

## A New Pimarane Diterpenoid from *Acacia raddiana*

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**ABSTRACT.** The extract of the stem bark of *Acacia raddiana* (family Leguminosae) afforded the known compounds: lupeol, betulin, betulinaldehyde, betulinic acid, oleanolic acid,  $\beta$ -sitosterol, stigmasterol and protocatechuic aldehyde, as well as a new diterpenoid, which was identified as  $3\beta$ ,  $11\beta$ -dihydroxy-8(14), 15-pimaradiene on the basis of spectral data.

### Introduction

The genus *Acacia* is very large. It has many complex botanical problems of nomenclature and classification<sup>[1]</sup>. Several papers have been published on gums from the genus *Acacia*; possibly because of the traditional use of "Arabic gum" as an article of commerce<sup>[2]</sup>. *Acacia raddiana* is a medicinal plant<sup>[3]</sup>, which has been investigated phytochemically only for polyphenols<sup>[4]</sup>. We now report the isolation and structure elucidation of a new pimarane diterpenoid, together with eight known compounds.

### Results and Discussion

Chromatographic separation of the extract of the stem bark of *Acacia raddiana* gave the known compounds: lupeol **1**<sup>[5]</sup>, betulin **2**<sup>[6]</sup>, betulinaldehyde **3**<sup>[7]</sup>, betulinic acid **4**<sup>[7]</sup>, oleanolic acid **5**<sup>[8]</sup>,  $\beta$ -sitosterol<sup>[5]</sup>, stigmasterol<sup>[5]</sup> and protocatechuic aldehyde<sup>[9]</sup>, as well as a new diterpenoid, which was identified as  $3\beta$ - $11\beta$ -dihydroxy-8(14),15-pimaradiene **6** on the basis of spectral data.

The known compounds were identified by spectral methods and their structures were confirmed by comparing with authentic spectra and/or literature spectral data.

Compound **6** gave a molecular ion peak  $[M]^+$  at  $m/z$  304 due to  $C_{20}H_{32}O_2$ . The MS spectrum showed fragment peaks at  $m/z$  287 due to loss of 17 amu from  $[M]^+$ , at  $m/z$

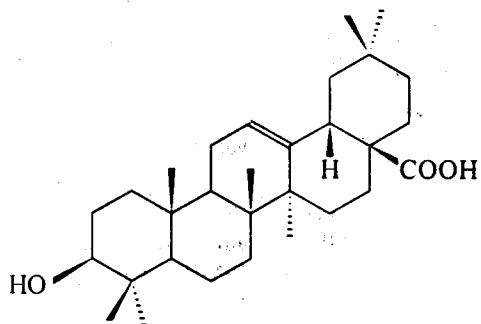
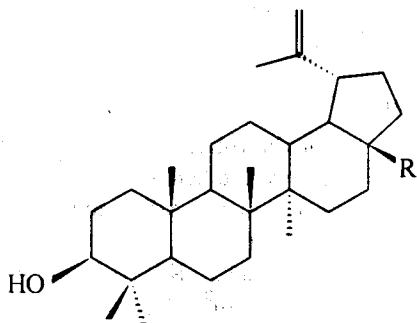
271 due to loss of  $\text{CH}_3$  and 18 amu from  $[\text{M}]^+$ , and at  $m/z$  253 due to loss of 18 amu from 271. This indicated that the oxygen functions are more likely to be two hydroxyl groups. This was in agreement with the IR spectrum, which showed a free hydroxyl absorption band at  $3391\text{ cm}^{-1}$ .

