, 313.
9. Buschi, C. A., Pomilio, A. B. and Gros, E. G. (1981) *Phytochemistry* **20**, 1179.
10. Rodrigues, E., Carman, N. J. and Mabry, T. J. (1972) *Phytochemistry* **11**, 409.
11. Rodrigues, E., Carman, N. J., Velde, G. V., McReynols, J. H., Mabry, T. J., Irwin, M. A. and Geissman, T. A. (1972) *Phytochemistry* **11**, 3509.
12. Harborne, J. B. and Mabry, T. J. (1982) *The Flavonoids, Advances in Research*. Chapman & Hall, London.
13. Mabry, T. J., Markham, K. R. and Thomas, N. B. (1970) *The Systematic Identification of Flavonoids*. Springer, New York.

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ALKALOIDS OF *ALSTONIA CORIACEA*

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Key Word Index— *Alstonia coriacea*; Apocynaceae; indole alkaloids; quinoline alkaloids; ^{1}H and ^{13}C NMR.

Abstract—Seven alkaloids have been identified from the stem bark of *Alstonia coriacea* from New Caledonia. They are gentianine, 10-methoxy deplancheine, vincamajine, desmethylquaternine, 10-methoxy-3-*epi*-α-yohimbine, corialstonine and cabucraline. Corialstonine is a novel member of the little represented quinoline alkaloid series.

INTRODUCTION

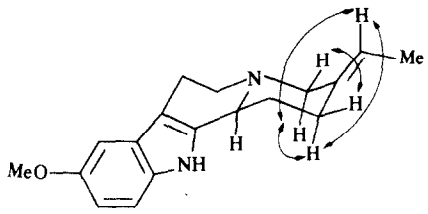
Alstonia coriacea Pancher ex S. Moore is a shrub from New Caledonia, which sometimes is mistaken for *A. lenormandii* [1]. After studying the alkaloid content of this latter species [2], we herein report our results on the alkaloids of the stem bark of *A. coriacea* collected by two of us (J. P. and S. L.) in the southern part of the island. Alkaloids were extracted in the standard fashion and from 3.3 kg of dried milled stem bark, there was obtained 17 g of alkaloids (yield 5.2 g/kg); some alkaloids were also isolated from the leaves but their low yield discouraged us from pursuing investigation.

RESULTS AND DISCUSSION

From the crude alkaloid mixture, seven alkaloids were isolated in a pure state and identified. They are gentianine, **1** (0.6% of alkaloid mixture (AM)), 10-methoxy deplancheine, **2** (1.5% AM), vincamajine, **3** (6.5% AM), desmethylquaternine **4** (56% AM), 10-methoxy-3-*epi*-α-yohimbine **5** (0.9% AM), corialstonine **6** (0.5% AM) and cabucraline, **7** (0.8% AM). Among these, alkaloids **1–3** and **7** are known compounds, available for direct comparison from the study of other *Alstonia* species. Alkaloid **4**, previously isolated from *A. legouixae*, was identified here by comparison of spectra [3]. To the best of our knowledge, alkaloids **5** and **6** are new; the structural elucidation of **6** has been reported in a preliminary note [4] and will not be detailed here. The novel isolation of **2–4** and **7** has provided the opportunity of obtaining complete ^{1}H and ^{13}C NMR assignments by means of 2D NMR experiments.

Deplancheine and 10-methoxydeplancheine 2 are rare alkaloids, isolated from *A. deplanchei* [5], *A. undulata* [6] and *A. lanceolifera* [7]. Previous structural assignment of **2** was based on comparison of the ^{1}H NMR spectra of **2** and of the corresponding fully synthetic 19,20-dihydro derivative. This is now done using ^{13}C NMR, to establish the gross structure of **2** and to settle the aromatic substitution, and ^{1}H NMR. Both spectra were assigned using δ–δ correlation experiments and the chemical shifts of the aromatic carbons were found to be close to the values reported for 10-methoxy indoles by Verpoorte *et al.* [8]. Ring junction H-3 was observed as a broad

† Part 125 in the series 'Plants from New Caledonia'. For part 124, see Ettouati, L., Ahond, A., Convert, O., Poupat. C. and Potier, P. (1988) *Bull. Soc. Chim. Fr.*, (in press).



