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ACHILLEOL A: A NEW MONOCYCLIC TRITERPENE SKELETON FROM *ACHILLEA ODORATA L.*

A. F. Barrero, E. J. Alvarez-Manzaneda R.* and R. Alvarez-Manzaneda R.

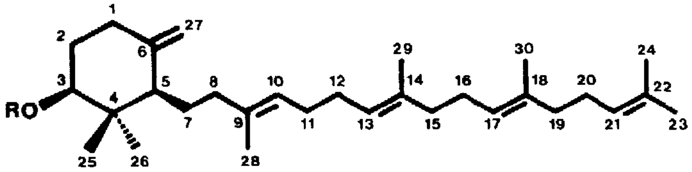
Departament of Organic Chemistry. Faculty of Sciences.
University of Granada, Granada, Spain.

Abstract: A new triterpene **1a** from *Achillea odorata L.* has been isolated, and its structure established on the basis of its spectroscopic properties as well as those of its acetylderivative **1b**. **1a** shows the first example of monocyclic triterpene skeleton, biosynthetized in the first step of cyclization of squalene oxyde.

During our studies on the chemical components of the *Achillea odorata L.* (Compositae), a new monocyclic triterpene **1a** has been isolated after saponification of a mixture of oleic and linoleic acid esters from the hexane extract [1].

1a R= H

1b R= Ac



1a had $[\alpha]_D$=-10.9° (c 0.9, $HCCl_3$), and mass spectrum [2] showed a molecular ion at m/z 426 and other characteristic fragments such as m/z 408, related with the loss of a molecule of water and the base peak at m/z 69 (3-methyl-2-butenyl), arised from the allylic rupture in the side chain. These data together with those from IR, ^{1}H- and ^{13}C-NMR spectra allowed to assign a molecular formula $C_{30}H_{50}O$.

The ^{13}C-NMR spectrum [3] showed the presence of four trisubstituted and one gem-disubstituted carbon-carbon double bonds, which implied the presence of a cycle in the structure of **1a**.

In the IR spectrum [4] appeared bands related with hydroxyl (3400 and 1085 cm^{-1}), exocyclic terminal methylene group (3070, 1644 and 892 cm^{-1}), as well as trisubstituted carbon-carbon double bond (1666 and 851 cm^{-1}).

The ^{1}H [3] and ^{13}C-NMR signals at δ 3.42 (1H, dd, J=10.0 and 4.5 Hz) and 77.4 ppm, respectively, demonstred the secondary nature and equatorial disposition on a cyclohexane ring of the hydroxyl group. The signals at δ 4.62 and 4.88 (^{1}H-NMR) and 147.3 and 108.4 (^{13}C-NMR) were also characteristic of a methylencyclohexane moiety. Signals of methyl groups at δ 0.72 (3H), 1.02 (3H), 1.60 (12H) and 1.69 (3H), a broad singlet at δ 2.02, assigned to methylene adjacent to a carbon-carbon double bond, and a multiplet at δ 5.12, corresponding to four vinylic protons, were also observed.

^{13}C-NMR assignments were made on the basis of DEPT experiments and by comparison with those reported for trixagol [5] and squalene [6] in relation with the cyclic and side chain moieties, respectively, and were in accordance with the proposed structure. The presence of an equatorial hydroxyl group at C-3 in **1a** was revealed by the β effect on C-2 and C-4 (Δ +9.4 and +5.7, respectively) respect to the same carbons in trixagol, which was in accordance with the data found in the literature for related terpenoids [7].

^{13}C-NMR chemical shifts of compounds 1a and 1b

	1a	1b		1a	1b		1a	1b
C- 1	32.31	31.66	C-11^{c}	26.76	26.86	C-21^{b}	124.50	124.51
C- 2	33.18	28.73	C-12^{c}	26.85	26.76	C-22	131.29	131.33
C- 3	77.40	78.71	C-13^{b}	124.37	124.35	C-23^{f}	25.76	25.78
C- 4	40.62	39.26	C-14^{a}	135.18	135.24	C-24	17.75	17.77
C- 5	50.99	51.40	C-15^{d}	39.81	39.83	C-25^{f}	25.96	26.20
C- 6	147.33	146.89	C-16^{e}	28.33	28.35	C-26^{f}	26.76	26.20
C- 7	23.82	24.01	C-17^{b}	124.45	124.51	C-27	108.45	109.34
C- 8	38.70	38.53	C-18^{a}	135.50	135.36	C-28	15.58	17.88
C- 9^{a}	134.97	134.98	C-19^{d}	39.84	39.83	C-29^{g}	16.10	16.14
C-10^{b}	124.35	124.35	C-20^{e}	28.38	28.35	C-30^{g}	16.10	16.09
$CH_3\underline{C}O$		170.78	$\underline{C}H_3CO$		21.40			

$^{a-g}$ Assignments bearing the same superscript may be reversed.

The S configuration at C-3 was established by the Horeau's method [8].

Conventional acetylation of **1a** yielded the corresponding acetylderivative **1b**, which showed the expected spectroscopic properties [9].

Notes and References

[1] *Achillea odorata L.* is a plant which grows in the mountains of mediterranean area. It was collected in May 1987 in Sierra Nevada (1700 m altitude) Granada (Spain). Extraction with hexane in a Soxhlet system of 1580 g of dried plant gave a residue (67.0 g), which was defatted ($HCCl_3$-MeOH) to yield a crude (36.4 g), that after saponification and subsequent chromatographies on silica gel column afforded **1a** (50 mg).

[2] Mass spectrum was obtained at 70 eV on a Hewlett-Packard 5988a spectrometer. Other significant fragments are m/z (rel. abundance): 81 (89) ($C_6H_9^+$), 82 (12)($C_6H_{10}^{+\cdot}$), 121 (28) ($C_9H_{13}^+$), 135 (24) ($C_{10}H_{15}^+$) and 149 (18) ($C_{11}H_{17}^+$).

[3] ^{1}H (80 MHz) and ^{13}C-NMR (75 MHz) spectra were performed on a Bruker WP 80 SY and a Bruker AM 300 spectrometers, respectively, in $DCCl_3$ solns. using TMS as int. standard.

[4] IR spectrum was recorded on a Perkin-Elmer 983 G instrument.

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[9] **1b** had $[\alpha]_D=+6.3°$ (c 0.9, $HCCl_3$). MS m/z (rel. abundance): 468 (1) ($M^{+\cdot}$), 408 (1) ($M^{+\cdot}$-AcOH), 339 (1), 284 (1), 203 (7), 175 (12), 149 (8), 135 (15), 121 (19), 81 (66), 69 (base peak). IR (film), ν: 3070, 1734, 1665, 1645, 894 and 849 cm^{-1}. ^{1}H-NMR: δ 0.80 (s, 3H), 0.95 (s, 3H), 1.60 (s, 12H), 1.69 (s, 3H), 2.02 (bs, 14H), 2.05 (s, 3H), 4.65 (m, 1H), 4.68 (dd, 1H), 4.90 (m, 1H), 5.12 (m, 4H).

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