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ATOMASINS A AND B, TETRANORTRITERPENOIDS FROM THE BARK OF *ENTANDROPHRAGMA CANDOLLEI*

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Key Word Index—*Entandrophragma candollei*, Meliaceae, tetranortriterpenoids; atomasins A and B

Abstract—Two new tetranortriterpenoids, atomasins A and B, were isolated from the trunk bark of *Entandrophragma candollei*. The structures of the new compounds were established from their spectroscopic data.

INTRODUCTION

The genus *Entandrophragma* contains a number of protolimonoids and limonoids [1]. Previous investigations [2] on *E. candollei* Harms [3] yielded sitosterol and candollein, a tetranortriterpenoid very closely related to entandrophragmin, which is the major constituent of several species of the genus *Entandrophragma*. In continuation with our studies on Cameroonian medicinal plants [4], we have investigated *E. candollei* and wish to report on the isolation and characterization, from the chloroform extract, of two new tetranortriterpenoids, for which we propose the names atomasin A (**1**) and atomasin B (**2**),‡ together with the known compounds sitosterol, odoratone, candollein and methyl angolensate obtained in our previous study [5]

RESULTS AND DISCUSSION

Atomasin A (**1**), mp 224–225°, showed a molecular ion peak at *m/z* 690 consistent with the formula $C_{35}H_{46}O_{14}$. It gave positive Liebermann–Buchard and Ehrlich tests, indicating that **1** was possibly a limonoid The IR spectrum exhibited absorptions due to hydroxyl (3400 cm^{-1}), ester (1720 cm^{-1}) and lactone (1750 cm^{-1}) groups and β-substituted furan ring (3150, 1500, 870 cm^{-1}). The ^1H NMR spectrum showed the presence of three tertiary methyl groups at δ0.86, 0.95 and 1.12, two secondary methyl groups at δ1.05 (3H, *d*, J = 7.0 Hz) and 1.12 (3H, *d*, J = 7.0 Hz), two acetate groups at δ2.03 and 2.30, a carbomethoxyl at δ3.73 and three carbinol protons of three secondary ester groups at δ4.98, 5.17 and 5.98 (1H each, *s*). The resonances at δ6.38 (1H, *m*), 7.38 (1H, *m*) and 7.39 (1H, *m*) confirmed the presence of the furan ring. The ^{13}C NMR spectrum of **1** showed resonances due to five ester groups at δ177.3, 174.6, 174.3, 170.4, 170.2, four olefinic carbon atoms at δ142.8, 140.0, 121.1, 109.8, seven carbon atoms attached to oxygen at δ86.2 (*s*), 85.1 (*s*), 78.0 (*s*), 75.1 (*s*), 84.3 (*d*), 83.1 (*d*), 66.8 (*d*), and carbomethoxyl at δ51.6. The aliphatic part of this spectrum consisted of seven methyl groups, five methylenes, three methines and four quaternary carbon atoms Closer analysis of ^{13}C NMR spectrum gave the formula $C_{35}H_{46}O_{14}$. Integration of the ^1H NMR spectrum indicated 46 protons as in the molecular formula deduced from the mass spectrum. Thus **1** contains three hydroxy groups.

The mass spectrum showed the characteristic cleavage of isobutyrate at *m/z* 71. This was supported in the ^1H NMR spectrum by the presence of an isopropyl with a deshielded methine proton at δ3.32 (1H, *m*), 1.12 (3H, *d*, J = 7.0 Hz) and 1.05 (3H, *d*, J = 7.0 Hz).

Spectroscopic data (^1H and ^{13}C NMR) of **1** suggested that it belongs to the phragmalin series. Evidence for this 1,29-cyclo methyl meliacate skeleton was supported by the nature of carbinol protons of three secondary ester groups at δ5.96, 5.17, 4.98, the presence of only three angular methyl groups and a methoxycarbonyl group [6]. Furthermore, its ^{13}C NMR data were similar to those of phragmalin [7] and candollein [8], and in particular showed a triplet at δ42.2 which may be ascribed to C-29 in this kind of bridged ring skeleton (phragmalin 40.0, candollein 40.2). The orthoacetate peaks which commonly appear on the ^1H and ^{13}C NMR spectra (at δ1.6 and 119.3 [8] respectively) of the members of this limonoids group are absent.