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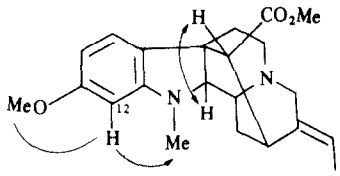

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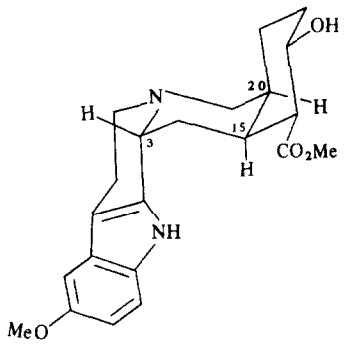

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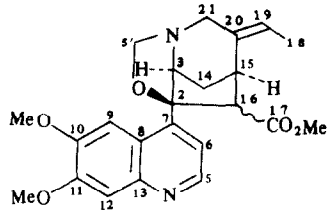

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doublet with $J = 10.9$ Hz at $\delta = 3.38$ ppm, indicating a *trans* quinolizidine arrangement. Among correlations observed on the COSY spectrum, a few unusual modulations due to long-range couplings deserve comments since the deplancheine unit is part of many more elaborate alkaloids; they are observed between H-21 axial and H-15 axial, H-21 equatorial and H-15 equatorial, H-18 and H-21 axial, H-19 and H-21 axial and H-15 axial. Not surprisingly, allylic and homoallylic couplings are found to have a larger value in the case of axial protons whose CH bonds are orthogonal to the plane of the olefin. It is also worthy of note that none of the couplings observed between allylic and vinylic groups allows establishment of the double bond configuration. This point is settled after the C-21 chemical shift (54.8 ppm) which favours a *E* configuration.

Vincamajine **3** and cabucraline **7** are ubiquitous *Alstonia* alkaloids; their ^1H and ^{13}C NMR spectra have been assigned using 2D-techniques (see Table 1 for ^{13}C and Experimental for ^1H). With regard to the original assignment of **7** [9], three pairs of carbons are interchanged; CH_2:5 and 21, 6 and 14 and CH:3 and 16. Similar changes will probably have to be made on the spectra of molecules containing cabucraline or derivatives thereof; this point is currently under investigation in our laboratory. The ^1H NMR spectrum of cabucraline was completely analysed by means of 2D spectroscopy and the only observed unexpected chemical shifts are those of H-2 (abnormally shielded at δ 2.56 ppm) and of H-15 (deshielded at δ 3.62 ppm). Whereas connectivities were not easily demonstrated using double resonance, there is no difficulty in following a path from H-2 to H-16 via H-3, H-14 and H-15. Some couplings such as $J_{2,3}$ are

Heteronuclear long range couplings

-C-2 ⟶ H-3 (^2J)	-C-5 ⟶ H-21 (^3J)
-C-20 ⟶ H-16 (^3J)	-C-2 ⟶ H-5 (^3J)
-C-20 ⟶ H-21 (^2J)	-C-8 ⟶ H-6 (^3J)
-C-20 ⟶ H-19 (^3J)	-C-8 ⟶ H-12 (^3J)
-C-20 ⟶ H-15 (^2J)	-C-13 ⟶ H-9 (^3J)

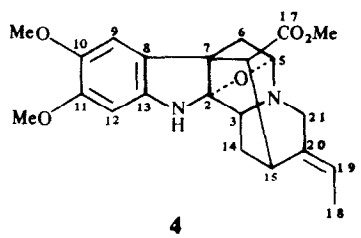

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Table 1. ^{13}C NMR of alkaloids **2**–**7** (75 MHz, $CDCl_3$; central line of $CDCl_3$ used as intl standard $\delta = 77$. ppm). In ref. [4], ^{13}C data for compound **4** have unfortunately been exchanged for those of the N(1) methylated derivative.

