PERGAMON

Phytochemistry 51 (1999) 445–448

PHYTOCHEMISTRY

A lupane triterpenoid from *Maerua oblongifolia*

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Received 26 October 1998; received in revised form 30 November 1998

Abstract

Separation of the extract of *Maerua oblongifolia* afforded, in addition to known compounds, three lupane triterpenoids; one of them is new natural product, which was identified, by one and two dimensional NMR, MS and IR spectra, as lup-20(29)-en-3β,30-diol. © 1999 Elsevier Science Ltd. All rights reserved.

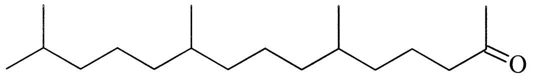
Keywords: *Maerua oblongifolia*; Capparaceae; Lupane triterpenoids; Hetero COSY; HMBC; NOESY

1. Introduction

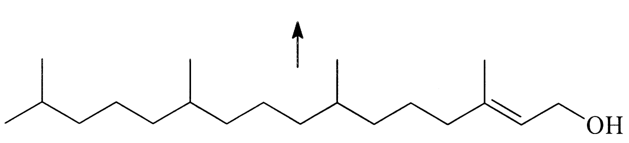
Maerua oblongifolia (Forssk.) A. Rich., a very commonly distributed plant species in Saudi Arabia, belongs to the family Capparaceae, a medium-sized family for Saudi Arabia which comprises some trees, like *Bocia angustifolia* and *Maerua crassifolia*, as well as shrubs and herbs (Collenette, 1985).

Only a few phytochemical investigations have been carried out on some species of this family (Rizk, 1986). Typical compounds are isothiocyanate glycosides (Gmelin, & Kjaer, 1970; Ahmed, Rizk, Hammouda, & Seif El-Nasr, 1972a), which are known to possess antithyroid activity (Michajlovskij, Sedlak, & Kostekova, 1970). The lipids, sterols, flavonoids and alkaloids of certain *Capparis* spp. were also studied (Mukhamdova, Akramov, & Yunusov, 1969; Ahmed, Rizk, Hammouda, & Seif El-Nasr, 1972b; Hammouda, Seif El-Nasr, & Rizk, 1975). The genus *Maerua* was still not investigated. A phytochemical investigation of this family is important because some Capparaceae species have characteristics in common with the Cruciferae and the Cleomaceae (Collenette, 1985).

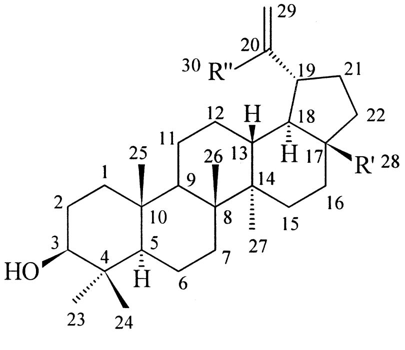
We now present the results of the phytochemical investigation of *Maerua oblongifolia* (Forssk.) A. Rich. and report the isolation of a new lupane triterpenoid from this plant species.



1



2



3; R' = CH_2OH, R'' = CH_3

4; R' = CHO, R'' = CH_3

5; R' = CH_3, R'' = CH_2OH

PII: S0031-9422(98)00771-7

2. Results and discussion

Chromatographic separation of the extract of the aerial parts of *Maerua oblongifolia* afforded two linear terpenoids **1** and **2**, six fatty acid derivatives, two sterols and three lupane triterpenoids **3–5**, one of which, **5**, was new. The fatty acid derivatives are palmitic acid (Bailey, & Pittman, 1971) as well as its methyl ester, stearic acid (Joshi, Bansal, & Singh, 1974) methyl ester, palmitoleic acid (Cronan, & Batchelor, 1974), oleic acid (Ackman, McLaughlan, Scrimgeour, & Watson, 1974) methyl ester and linoleic acid (Ackman et al., 1974) methyl ester. These methyl esters were, more likely formed due to methanolysis of fat material during extraction. The sterols are sitosterol (Abdel-Mogib, Jakupovic, Dawidar, Metwally, & Abou-Elzahab, 1990) and stigmasterol (Abdel-Mogib et al., 1990). The triterpenoids are betulin **3** (Abdel-Mogib, Ezmirly, & El-Shamy, 1996), betulinaldehyde **4** (Abdel-Mogib et al., 1996) and a new one, lup-20(29)-en-3β,30-diol (**5**).