According to the fact that 1,29-cyclo methyl meliacate derivatives are generally substituted at C-1, C-2, C-3, C-8, C-9 and C-30 [9], and on the basis of a biogenetical scheme for phragmalin [9] and because of steric hindrance [6], we attributed the hydroxy groups to C-1, C-8 and C-9 and the ester groups to C-2, C-3 and C-30. The problem of attachment of these ester groups was solved by 2D δ_H/δ_C direct and long range correlations [10] H-30 showed a strong correlation with a carbonyl at δ174.6. This carbonyl was also coupled through long range with the protons of the isopropyl group Hence, the isobutyrate is linked to C-30 and the acetates to C-2 and C-3. These observations are consistent with structure **1** for atomasin A.

Atomasin B (**2**), $C_{34}H_{44}O_{14}$, $[M]^+$ ion peak at *m/z* 676, was isolated as colourless needles, mp 234–235°. Preliminary Lieberman–Buchard and Ehrlich tests and

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‡The name atomasin refers to the vernacular name 'Atom Assie' given to *Entadrophragma candollei*

the IR spectrum (3150, 1500 and 875 cm^{-1}) indicated that **2** was also a limonoid The ^1H and ^{13}C NMR data of **2** as shown in Tables 1 and 2, revealed that it was structurally close to atomasin A (**1**) and differed only by replacement of the isobutyrate at C-30 in atomasin A (**1**) by a propionate in atomasin B (**2**) These findings are confirmed by the mass spectra of atomasin A [M^+ at *m/z* 690] and atomasin B [M^+ at *m/z* 676], where the difference of 14 units is due to the lack of a CH_2 fragment.

The occurrence of atomasin A and atomasin B from *E. candollei* is of great interest, as they may be considered as potential intermediates in the biogenesis [8] of the phragmalin limonoid group

EXPERIMENTAL

General Mps. uncorr, NMR 25°, $CDCl_3$ unless otherwise mentioned 200 13 MHz for ^1H (shifts relative to $CDCl_3$ at δ_H 7 25) and 50 32 MHz for ^{13}C (shifts relative to $CDCl_3$ at δ 77 ppm) EIMS were obtained at 70 eV

Plant material The bark of *E candollei* was collected at Awae, near Akonolinga, Cameroon, in October 1985 A voucher specimen has been deposited at the National Herbarium, Yaounde

Extraction and isolation of constituents The air-dried and finely powdered stem bark of *E candollei* (6 5 kg) was extracted with hexane (20 l) The defatted material obtained after hexane extraction was then extracted with $CHCl_3$ The syrup obtained (100 g) after concn of $CHCl_3$ soln was chromatographed repeatedly on a silica gel column and eluted with mixtures of $CHCl_3$–EtOAc to give sitosterol (2 3 g), methyl angolensate (50 mg), odoratone (90 mg), candollein (50 mg), **1** (240 mg), **2** (110 mg) Known compounds were identified by direct comparison (mp, UV, IR, ^1H NMR) with authentic samples and are therefore not described here

Table 1 ^1H NMR data of compounds **1** and **2** (recorded at 200 13 MHz, $CDCl_3$, TMS)

H	1	2
21	7 39 *m*	7 36 *m*
23	7 38 *m*	7 35 *m*
22	6 38 *m*	6 34 *m*
17	4 98 *s*	4 98 *s*
30	5 98 *s*	6 01 *s*
3	5 17 *s*	5 16 *s*
CO_2Me	3 72 *s*	3 69 *s*
OAc	2 30 *s*	2 24 *s*
OAc	2 03 *s*	2 04 *s*
Me*	1 12 *s*	1 08 *s*
	0 97 *s*	0 94 *s*
	0 88 *s*	0 84 *s*
H-2′	2 38 *m*	2 20 *q*
Me-2′	1 12 *d* (7 2)†	1 07 *t* (8 5)
	1 05 *d* (7 0)	–
OH	4 97 *s*	4 90 *s*
	4 69 *s*	4 81 *s*
	4 68 *s*	4 70 *s*

*Skeletal methyl groups

†Coupling constants (value in Hz in parentheses)

Atomasin A (**1**) Colourless needles from $CHCl_3$–Et_2O, mp 224–225° Found M^+ 690 1, $C_{35}H_{46}O_{14}$ requires 690 1 IR ν_{max}^{KBr} cm^{-1} 3400, 3150, 2980, 1750, 720, 1500, 1440, 1380, 1360, 870, ^1H and ^{13}C NMR see Tables 1 and 2, respectively, EIMS *m/z* (rel int) 313 (13), 135 (7), 95 (10), 71 (15), 43 (100)