C	2	3	4	5	6	7
2	135.5	74.7	107	132.4	89.7	78.2
3	59.8	53.2	52.1	53.9	73.4	47.6
5	52.9	61.8	87.5	51.0	146.9	50.2
6	21.4	35.3	40.6	16.6	115.2	29.9
7	107.7	56.8	52.1	107.6	146.5	42.1
8	127.6	130.0	128.2	127.9	122.2	132.4
9	100.5	124.5	110.2	100.3	107.9	121.3
10	153.7	119.2	141.5	154.1	152.0	103.6
11	110.7	129.5	145.4	111.3	148.9	159.9
12	111.1	109.2	96.5	111.8	105.8	97.4
13	130.9	154.3	149.4	130.9	148.0	154.1
14	30.6	21.8	26.1	24.0	31.4	32.3
15	33.7	30.1	31	32.3	40.2	33.8
16	—	59.6	52.2	54.0	59.4	52.6
17	—	74.6	—	65.8	—	—
18	12.6	12.8	12.7	33.3	12.9	13.1
19	118.6	117	120.1	23.7	119.5	121.8
20	133.6	136.2	138.4	35.6	135.8	135.1
21	54.8	55.5	46.4	49.6	53.1	54.3
Ar-OMe	55.7	—	56.9 56.1	55.9 —	55.9 55.7	55.3 —
CO_2Me	—	51.6	51.4	51.8	50.8	51.6
CO	—	173.1	172.7	174.6	169.2	172.5
N-Me	—	34.3	—	—	—	33.2

better seen when delays (0.1 sec) are introduced in the sequence before and after the mixing pulse. Under these conditions, one observes correlations between the aromatic narrow doublet ($\delta = 6.18$ ppm) and the methoxy and N-methyl groups; this experiment represents a simple means of locating a methoxy on a N-methyl indole derivative. The same results are deduced from a NOESY experiment using a 900 msec mixing time (for a 300 MHz field); in the NOESY spectrum a meaningful through-space correlation is found between H-2 and H-16, thus allowing the configurations of the C-2 and C-16 stereocentres to be determined.

N(1) Desmethyl quaternine **4** is the major alkaloid from the plant, obtained here in a crystalline form with mp 197° (from diethyl ether). Its IR, UV and mass spectra are superimposable with the corresponding spectra of the alkaloid from *A. legouixae*, kindly provided by Prof. Poisson [3]. High field ^1H and ^{13}C data were fully assigned as described above and we wish to analyse here some of the observations deduced from a Kessler experiment optimized for $J = 10$ Hz. As noticed by others ^2J have smaller values than ^3J especially in the aromatic area; ^3J have a Karplus-type angular dependance and are useful in the assignment of proton configurations. Thus, C-13 resonance is modulated by H-9 frequency but not by H-12; correlations between C-8 and H-12 on one hand and H-6 on the other allow the establishment of a link between ring A and C through two quaternary carbon atoms. Other unexpected correlations are observed between C-2 and H-5, C-5 and H-21, through oxygen and nitrogen heteroatoms, respectively.

The first novel compound from the plant, alkaloid **5** is 10-methoxy-3-*epi*-α-yohimbine. According to its mass spectrum, it is an isomer of quaternatine (= 11-methoxy-3-*epi*-α-yohimbine) from *A. quaternata* [10]. Comparison of the high field parts of the ^{13}C NMR spectra of **5** and of the series of yohimbinoids described by Wenkert *et al.* [11] allows identification of the configurations of the asymmetric centres of **5** and its assignment to the 3-*epi*-α-series.

Confirmation of the stereochemistry of **5** is obtained, in part, from the analysis of the high field ^1H NMR spectrum, where several important protons are observable: H-3 (*br s*) at δ 4.41 ppm thus indicating a *cis* quinolizidine ring junction, H-17 (doublet of triplets, $J = 4.5$, 11 Hz) at δ 4.08 ppm showing that H-17 and H-16 are *trans* diaxially oriented and H-16 (doublet of doublets, $J = 3.5$, 10.4 Hz) at δ 2.43 ppm which is *cis* related to H-15. The H-21 are a *br d* ($\delta = 2.5$ ppm, $J = 12.4$ Hz) and a doublet of *d* ($\delta = 3.02$ ppm, $J = 12.4$, 4.2 Hz) and this proves that H-20 is equatorial in ring D and thus is α. Location of the aromatic methoxy substituent is based on ^{13}C increments and comparison with literature data [8].

Corialstonine **6** is a minor alkaloid from *A. coriacea* and it remains one of the rare members of the quinoleine alkaloids family. As many other quinoline alkaloids, it might be formed by oxidation and rearrangement of an indole precursor

Alstonia coriacea shares with the varieties of *A. lenormandii* the feature of producing large amounts of alkaloids with the 10,11-dimethoxy picraline skeleton; they differ however in the nature of their minor bases (indoloquinolizidines in *A. coriacea* and anilinoacrylic esters in *A. lenormandii*).

