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Cycloeucalen-3ß-(2-methyl Butanoate). New Cycloeucalen Isolated from the Espeletia *barclayana* Cuatr (Asteraceae)

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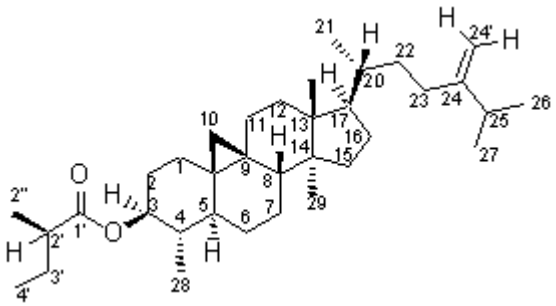


Continuing our studies of the *Espeletia barclayana Cuatr*. [1,2] we describe the isolation and characterization of another new cycloeucalen triterpene, cycloeucalen-3ß-(2'-methyl butanoate). It's structure was established using spectroscopic methods ^{1}H and ^{13}C NMR: 600 MHz, and 150 MHz (1D:1H, ^{13}C-JMOD; 2D:COSY, NOESY, HMBC).

The sample of *E. barclayana Cuatr*. was collected at páramo del Tablazo, Subachoque, Cundinamarca, Colombia, and identified by Mr. Santiago Diaz of the Herbario Nacional Colombiano (Col. 332528). The dried and ground leaves (1kg) of *E. barclayana* were extracted with petrol and 20g of this extract was subjected to column chromatography over Si-gel using petrol and EtOAc as eluents. The petrol fraction gave a mixture of two compounds that were separated using TLC preparative development repeatedly with n-hexane:benzene (1:1). Cycloartan-3ß-(2-methyl butanoate) [1] and a new cycloeucalen derivative were obtained and purified by several times of recrystallization with $CHCl_3$ and MeOH.

^{1}H NMR spectra of the cycloeucalene showed doublet signals at d 0.15 and 0.40 with J=3.7 Hz for CH_2 of cyclopropane ring and d 4.66 4.67 for $=CH_2$. The chemical shifts of the cyclopropyl methylene protons (d 0.15 and 0.40) are consistent with the presence of only one methyl group at C-4 [3,4]. The presence of the methylene group was confirmed by the ^{13}C NMR signal at d 105.9 and its position on C-24 was determined using ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY spectra (see data in Table 1). The ^{1}H NMR spectrum clearly indicated the b-equatorial nature of the C-3 ester group (4.5, heptuplet, J_{ax-eq} =5 Hz , J_{ax-ax} = 11Hz, 3aH).

Mp 132-134 ^{o}C

$[a]^{20}_{D}$ = +47 º (0.0068 g/mL, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): 0.85 (d, H_3-21), 0.91 (9H, H_3-21, H_3-29, H_3-4'), 0.97 (s, H_3-18), 1.02 and 1.03 (H_3-26 and H_3-27), 1.14 (d, H_3-H-2''), 0.15 (d, J=3.7 Hz, H-19a) and 0.40 (d, J=3.7Hz, H-19ß), 2.24 (heptuplet, J=7Hz, H-25), 2.35 (hexuplet, J= 7Hz, H-2'), 4.5 (m, heptuplet, J_{ax-eq}=5, J_{ax-ax}=11, CH-O H-3), 4.66-4.67 (d, $=CH_2$) .

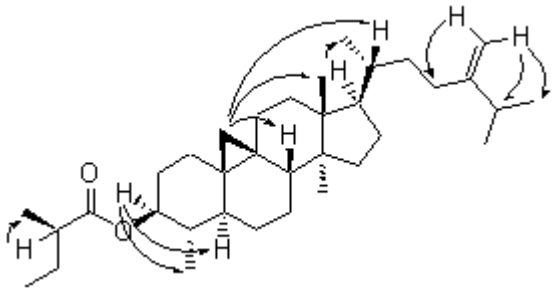
^{13}C NMR (150 MHz, $CDCl_3$): 30.9(C-1), 27.2 (C-2), 78.2 (C-3), 41.3 (C-4), 43.0 (C-5), 25.1 (C-6), 24.7

(C-7), 46.9 (C-8), 23.6 (C-9), 29.3 (C-10), 30.5 (C-11), 32.8 (C-12), 48.9 (C-13), 45.8 (C-14), 35.3 (C-15), 28.1 (C-16), 52.2 (C-17), 17.8 (C-18), 26.9 (C-19), 36.12 (C-20), 18.3 (C-21), 34.9 (C-22), 31.3 (C-23), 156.9 (C-24), 33.7 (C-25), 21.8 (C-26), 22 (C-27), 14.3 (C-28), 19.1 (C-29), 18.3 (C-30), 105.9 (C-24') 176.0 (C-1'), 41.6 (C-2'), 26.7 (C-3'), 11.7 (C-4'), 16.7 (C-2").

Table 1. Spectral data and assigments for proton and carbon on ^{1}H NMR and ^{13}C NMR:

No. H	δ (ppm)	multiplicity	H-X-C-C-C
H-24'	4.66-4.67	(d, $=CH_2$)	33.7(C25), 31.3(C23)
H-3	4.5	(m, J=5, CH-O)	
H-23	2.1-1.9		156.9(C24)
H-5	1.66	(m)	
H-25	2.24	(heptete,J=7Hz)	156.9(C24), 21.8(C27), 22(C29)
H-6	1.55 - 0.6	(dq, J= 2.4,12.6 Hz)	
H-17	1.6	m.	48.9(C13),45.8(C14), 36.12(C20), 17.8(C18)
H-18	0.97	(s, H_3)	52.16(C17)
H-19α	0.15	(d, J=3.7 Hz,)	
H-19β	0.40	(d, J=3.7Hz,)	
H-20	1.42	CH	52.16(C17)
H-26-27	1.02-1.03	2 CH_3	156.9(C24),
H-21	0.85	(d, CH_3)	
H-2'	2.35	(sextete,J=7Hz)	176(C1'), 26.8(C3'), 16.8(C2")
H-2"	1.14	(d, CH_3)	176(C1')
H-3'	1.69-1.49		176(C1')
H-4'	0.94	(CH_3)	

Some correlation observed on HMBC and NOESY spectra:



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Sample Availability: available from MDPI. MDPI 18995.