Compound **1** was identified by the GC/MS technique in which a computer matching with stored authentic spectra is available. The mass spectrum was in good agreement with that of 6,10,14-trimethyl-2-pentadecanone (hexahydrofarnesyl acetone) **1**. It is probable that **1** is an artifact formed from phytol (**2**) (Böhlmann, & Ziesche, 1980) that was identified also by the GC/MS analysis.

The structure of compound **5** was elucidated from spectral measurements. ^{1}H NMR spectrum of **5** (Table 1) showed a triterpenoid pattern with six methyl singlets in the up-field. In the down-field region of the spectrum, there are five proton-signals; at δ 4.95 d (1.4 Hz), 4.88 s, 4.11 d (14.8 Hz), 4.06 d (14.8 Hz) and 3.16 dd (10.5, 5.7 Hz). The former two signals correlated, in the hetero COSY spectrum, with an olefinic carbon at δ 106.30 and showed two cross peaks in the HMBC spectrum (Table 3) with a carbon peak at δ 64.43, which in turn correlated in the hetero COSY spectrum with the two doublets at δ 4.11 and 4.06. Thus a lupane triterpenoid with two hydroxyl groups, one of them at C-30 is probable. The signal at δ 3.16 in the proton spectrum showed a cross peak with a carbon peak at δ 78.65 in the hetero COSY spectrum and two cross peaks with the peaks of C-23 and C-24 at δ 28.03 and 16.11, in the HMBC spectrum, respectively, due to ^{3}J couplings. Thus the second hydroxyl group was located at C-3 in the β-orientation, in agreement with the diaxial coupling of 10.5 Hz with H-2β. ^{1}H NMR and ^{13}C NMR signals were assigned on the basis of the hetero COSY and HMBC spectra. The structure and configuration of **5** were confirmed by comparing the ^{13}C NMR data with those of betulin (Tinto, Blair, Ali, Reynolds, & McLean, 1992) as well as those of 30-hydroxylup-20(29)-en-3-one (Tinto et al., 1992).

The NOE effects contained in the NOESY spectrum Table 4 not only supported the configuration around the chiral centers, but also supported the proposed structure.

3. Experimental

3.1. General

M.p.'s were measured on a Bock Monoscop, hot

Table 1
^{1}H NMR data of compound **5** (400 MHz, CDCl$_3$)

H-atom	δ value, multiplicity	H-atom	δ value, multiplicity
H-1α	1.65 m	H-16	1.48 m
H-1β	0.89 m	H-16′	1.35 m
H-2α	1.71 m	H-18	1.44 m
H-2β	1.59 m	H-19	2.27 ddd (11, 11, 5.4)
H-3	3.16 dd (10.5, 5.7)	H-21β	2.05 dddd (11.6, 11, 10.4, 10.2)
H-5	0.67 brd (9.4)	H-21α	1.34 m
H-6α	1.51 m	H-22β	1.38 m
H-6β	1.38 m	H-22α	1.27 m
H-7α	1.40 m	H-23	0.96 s
H-7β	1.19 m	H-24	0.76 s
H-9	1.23 m	H-25	0.82 s
H-11α	1.40 m	H-26	1.02 s
H-11β	1.24 m	H-27	0.94 s
H-12	1.42 m	H28	0.78 s
H-12′	1.11 m	H-29	4.95 d (1.4)
H-13	1.67 m	H-29′	4.88 s
H-15	1.41 m	H-30	4.11 d (14.8)
H-15′	0.98 m	H-30′	4.06 d (14.8)

Table 2
^{13}C NMR data of compound **5** ($CDCl_3$, 100 MHz)

C-atom	δ-value, multiplicity[a]	C-atom	δ-value, multiplicity[a]
1	38.70 t	16	35.44 t
2	27.36 t	17	42.74 s
3	78.65 d	18	48.72 d
4	38.85 s	19	43.77 d
5	55.26 d	20	154.87 s
6	18.29 t	21	31.70 t
7	34.26 t	22	39.83 t
8	40.80 s	23	28.03 q
9	50.34 d	24	16.11 q
10	37.11 s	25	15.96 q
11	20.97 t	26	15.48 q
12	26.53 t	27	14.52 q
13	37.96 d	28	17.69 q
14	42.97 s	29	106.30 q
15	27.36 t	30	64.43 q

[a] Multiplicity was concluded from DEPT 135 and DEPT 90 experiments.

plate-type melting point apparatus and were uncorr.; GC/MS spectra were taken on a QP-7000 Shimadzu, with fused silica capillary column (30 m×0.25 mm ID), film (5% phenyl, 95% methylsilicon) thickness 0.25 µm and the output of an IBM computer with software Class 500 and NIST library for comparison; NMR spectra were recorded on Bruker FT-400 MHz; IR spectra were taken on a Nicolet Magenta 550 FT IR spectrometer.