Atomasin B (**2**) Colourless needless from $CHCl_3$–Et_2O, mp 234–235° Found M^+ 676 320, $C_{34}H_{44}O_{14}$ requires 676 321 IR ν_{max}^{KBr} cm^{-1} 3400, 3150, 2980, 1750, 1710, 1500, 1400, 1380, 1360, 875, ^1H and ^{13}C NMR see Tables 1 and 2, respectively

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Table 2 ^{13}C NMR data of compounds **1** and **2** (recorded at 50 32 MHz, $CDCl_3$, TMS)

C	1	2
1	86 2 *s*	86 2 *s*
2	85 1 *s*	85 6 *s*
3	84 3 *d*	83 7 *s*
4	41 9 *s*	41 9 *s*
5	37 6 *d*	37 4 *d*
6	32 7 *t*	32 7 *t*
7	177 3 *s*	177 2 *s*
8	78 2 *s*	78 0 *s*
9	75 1 *s*	75 1 *s*
10	51 6 *s*	51 4 *s*
11	27 5 *t*	27 4 *t*
12	30 2 *t*	30 1 *t*
13	36 1 *s*	36 2 *s*
14	46 2 *d*	46 2 *d*
15	32 2 *t*	32 1 *t*
16	174 3 *s*	174 6 *s*
17	83 1 *d*	83 1 *d*
18	25 2 *q*	24 9 *q*
19	16 4 *q*	16 4 *q*
20	121 1 *s*	121 0 *s*
21	140 0 *d*	140 0 *d*
22	109 9 *d*	109 8 *d*
23	142 9 *d*	142 8 *d*
28	16 3 *q*	16 1 *q*
29	42 5 *t*	42 2 *t*
30	66 8 *d*	66 6 *d*
1′	174 6 *s*	172 0 *s*
2′	34 1 *d*	27 3 *t*
3′	19 2 *q**	19 0 *q*
4′	18 5 *q**	
Ac	170 4 *s*	170 1 *s*
Ac	170 2 *s*	170 0 *s*

*Assignments may be interchanged

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A QUASSINOID GLYCOSIDE FROM THE ROOTS OF *EURYCOMA LONGIFOLIA*

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Key Word Index—*Eurycoma longifolia*, Simaroubaceae, eurycomanol-2-*O*-β-D-glucopyranoside, eurycomanol, quassinoid, antimalarial

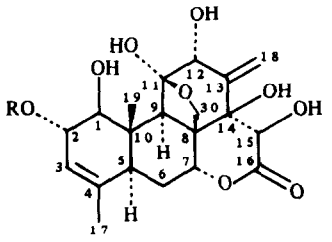
Abstract—A new quassinoid glycoside, eurycomanol-2-*O*-β-D-glycopyranoside, and eurycomanol have been isolated as antimalarial components of *Eurycoma longifolia*.

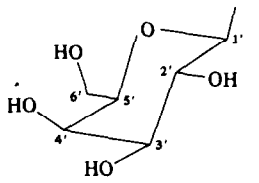
INTRODUCTION

As part of our search for antimalarial constituents among local medicinal herbs, we have studied *Eurycoma longifolia* Jack., known locally as 'Tongkat Ali'. This plant is used as a traditional treatment for persistent fevers and tertian malaria [1]. In previous study [2], we reported on the isolation and antimalarial activities of several quassinoids, the bitter principles of this plant. This communication describes the structural determination of eurycomanol-2-*O*-β-D-glycopyranoside (**1**), a new quassinoid glycoside, and the antimalarial activity of **1** and that of eurycomanol (**2**), also isolated from the same source.

RESULTS AND DISCUSSION

The *n*-butanol extract of *E longifolia* roots, on silica gel column chromatography, gave several fractions with antimalarial activity. Further purification of these fractions afforded the glycoside (**1**) and eurycomanol (**2**). The latter (**2**) was identified from spectroscopic data and by direct comparison with an authentic specimen [2, 3]. The glycoside **1** gave peaks at *m/z* 573 $[M+H]^+$, 595 $[M+Na]^+$ and 665 $[M+glycerol+H]^+$ in positive SIMS, from which the molecular formula, $C_{26}H_{36}O_{14}$, was deduced and confirmed by an elemental analysis as $C_{26}H_{36}O_{14}\cdot 2H_2O$. It was a hexoside from a peak at *m/z* 411 corresponding to $[M-C_6H_{10}O_5+H]^+$. Acid hydrolysis of **1** with 0.1 M HCl at 45° gave several degraded



1 R = 

2 R = H