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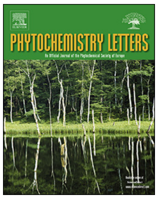

Welwitschiilactone A, B and C, three new 30-norfriedelane triterpenes from the roots of *Caloncoba welwitschii* (Oliv.) Gilg (Achariaceae)

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ABSTRACT

Three new 30-norfriedelane triterpenoids named, 3*β*,21*β*-dihydroxy-27-oxo-30-nor-(D:A)-friedo-olean-20(29)-en-27,19*α*-lactone (welwitschiilactone A) (**1**), 21*β*-hydroxy-3,27-dioxo-30-nor-(D:A)-friedo-olean-20(29)-en-27,19*α*-lactone (welwitschiilactone B) (**2**) and 2*β*,21*β*-dihydroxy-27-oxo-30-nor-(D:A)-friedo-olean-20(29)-en-27,19*α*-lactone (welwitschiilactone C) (**3**) along with seven known compounds were isolated from the methanol extract of the roots of *Caloncoba welwitschii*. Their structures were determined by comprehensive spectroscopic analyses (1D and 2D NMR, EI-, ESI- and HRESI-MS). The relative configuration of the 19-oxymethine and the 21-hydroxy have been established by using the NOESY spectrum.

1. Introduction

Caloncoba welwitschii (Oliv.) Gilg belonging to the family of Achariaceae is an understory shrub or a tree up to 14 m tall, mainly distributed in tropical Africa (Sleumer, 1975). It is widely used in traditional medicine in Central Africa: leaves and bark are applied for the treatment of rheumatism and as poultice to cure abscesses; leaf-sap is taken against headache and seed oil against leprosy, while in Gabon the fruit pulp is consumed. Unspecified parts of the plant are as well used against body-lice (Burkill, 1994). Pharmacological studies carried out on several species of the genus *Caloncoba* identified the ethanolic crude extract of the leaves of *C. welwitschii* to possess anti-sickle-cell anaemia activity (Mpiana et al., 2017; Sahu et al., 2012). The genus *Caloncoba* was reported to produces a wide range of secondary metabolites, including alkaloids (Agbo et al., 2017), cyclopentanoid amino acids (Clausen et al., 2002), flavonoids (Douanla et al., 2018) as well as pentacyclic and tetracyclic-type triterpenoids derivatives (Ziegler et al., 2002; Giner-Pons et al., 1992, 1993; Tchuendem et al., 1996; Mpetga et al., 2012a,b, 2014). While the leaves of *C. welwitschii* had previousl delivered flavonol, friedelane triterpenoids and phytosterols (Douanla et al., 2018), this article reports first compounds from its roots. The isolation and structural elucidation of three new 30-norfriedelane triterpenes lactones, welwitschiilactone A–C together with seven known compounds are presented.

2. Results and discussion

The roots of *C. welwitschii* were extracted with MeOH and subjected to column chromatography carried out on silica gel and preparative thin layer chromatography (pTLC) to afford three new 30-norfriedelane triterpenes lactones and seven known compounds (Fig. 1). By comparison with the reported data, the known compounds were identified as friedelane, stigmastane-3,6-dione, a mixture of *β*-sitosterol and stigmasterol, a mixture of *β*-sitosterol and stigmasterol glucoside (Douanla et al., 2018), (2*S*,3*S*,4*R*,5*R*) *N*-(1,3,4,5-tetrahydroxyundecan-2-yl)tetradecanamide (Happi et al., 2013) and 1-*O*-*β*-*D*-glucopyranosyl-(2*S*,3*R*,8*E*)-2-[(2′*R*)-2-hydroxylpalmitoylamino]-8-octadecene-1,3-diol (Ling et al., 2006), while the new triterpenes were identified by comprehensive spectroscopic analyses.