$^1\text{H-NMR}$  spectrum (Table 1) showed a diterpenoid pattern of signals with four tertiary methyl singlets in the up-field [at  $\delta$  1.21, 1.20, 1.00 and 0.96] as well as four olefinic proton signals in the down-field, three of them were assigned to a vinyl group [ $\delta$  5.93 *dd* ( $J = 10, 16\text{ Hz}$ ), 5.07 *dd* ( $J = 16, 2\text{ Hz}$ ), 5.05 *dd* ( $J = 10, 2\text{ Hz}$ )] and the fourth one was a singlet at  $\delta$  5.44 indicated a trisubstituted double bond. This was found in agreement with a pimara-8(14), 15-diene<sup>[10]</sup> carbon skeleton. The proton spectrum also showed two signals of protons geminal to secondary hydroxyl groups at  $\delta$  3.64 and 3.98 ppm. The first signal at  $\delta$  3.64 appeared as a quartet with coupling of 7.3 Hz. This is a special case of three-fold doublet with equal couplings of 7.3 Hz in coincidence with an equatorial proton either at C-6 or at C-11, geminal to the second hydroxyl group. The presence of a double of doublet at  $\delta$  2.00 with couplings of 7.3 and 1 Hz, assigned to the axial H-9 ( $J_{9a, 11e} = 7.3$ ;  $J_{9a, 14} = 1\text{ Hz}$ ), suggested the location of this hydroxyl group at C-11 in the axial orientation. The molecular model showed approximately equal dihedral angles between  $\text{H}_{11e}, \text{H}_{12a}$ ;  $\text{H}_{11e}, \text{H}_{12e}$  and  $\text{H}_{11e}, \text{H}_{9a}$ , in agreement with the observed equal couplings of 7.3 Hz. The second one (at  $\delta$  3.98) appeared as a double of doublet with couplings of 9 and 6 Hz, suggesting the location of the hydroxyl group between a tetrasubstituted  $\text{SP}^3$  carbon atom and a methylene group as C-1 or C-3. The chemical shifts of the C-18, C-19 and C-4 carbons of **6** were in good agreement with  $3\beta$ -hydroxy derivatives<sup>[11]</sup>.

TABLE 1  $^1\text{H-NMR}$  data of compound **6** [ $\delta$  value, multiplicity (J Hz),  $\text{CDCl}_3$ , 400 MHz].

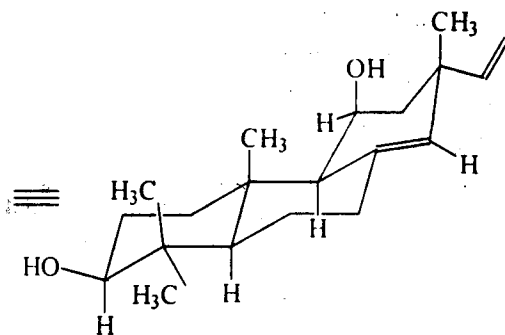
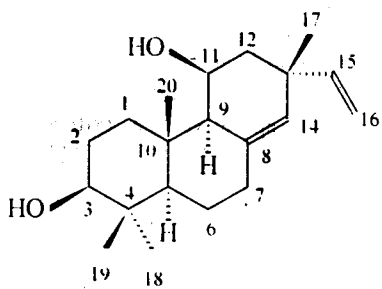
H	<b>6</b>
1	3.98 <i>dd</i> (9,6)
7 $\alpha$	2.18 <i>ddd</i> (12,11,7)
7 $\beta$	2.40 <i>ddd</i> (12,12,8)
9	2.00 <i>dd</i> (7.3,1)
11	3.64 <i>q</i> (7.3)
14	5.44 <i>s</i>
15	5.93 <i>dd</i> (10,16)
16	5.05 <i>dd</i> (10,2)
16'	5.07 <i>dd</i> (16,2)
17	1.21 <i>s</i>
18	1.20 <i>s</i>
19	0.96 <i>s</i>
20	1.00 <i>s</i>
OH	4.01 <i>s</i>

The close coincidence in  $\delta$  values in  $^{13}\text{C-NMR}$  between ring C carbon atoms of both **6** and **7**<sup>[12]</sup>, especially those of C-12, C-13, C-15, C-16 and C-17, revealed the same stereochemistry at C-13. Thus, compound **6** was identified as  $3\beta$ -dihydroxy-8(14), 15-pimaradiene.

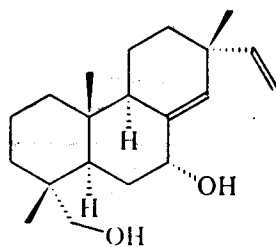


1. R = CH<sub>3</sub>
2. R = CH<sub>2</sub>OH
3. R = CHO
4. R = COOH

5



6



7

A number of diterpenoids have been isolated from a few *Acacia* species. Two casane diterpenoids were isolated from the roots of *A. jacquemontii*<sup>[13]</sup>. The root bark of *A. leucophloea* yielded three pimarane diterpenoids<sup>[10,14]</sup>.

### Experimental

The plant material was collected in December 1991 at Cairo-Suez desert road and identified by the third author. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were taken at 400 and 100 MHz, respectively, on a Bruker DPX 400 FT NMR spectrometer. MS spectra were taken on GC/MS Shimadzu with glass capillary column and EI 70 eV. Both NMR and MS spectrometers at MFMRC, King Abdulaziz University, Jeddah, K.S.A. IR spectra were measured on Magenta 550 FT IR spectrometer at Faculty of Science, King Abdulaziz University.

