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DAMMARANE SAPONINS FROM *ZIZYPHUS LOTUS*

JEAN-HUGUES RENAULT, KAMEL GHEDIRA,* PHILIPPE THEPENIER, CATHERINE LAVAUD, MONIQUE ZECHES-HANROT† and LOUISETTE LE MEN-OLIVIER

Faculté de Pharmacie (URA au CNRS 492), 51, rue Cognacq-Jay, 51096 Reims Cedex, France; *Faculté de Monastir, rue Avicenne, 5000 Monastir, Tunisia

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Key Word Index—*Zizyphus lotus*; Rhamnaceae; root bark; dammarane saponins; jujubosides A and C; lotosides I and II.

Abstract—Four dammarane-type saponins were isolated by means of centrifugal partition chromatography from the root bark of *Zizyphus lotus*. Their structures were elucidated using a combination of 1D and 2D ^{1}H and ^{13}C NMR spectra and mass spectroscopy. One of these glycosides is the known jujuboside A. The others are three new dammarane saponins, identified as 3-*O*-*β*-D-glucopyranosyl(1 → 6)-*β*-D-glucopyranosyl (1 → 3)-[α-L-rhamnopyranosyl(1 → 2)]-α-L-arabinopyranosyl jujubogenin = jujuboside C, 3-*O*-α-L-rhamnopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)]-*β*-D-galactopyranosyl lotogenin = lotoside I, and 3-*O*-α-L-rhamnopyranosyl(1 → 2)-[*β*-D-glucopyranosyl(1 → 3)]-*β*-D-glucopyranosyl lotogenin = lotoside II. Lotogenin is a new dammarane derivative identified as (15*R*, 16*R*, 20*R*, 22*R*)-16*β*,22-epoxydammar-24-ene-3*β*,15α,16α,20*β*-tetraol. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

Plants of the *Zizyphus* genus are often used in folk medicine. Chemical analysis of these species has led to the isolation of several cyclopeptide alkaloids with antibacterial and antifungal activities [1, 2] and also of dammarane-type glycosides, which are sweetness inhibitors [3–5]. In the framework of a collaborative research programme on medicinal plants of Tunisia, we have previously studied the alkaloidal content of the root bark of *Z. lotus* (L.) Desf., which is used as an antidiabetic in traditional medicine. This study resulted in the isolation of a series of six new cyclopeptides: lotusines A–F [6, 7]. The present paper reports an investigation of the polar extract of the same vegetal material from which four dammarane saponins, three of which being new, were isolated by means of centrifugal partition chromatography (CPC). Structural elucidation of these compounds was mainly based on NMR data [8].

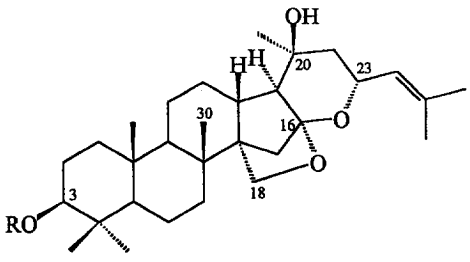
RESULTS AND DISCUSSION

The root bark of *Z. lotus* was extracted successively with hexane, chloroform and methanol. A crude saponin mixture was obtained from the methanol extract by precipitation with acetone. After dialysis against pure water, the extract was fractionated by chromatography on a silica gel column. One of the fractions was purified by CPC to afford four pure compounds: the known jujuboside A (**1**) and three new saponins named jujuboside C (**2**), lotoside I (**3**) and lotoside II (**4**). This liquid–liquid chromatographic method is derived from DCCC, previously used for the separation of several saponins from *Z. jujuba* [9]. The ternary biphasic solvent system ethyl acetate–*n*-butanol–water was selected as the most appropriate for running a gradient in the normal phase mode (ascending mode) [10]. This was a method successfully used in the laboratory for saponins isolation [11]. Part of the effluent was monitored with an evaporative light scattering detector (ELSD), which is a convenient method for the detection of compounds with a chromophore of weak intensity [11]. In this way, the four saponins **1**, **2**, **3** and **4** were obtained in one CPC run, in a pure state. Their structures were assigned as shown.

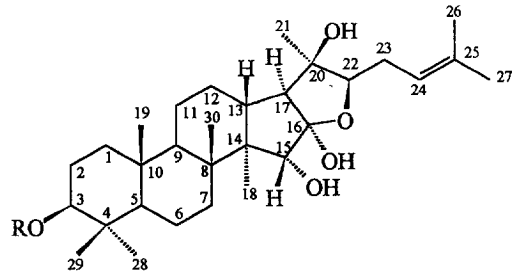
Compound **1** was identified as jujuboside A, previously isolated from *Z. jujuba* [9, 12, 13]. Its positive-ion FAB mass spectrum showed a quasimolecular ion peak at *m/z* 1229 $[M+Na]^+$, $C_{58}H_{94}O_{26}Na$. The NMR data (Tables 1 and 2) were in full agreement with those described for jujuboside A and jujubogenin [5, 12].