Compound **1** was purified as a white powder with $[\alpha]_D^{20}$ + 69.4°. It responded positively to the Liebermann-Buchard test, suggesting that the compound was a triterpenoid. The molecular composition was found to be $C_{29}H_{44}O_4$ by HR-ESIMS ($[M+H]^+$ at *m/z* 457.3325, calcd 457.3318), accounting for eight degrees of unsaturation. The IR spectrum indicated the presence of hydroxyl (υ_{max} = 3440 cm^{-1}), lactone (υ_{max} = 1780 cm^{-1}) and C=C (υ_{max} = 1630 cm^{-1}) groups. The ^{1}H-NMR spectrum of **1** (Table 1) showed singlets due to four tertiary methyl groups at δ_H 0.92 (s, H-24), 0.96 (s, H-25), 0.98 (s, H-26) and 1.06 (s, H-28) as well as a doublet for one secondary methyl at δ_H 0.93 (d, *J* = 8.4 Hz, H-23) as characteristic signals of a friedelane triterpene skeleton (Douanla et al., 2018). Additional features of the ^{1}H-NMR

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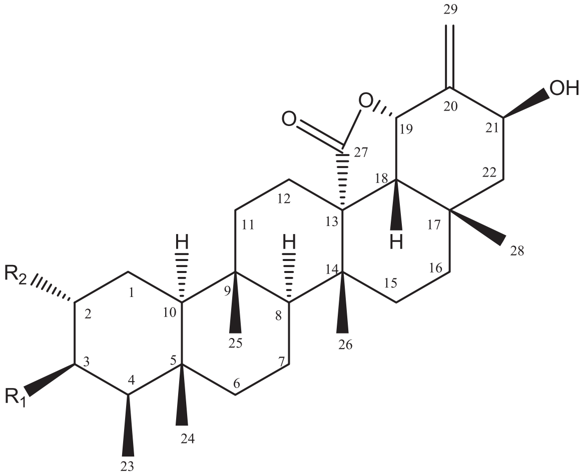

1. $R_1 = \text{OH}$, $R_2 = \text{H}$

2. $R_1 = \text{O}$, $R_2 = \text{H}$

3. $R_1 = \text{O}$, $R_2 = \text{OH}$

Fig. 1. Chemical structures of compounds **1** – **3**.

spectrum revealed the presence of three oxymethine at δ_H 3.73 (brd, *J* = 3.6 Hz, H-3), 4.63 (brd, *J* = 7.7 Hz, H-21), and 5.02 (d, *J* = 4.7 Hz, H-19) and an exocyclic methylene at δ_H 5.38 and 5.46 (each 1H, d, *J* = 1.7 Hz, H-29).

The friedelane triterpene skeleton of compound **1** was confirmed by the presence of a characteristic signal observed in the ^{13}C-NMR and DEPT spectra at δ_C 11.74 (C-23) (Mpetga et al., 2014; Mahato and Kundu, 1994). Furthermore, the ^{13}C-NMR showed the presence of four tertiary methyl groups at δ_C 16.6 (C-24), 16.8 (C-26), 19.2 (C-25) and 32.6 (C-28), three oxymethines at δ_C 66.6 (C-21), 72.8 (C-3) and 79.3 (C-19), one exocyclic double bond at δ_C 114.3 (C-29) and 146.2 (C-20) and one carboxyl group at δ_C 178.2 (C-27). These ^{1}H- and ^{13}C-NMR signals indicate the absence of the 30-methyl which was probably eliminated during the biosynthesis of the compound. The exact position of the carbonyl, olefinic and oxymeyhine groups was assigned by the 2D-NMR experiments (COSY, HMBC and NOESY). The COSY correlations between H-3 and H-4 on the one hand and on the other hand, the HMBC correlations between H-3 and C-1 and C-5 as well as the biogenetic considerations confirmed the position of one hydroxyl group at C-3. The position of a second hydroxyl group at C-21 was suggested by the HMBC correlations between H-21 and C-17, C-19, C-20, C-22 and C-29, as well as between O-H-21 and C-20, C-21 and C-22. Furthermore, the position of the third oxymethine proton at δ_H 5.02 at C-19 was suggested by the COSY correlations between H-18 and H-19. Hereby, the position at C-19 was confirmed by long-range correlations between

Table 1
^{1}H (500 MHz) and ^{13}C (125 MHz) NMR assignments for compounds -**3** in $CDCl_3$.