The crude alkaloid mixture was assayed for pharmacological activities in the central nervous system domain and for cardiovascular, antibiotic and anti-inflammatory activities; no significant properties were observed.

EXPERIMENTAL

General. Plant material was collected at 'Forêt Cachée' in 'Plaine des Lacs'. A herbarium specimen is deposited at the Herbarium of Orstom Centre in Nouméa. ^1H and ^{13}C NMR were measured at 300 and 75 MHz, respectively.

Extraction and isolation of alkaloids. Dried, powdered stem bark of *A. coriacea* (3.3 kg) was wetted with 50% NH_4OH and lixiviated with 60 l of EtOAc. The lixiviate was extracted with 2% H_2SO_4 and the aq. phase made alkaline with NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ layers were dried (Na_2SO_4) and evapd *in vacuo* to give 17 g of crude alkaloid mixt. (yield 5.2 g/kg). Alkaloid **4** was obtained by crystallization of the crude AM from Et_2O (yield 9.5 g). The mother liquors of crystallization were placed on a silica gel column packed in $CHCl_3$ and eluted with $CHCl_3$ (600 ml, fractions 1–5). $CHCl_3$–MeOH (49:1; 500 ml Fr. 6–15), $CHCl_3$–MeOH (19:1; 500 ml, Fr. 16–31), $CHCl_3$–MeOH (9:1; 500 ml, Fr. 32–38), $CHCl_3$–MeOH (17:3; 250 ml, Fr. 39–55) and $CHCl_3$–MeOH (4:1; 200 ml, Fr. 56–69). Gentianine **1** was in Fr. 1–5; alkaloids **3**, **5**, **6**, were in Fr. 6–31; alkaloid **2** was in Fr. 32–38 and alkaloid **7** in Fr. 32–55.

Description of new alkaloids. 10-*Methoxy*-3-epi-α-*yohimbine* **5**, (ceric sulphate TLC (CR) pale green): $[\alpha]_D$ −66° $CHCl_3$; *c* 1; UV: λ_{max}^{MeOH} nm: 227, 285, 310, 335: IR: $\nu_{max}^{CHCl_3}$ cm^{-1}: 3380, 1720, 1620, 1590, 1480, 1460, 1430, 1305, 1210; MS *m/z* (rel. int.): 384 ($[M]^+$; $C_{22}H_{28}N_2O_4$, 100), 383 (95), 369 (10), 353 (10), 325 (5), 258 (15), 222 (20), 214 (20), 200 (15), 199 (12), 174 (10); ^1H NMR (300 MHz, $CDCl_3$): δ 7.21 (*d*, *J* = 8.7 Hz, H-12), 6.93 (*d*, *J* = 2.3 Hz, H-9), 6.82 (*dd*, *J* = 8.7 2.3 Hz, H-11), 4.41 (*br s*, $W_{\frac{1}{2}}$ = 4 Hz, H-3), 4.08 (*dt*, *J* = 4.5, 11 Hz, H-17), 3.86 (*s*, ArOMe), 3.84 (*s*, CO_2Me), 3.23 (*m*, 2H, H-5), 3.02 (*dd*, *J* = 12.4, 4.2 Hz, H-21), 2.94 (*m*, H-6), 2.5 (*br d*, *J* = 12.4 Hz, H-21), 2.48 (*m*, H-6), 2.43 (*dd*, *J* = 10.4, 3.5 Hz, H-16), 2.16 (*br s*, H-15), 2.14 (*m*, H-14), 2.13 (*m*, H-19), 2.1 (*m*, H-18), 1.69 (*m*, H-14), 1.55 (*m*, H-20), 2.35 (*m*, H-19), 1.28 (*m*, H-18).