Compound **2** was isolated as an amorphous powder. Its positive-ion FAB mass spectrum exhibited a quasimolecular peak at *m/z* 1097 $[M+Na]^+$, $C_{53}H_{86}O_{22}Na$. A positive fragment ion at *m/z* 949 cor-

†Author to whom correspondence should be addressed.

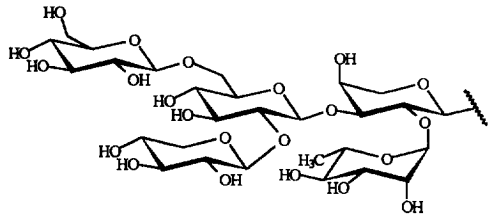


Jujubogenin R = H

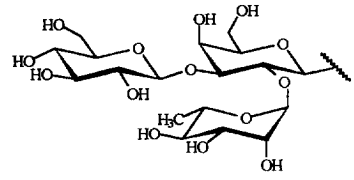


Lotogenin R = H

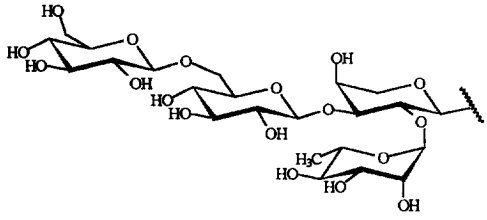
• Jujuboside A (**1**)
R =



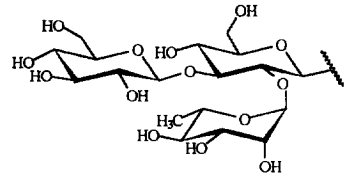
• Lotoside I (**3**)
R =



• Jujuboside C (**2**)
R =



• Lotoside II (**4**)
R =



responded to the loss of a terminal desoxyhexose and the one at *m/z* 455 to the aglycone moiety. The ^{1}H and ^{13}C NMR chemical shifts of the aglycone moieties of **1** and **2** were almost superimposable. So, the genin structure was assigned as jujubogenin on the basis of ^{1}H and ^{13}C NMR spectra and homo- and heteronuclear correlations observed in ^{1}H–^{1}H COSY, HMQC and HMBC experiments. Most of the ^{13}C NMR signals were assigned through $^{2}J_{H\text{-}C}$ and $^{3}J_{H\text{-}C}$ couplings of the seven methyls and are in agreement with literature data [3, 5, 14, 15] (Table 1). In the ROESY spectrum of **2** the correlations observed between H-13 and CH_3-30 confirmed a β-orientation of H-13 (Fig. 1). ROE correlations between H-17 and Me-21 and the coupling constant between H-13 and H-17 ($J_{13\text{-}17} = 7$ Hz) are in agreement with the α-orientation of H-17 and Me-21 [13]. The configuration at C-23 was deduced from the coupling constant between H-23 and H-22α ($J = 10$ Hz).

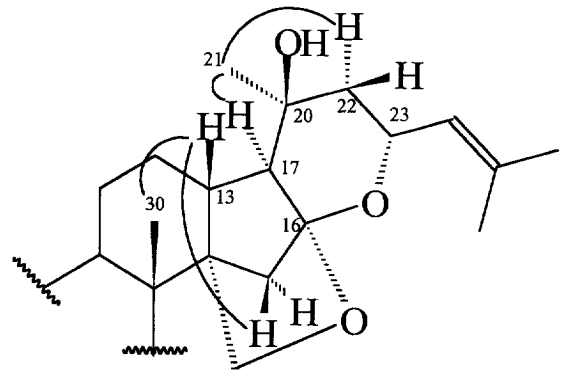


Fig. 1. Most significant correlations from the ROESY experiment for compound **2**.