The stem bark of *Acacia raddiana* (770 g) was extracted by soaking at room temperature in a mixture of pet.ether-ether-MeOH (1:1:1) for 24 hours. The extract was defatted using cold MeOH giving 14,83 g defatted material, which was fractionated by silica gel CC into three main fractions. Fraction I (800 mg, eluted from the column by pet.ether-ether 9:1) afforded, 200 mg of which, by preparative TLC (silica gel, pet.ether-ether 4:1) lupeol **1** (60 mg, R<sub>f</sub> 0.32) and betulinaldehyde **3** (32 mg, R<sub>f</sub> 0.25). Fraction II (2.2 g, eluted from the column by pet.ether-ether 1:1) was separated, 200 mg of which, by preparative TLC (silica gel, pet.ether-ether 3:2) into two bands at R<sub>f</sub> values of 0.38 and 0.33. The first band was proved to be a mixture of β-sitosterol, stigmasterol and protocatechuic aldehyde (25 mg, 1:1:2). The second band was found to contain betulin **2** together with protocatechuic aldehyde (37 mg, 1:2). Fraction III (4g, eluted from the column by ether) gave, 250 mg of which, by preparative TLC (silica gel, pet.ether-ether 1:4) a mixture of betulinic acid **4** and oleanolic acid **5** at R<sub>f</sub> 0.46 (41 mg, 1:1) and the new diterpenoid **6** (28 mg, R<sub>f</sub> 0.37).

#### 3-β, 11β-dihydroxy-8(14), 15-pimaradiene **6**.

Yellowish gum; IR  $\nu_{\max}^{\text{CHCl}_3}$  cm<sup>-1</sup> : 3391 (OH), 2935 (CH str.), 2872 (C = C-H str.), 1635 (C = C), 1559, 1383, 1223, 1045, 999, 911, 758; MS, m/z (rel. int.) : 304 [M]<sup>+</sup> (4%), 287 [M-OH]<sup>+</sup> (32%), 271 [M-Me-H<sub>2</sub>O]<sup>+</sup> (27%), 253 [271-H<sub>2</sub>O]<sup>+</sup> (27%), 228 (15%), 213 (20%), 200 (49.5%), 189 (100%), 171 (24%), 119 (24%), 105 (40%), 79 (51%), 55 (90%); <sup>1</sup>H-NMR : Table 1; <sup>13</sup>C-NMR : Table 2.

TABLE 2. <sup>13</sup>C-NMR data of compounds **6** (δ values, multiplicity<sup>#</sup>, CDCl<sub>3</sub>, 100 MHz), and **7**<sup>▼</sup>

Carbon No.	<b>6</b>	<b>7</b>
1	30.4 t	38.76
2	22.2 t	18.38
3	77.0 d	35.21
4	39.1 s	37.79
5	43.0 d	39.56
6	18.2 t	28.74
7	35.6 t	73.34
8	13.7 s	139.40

TABLE 2. Contd

Carbon No.	6	7
9	47.7 <i>d</i>	46.32
10	42.0 <i>s</i>	38.30
11	73.0 <i>d</i>	18.38
12	34.9 <i>t</i>	34.35
13	37.6 <i>s</i>	37.59
14	129.5 <i>d</i>	134.14
15	148.5 <i>d</i>	148.38
16	110.5 <i>t</i>	110.67
17	25.7 <i>q</i>	25.78
18	28.2 <i>q</i>	70.98
19	15.5 <i>q</i>	18.07
20	15.0 <i>q</i>	14.86

\*The multiplicity was concluded from off-resonance  $^{13}\text{C}$ -NMR experiment.

▼from reference [12].

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## ترين ثنائي جديد من نوع اليماران من نبات الطلح «أكاشيا راديانا»

مدوح عبد المجيب، وصالح بن طاهر إزمري و مها محمد عبد المنعم الشامي\*  
 قسم الكيمياء، كلية العلوم، جامعة الملك عبد العزيز، جدة - المملكة العربية السعودية  
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المستخلص . من مستخلص لحاء ساق نبات الطلح «أكاشيا راديانا» تم فصل ثمانية منتجات طبيعية معروفة وهي : ليوبول ، بتيولين ، بتيولين ألدهيد ، حامض بتولينك ، حامض أوليانوليك ، بيتا سيتو استيرول ، إستجما استيرول وبروتاكاتشويك ألدهيد بالإضافة إلى ترين ثنائي جديد عُرف ٣-بيتا ، ١١-بيتا-ثنائي هيدروكسي-٨(١٤)، ١٥-بيماراديين بناءً على القياسات الطيفية .