3.2. Plant material

Maerua oblongifolia (Forssk.) A. Rich. (family Capparaceae) was collected in September 1997 from the campus of King Abdulaziz University, Jeddah, K.S.A., and identified by Professor Dr. Abdulaziz Faied, Botany Department, Faculty of Science, King Abdulaziz University. The aerial parts of the plant were dried in an electric oven at 40°C for 3 days and ground using an electrical mill.

3.3. Processing of the plant material

The dried, ground aerial parts (1400 g) of *Maerua oblongifolia* were extracted by soaking at room temp. in petrol–Et_2O–MeOH (1:1:1) for 24 h. The crude extract (75 g) was defatted using cold MeOH, giving the defatted extract.

Table 4
NOE effects, from NOESY spectrum of compound **5**

H-irradiated	H-affected
H-29	18, 22, 30
H-30	18, 22, 29
H-3	5, 23, 1α
H-19	28, 30, 29
H-21β	28
H-5	23, 9, 7α, 6α, 3
H-24	6β, 2β
H-28	13, 21β, 19
H-25	11β, 6β
H-27	7α
H-23	3
H-26	13

3.4. Separation of the compounds

The defatted extract (38 g) was chromatographed on a silica gel column into 3 fractions. Fraction I (90 mg, eluted with petrol–Et_2O, 3:1) afforded by GC/MS **1** (8.3%, R_t 12.54 min), methyl palmitate (10.8%, R_t 13.44 min), methyl linoleate (15.0%, R_t 15.22 min), methyl oleate (25.0%, R_t 15.29 min) and methyl stearate (16.7%, R_t 15.56 min). Fraction II was eluted as two successive subfractions IIa (20 mg) and IIb (50 mg) by the eluent petrol–Et_2O (1:1). Fraction IIa afforded by GC/MS palmitic acid (4.7%, R_t 13.66 min), palmitic acid (41.1%, R_t 13.94 min), methyl oleate (1.4%, R_t 15.29 min) and phytol (**2**) (12.3%, R_t 15.42 min). Fraction IIb gave on Sephadex LH20 CC (eluted with $CHCl_3$–MeOH 1:1) a mixture 9:3:4:2 of β-sitosterol, stigmasterol, betulin (**3**) and betulinaldehyde (**4**). Fraction III (1.26 g, eluted with Et_2O) gave by washing with Et_2O the triterpenoid **5** (700 mg) as a white solid insoluble in both Et_2O and MeOH, but soluble in $CHCl_3$.

3.5. Lup-20(29)-en-3β,30-diol (5)

White crystals ($CHCl_3$); m.p. 230–232°C; IR, $\nu_{max}^{CHCl_3}$,

Table 3
The important correlations of compound **5** in HMBC spectrum

H-atom	Correlated with C-atom (J)	H-atom	Correlated with C-atom (J)
H-29	30 (^3J), 19 (^3J).	H-23	24 (^3J), 3 (^3J), 5 (^3J).
H-30	20 (^2J), 29 (^3J).	H-27	8 (^3J), 14 (^2J), 13 (^3J).
H-3	23 (^3J), 24 (^3J).	H-25	5 (^3J), 9 (^3J), 1 (^3J).
H-19	20 (^2J), 29 (^3J).	H-28	22 (^3J), 16 (^3J), 17 (^2J).
H-26	9 (^3J), 14 (^3J), 7 (^3J).	H-24	23 (^3J), 5 (^3J), 3 (^3J).

cm^{-1}: 3361.8 (OH), 2938.8 and 2859.0 (str. CH, CH_2, CH_3), 1454.6, 1383.7 and 1045.3; ^{1}H NMR: Table 1; ^{13}C NMR: (Table 2); HMBC data: (Table 3); NOESY data: (Table 4); MS, *m*/*z* (rel. int.): 442 $[M]^+$ (8.5) (corresponding to $C_{30}H_{50}O_2$), 424 $[M-H_2O]^+$ (8.5), 405 (12.7), 385 (12.8), 341 (17.6), 328 (19.7), 308 (17.6), 295 (26.1), 287 (18.3), 268 (100), 257 (44.4), 246 (21.8), 232 (21.1), 213 (66.0), 196 (50.7), 180 (83.1), 138 (75.4), 111 (71.8), 85 (64.8), 73 (28.9), 64 (59.9).

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