Corialstonine **6**. $[\alpha]_D$ +102° ($CHCl_3$; *c* 1), UV λ_{max}^{MeOH} nm; 218, 238, 317, 330; (MeOH + HCl) = 220, 246, 354; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: (1745, 1620, 1580, 1500, 1480, 1430, 1345, 1250, 1160; MS: *m/z* (rel. int.): 424 ($[M + 14,5]^+$], 410 ($[M]^+$, $C_{23}H_{26}N_2O_5$, 30), 258 (10), 188 (12), 135 (25), 122 (40), 121 (100); ^1H NMR (300 MHz, $CDCl_3$): δ 8.65 (*d*, *J* = 4.8 Hz, H-5), 8.32 (*s*, H-12), 7.4 (*s*, H-9), 7.08 (*d*, *J* = 4.8 Hz, H-6), 5.4 (*br q*, *J* = 7 Hz, H-19), 4.7 (*d*, *J* = 6.7 Hz, H-5′), 4.35 (*d*, *J* = 6.7 Hz, H-5′), 4.3 (*d*, *J* = 4.1 Hz, H-3), 4.02 (*s*, 3H, ArOMe), 4.0 (*s*, 3H, ArOMe), 3.95 (*dq*, *J* = 16.5, 2.4 Hz, H-21), 3.65 (*br s*, H-15), 3.45 (*s*, 3H, CO_2Me), 3.2 (*br d*, *J* = 16.5 Hz, H-21), 2.85 (*d*, *J* = 5.1 Hz, H-16), 2.5 (*d*, *J* = 13.2 Hz, H-14), 2.1 (*dt*, *J* = 13.2, 4.1 Hz, H-14), 1.5 (*dd*, 3H, *J* = 7, 2.4 Hz, Me-18).

Complementary data for known alkaloids. 10-*Methoxy deplancheine* **2**. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.85 (*br s*, NH), 7.18 (*d*, *J* = 8.5 Hz, H-12), 6.92 (*d*, *J* = 2.6 Hz, H-9), 6.78 (*dd*, *J* = 8.5, 2.6 Hz, H-11), 5.35 (*br q*, *J* = 6.8 Hz, H-19), 3.85 (*s*, 3H, OMe), 3.8 (*br d*, *J* = 12.4 Hz, H-21), 3.38 (*d*, *J* = 10.9 Hz, H-3), 3.15 (*dd*, *J* = 10.6, 6 Hz, H-5), 2.98 (*dddd*, *J* = 2.2, 5.8, 10, 12 Hz, H-6), 2.77 (*d*, *J* = 12.4 Hz, H-21), 2.7 (*dd*, *J* = 10.6, 6 Hz, H-5), 2.68 (*m*, H-6), 2.38 (*br d*, *J* = 13.4 Hz, H-15), 2.25 (*br t*, *J* = 13.4 Hz, H-15), 2.1 (*ddt*, *J* = 12.3, 2.5, 1.4 Hz, H-14), 1.67 (*d*, *J* = 6.8 Hz, Me-18), 1.62 (*dq*, *J* = 4.5, 13.4 Hz, H-14).

Vincamajine **3**. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.18 (*dt*, *J* = 7.1, 1.1 Hz, H-11), 7.15 (*br d*, *J* = 7.5 Hz, H-9), 6.8 (*dt*, *J* = 7.5, 1.1 Hz, H-10), 6.66 (*br d*, *J* = 7.1 Hz, H-12), 5.27 (*br q*, *J* = 7 Hz, H-19), 4.24 (*br s*, H-17), 3.7 (*s*, 3H, CO_2Me), 3.56 (*m*, H-3), 3.51 (*m*, H-5), 3.5 (*m*, 2H, H-21), 3.42 (*br s*, H-15), 3.24 (*d*, *J* = 4.6 Hz, H-2), 2.64 (*s*, N-Me), 2.62 (*dd*, *J* = 11, 4.5 Hz, H-6), 2.45 (*dd*, *J* = 14.5 Hz, H-14), 2.1 (*br s*, OH), 1.75 (*d*, *J* = 11 Hz, H-6), 1.6 (*dt*, *J* = 7, 1.5 Hz, Me-18), 1.54 (*dd*, *J* = 14, 9.5 Hz, H-14).