Attribution	1		2		3	
	^{13}C	^{1}H (m, *J* in Hz)	^{13}C	^{1}H (m, *J* in Hz)	^{13}C	^{1}H (m, *J* in Hz)
1	15.9	1.56 (m)	22.4	1.74 (m)	32.6	2.35 (m)
		1.59 (m)		1.94 (m)		2.40 (m)
2	34.9	1.54 (m)	41.4	1.37 (m)	74.8	4.15 (brt, *J* = 8.9)
		1.84 (m)		1.75 (m)		
3	72.9	3.73 (d, *J* = 3.6)	213.3	–	212.6	–
4	48.9	1.83 (m)	58.9	1.84 (m)	55.4	1.76 (m)
5	37.8	–	42.1	–	43.1	–
6	41.3	1.12 (m)	40.8	1.43 (m)	40.7	1.40 (m)
		1.74 (m)		1.74 (m)		1.78 (m)
7	17.2	1.47 (m)	17.2	1.58 (m)	17.7	1.33 (m)
		1.50 (m)		1.60 (m)		1.63 (m)
8	47.1	2.47 (dd, *J* = 12.2, 1.8)	47.1	2.57 (dd, *J* = 12.0, 1.4)	47.9	2.61 (dd, *J* = 12.0, 1.4)
9	37.1	–	37.4	–	37.1	–
10	60.0	1.11 (m)	57.8	1.73 (m)	55.3	1.74 (m)
11	36.0	1.63 (m)	35.3	1.57 (m)	35.3	1.59 (m)
		1.65 (m)		1.59 (m)		1.61 (m)
12	25.4	1.75 (m)	25.2	1.80 (m)	25.3	1.79 (m)
		1.79 (m)		1.83 (m)		1.82 (m)
13	52.0	–	52.0	–	51.9	–
14	37.2	–	37.1	–	37.3	–
15	29.1	1.47 (m)	29.2	1.48 (m)	29.3	1.49 (m)
		1.60 (m)		1.50 (m)		1.50 (m)
16	35.3	1.56 (m)	35.9	1.31 (m)	35.9	1.31 (m)
		1.59 (m)		1.33 (m)		1.34 (m)
17	31.3	–	31.3	–	31.3	–
18	60.0	2.07 (d, *J* = 4.7)	51.8	2.09 (d, *J* = 4.8)	51.8	2.12 (d, *J* = 5.0)
19	79.3	5.02 (d, *J* = 4.7)	79.5	5.04 (d, *J* = 4.8)	79.5	5.07(d, *J* = 5.0)
20	146.2	–	146.9	–	145.9	–
21	66.6	4.63 (brd, *J* = 7.5)	66.5	4.62 (brt, *J* = 6.8)	66.5	4.64 (brs)
22	43.8	2.50 (dd, *J* = 15.7, 7.5)	43.8	2.51 (dd, *J* = 15.7,7.6)	43.7	2.53 (dd, *J*= 15.7, 7.7)
		1.19 (brd, *J* = 15.7)		1.20 (d, *J* = 15.7)		1.20 (d, *J* = 15.7)
23	11.7	0.93 (d, *J* = 8.4)	6.9	0.87 (d, *J* = 6.7)	6.7	0.96 (d, *J* = 6.7)
24	16.6	0.92 (s)	14.9	0.74 (s)	14.9	0.70 (s)
25	19.2	0.96 (s)	18.9	0.99 (s)	19.1	0.99 (s)
26	16.8	0.98 (s)	17.1	0.94 (s)	17.0	0.94 (s)
27	178.2	–	178.3	–	178.3	–
28	32.6	1.06 (s)	32.6	1.07 (s)	32.6	1.07 (s)
29	114.4	5.38 (d, *J* = 1.7)	114.6	5.39 (d, *J* = 1.8)	114.6	5.51 (d, *J* = 1.6)
OH		5.46 (d, *J* = 1.7)		5.48 (d, *J* = 1.8)		5.43 (d, *J* = 1.6)
		–		–		3.70 (d, *J* = 3.3)