Desmethylquaternine **4**. CR green then pink; mp 197–200° (Et_2O); $[\alpha]_D$ −19° ($CHCl_3$; *c* 1); UV λ_{max}^{MeOH} nm: 210, 235, 300; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3340, 1735, 1615, 1495, 1130, 1070, 990, 865, 815; MS: *m/z* (rel. int.): 398 (100), 383 (20), 380 (20), 339 (30), 299 (70), 262 (55), 254 (20), 204 (15), 190 (15), 136 (30), ^1H NMR (300 MHz, $CDCl_3$) δ: 6.78 (*s*, H-9), 6.4 (*s*, H-12), 5.41 (*br q*, *J* = 6.7 Hz, H-19), 4.83 (*d*, *J* = 2.1 Hz, H-5), 3.81 (*s*, OMe), 3.76 (*s*, Me), 3.75 (*m*, H-21), 3.66 (*s*, Me), 3.57 (*d*, *J* = 4.6 Hz, H-3), 3.36 (*d*, *J* = 13.6 Hz, H-6), 3.28 (*br s*, H-5), 3.08 (*d*, *J* = 17.6 Hz, H-21), 2.42 (*d*, *J* = 3.6 Hz, H-16), 2.24 (*dd*, *J* = 13.6, 2.4 Hz, H-6), 2.14 (*dt*, *J* = 13.0, 3.9 Hz, H-14), 1.85 (*dd*, *J* = 13, 2 Hz, H-14), 1.48 (*dd*, *J* = 7, 2 Hz, Me-18).

Cabucraline **7**. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.8 (*d*, *J* = 7.9 Hz, H-9), 6.2 (*dd*, *J* = 7.9, 2.2. Hz, H-10), 6.18 (*d*, *J* = 2.2 Hz, H-12), 5.46 (*br q*, *J* = 7 Hz, H-19), 4.28 (*d*, *J* = 4.8 Hz, H-3), 4.05 (*br d*, *J* = 15.7 Hz, H-21), 3.83 (*dt*, *J* = 5.4, 13.5 Hz, H-5), 3.77 (*s*, OMe), 3.73 (*s*, ArOMe), 3.62 (*br s*, H-15), 3.12 (*dt*, *J* = 6.6, 13.5 Hz, H-6), 3.03 (*d*, *J* = 15. Hz, H-21), 2.92 (*d*, *J* = 3.9 Hz, H-16), 2.71 (*dd*, *J* = 6.6, 13.5 Hz, H-5), 2.64 (*s*, N-Me), 2.56 (*s*, H-2), 2.35 (*ddd*, *J* = 2.9, 4.8, 14.2 Hz, H-14), 1.63 (*br dd*, *J* = 14.2, 2 Hz, H-14), 1.48 (*dd*, *J* = 7,2 Hz, Me-18).

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REFERENCES

1. Boiteau, P., Allorge, L. and Sèvenet, T. (1977) *Adansonia* **16**, 465.
2. Legseir, B., Chérif, A. Richard, B., Pusset, J., Labarre, S., Massiot, G. and Le Men-Olivier, L. (1986) *Phytochemistry* **25**, 1735.
3. Lewin, G., Tamini, O., Cabalion, P. and Poisson, J. (1981) *Ann. Pharm. Fr.* **39**, 273.
4. Cherif, A., Massiot, G. and Le Men-Olivier, L. (1987) *Heterocycles*, **26**, 3055.
5. Besselievre, R., Cosson, J.-P., Das B. C. and Husson, H.-P. (1980) *Tetrahedron Letters* 63.
6. Petitfrère -Anvray, N., Vercauteren, J., Massiot, G., Lukacs, G., Sévenet, T. and Le Men-Olivier, L. (1981) *Phytochemistry* **20**, 1987.
7. Guillaume, D., Morfaux, A. M., Richard, B., Massiot, G., Le Men-Olivier, L., Pusset, J. and Sèvenet, T. (1984) *Phytochemistry* **23**, 2407.
8. Verpoorte, R., Van Beek, T. A., Riegman, R. L. M., Hylands, P. J. and Bisset, N. G. (1984) *Org. Magn. Reson.* **22**, 328.
9. Massiot, G., Vercauteren, J., Jacquier, M. J., Lévy, J. and Le Men-Olivier, L. (1981) *C. R. Acad. Sci.* **292**, 191.
10. Mamatas-Kalamaras, S., Sèvenet, T., Thal, C. and Potier, P. (1975) *Phytochemistry* **14**, 1849.
11. Wenkert, E., Chang, C. J., Chawla, H. P. S., Cochran, D. W., Hagaman, E. W., King, J. C. and Orito, K. (1976) *J. Am. Chem. Soc.* **98**, 3645.