The presence of a four-sugar residue followed from the observation of four anomeric carbons at δ 105.3, 104.8, 104.2 and 102.0 which are, respectively, bound

to anomeric protons at δ 4.45 (*d*, $J = 5$ Hz), 4.34 (*d*, $J = 8$ Hz), 4.49 (*d*, $J = 7.5$ Hz) and 5.20 (*d*, $J = 1.5$ Hz) according to the HMQC spectrum. Identification of the sugars was done by means of a ^1H–^1H COSY experiment and by comparison with the NMR data for **1** (Tables 1 and 2). These data also showed that **2** corresponded to **1** without the terminal β-D-xylose. The absence of a sugar on the inner glucose C-2 in **2** shifted this carbon and its attached proton ($\Delta\delta_C = -7.5$ ppm and $\Delta\delta_H = -0.24$ ppm) upfield. Observations of ROE correlation between H-3 of the genin and H-1 of the arabinose, and of HMBC correlation between C-3 of the genin and H-1 of the arabinose, confirmed the attachment of the sugar chain on position C-3 of jujubogenin. Sequencing of the sugar chain was confirmed by ROESY and HMBC experiments. In the ROESY spectrum, through-space interactions across glycosidic bonds were observed between H-1 of the inner glucose and H-3 of arabinose, between H-1 of rhamnose and H-2 of arabinose and between H-1 of the terminal glucose and H-6 of the inner glucose. Moreover, in the HMBC spectrum, intense long-range correlations between H-1 of the inner glucose and C-3 of the arabinose, between H-1 of rhamnose and C-2 of arabinose and between H-1 of the terminal glucose and H-6 of the inner glucose were also observed. Thus, **2** is 3-*O*-β-D-glucopyranosyl(1 → 6)-β-D-glucopyranosyl(1 → 3)-[α-L-rhamnopyranosyl (1 → 2)]-α-L-arabinopyranosyl jujubogenin.

Compound **3** was obtained as a white amorphous powder. Its positive-ion FAB mass spectrum exhibited a quasimolecular ion peak at *m/z* 968.2 $[M + Li]^+$, $C_{48}H_{80}O_{19}Li$. The ^{13}C NMR spectrum showed 18 signals for three hexosyl moieties and 30 signals for an aglycone moiety. *J*-modulated ^{13}C and HMQC spectra revealed that these 30 carbons consisted of eight methyls, seven methylenes, eight methines and seven quaternary carbons, indicating a genin different from jujubogenin. A combination of the ^1H, ^{13}C, COSY, HMQC, HMBC and ROESY experiments allowed full assignment of the sugar moieties. The presence of three sugar residues was established by the observation of anomeric carbons at δ 105.9, 105.3 and

Table 1. ^{13}C NMR spectral data for compounds **1**–**4** (in CD_3OD; 75 MHz; δ-ppm)

C*	1	2	3	4	C	1	2	3	4
1	39.9	40.0	40.8	40.8		α-L-Ara	α-L-Ara	β-D-Gal	β-D-Glu (inner)
2	27.2	27.3	27.5	27.4	1	104.8	105.3	105.9	105.4
3	89.8	89.6	90.0	90.0	2	76.0	75.5	75.3	77.7
4	40.5	40.5	40.5	40.5	3	82.2	82.8	86.0	88.7
5	57.5	57.5	58.0	57.9	4	68.8	68.6	70.0	70.2
6	19.0	19.1	19.3	19.1	5	63.8	65.0	75.8	78.4
7	36.9	36.9	37.0	37.1	6			62.3	62.6
8	38.3	38.3	42.3	42.3		α-L-Rha	α-L-Rha	α-L-Rha	α-L-Rha
9	54.1	54.2	52.4	52.4	1	101.7	102.0	101.4	101.8
10	38.5	38.5	38.2	38.2	2	72.1	72.1	72.1	72.2
11	22.5	22.5	22.4	22.4	3	72.1	72.1	72.1	72.2
12	30.5	30.2	27.0	27.0	4	73.9	73.8	73.9	73.8
13	38.0	38.0	36.9	36.9	5	70.4	69.7	70.1	70.2
14	54.6	54.6	53.8	54.0	6	18.0	18.0	18.0	18.0
15	37.1	37.1	77.6	77.4		β-D-Glu (inner)	β-D-Glu (inner)	β-D-Glu	β-D-Glu
16	111.6	111.4	111.0	111.0	1	103.6	104.2	105.3	104
17	54.3	54.4	63.5	63.5	2	82.6	75.1	75.2	75.3
18	66.8	66.8	9.9	9.9	3	77.8	78.0	78.3	78.0
19	16.9	17.1	17.2	17.2	4	71.5	71.6	71.1	72.2
20	69.8	70.2	79.0	78.8	5	76.7	77.0	78.0	78.2
21	29.6	29.6	26.7	26.7	6	70.2	69.4	62.3	62.7
22	45.3	45.4	89.5	89.5		β-D-Glu	β-D-Glu		
23	70.2	69.7	28.2	28.2	1	104.9	104.8		
24	126.3	126.3	122.7	122.7	2	75.0	75.0		
25	136.7	136.7	133.5	133.4	3	77.9	78.0		
26	25.8	25.7	26.0	25.9	4	71.7	71.6		
27	18.4	18.4	18	18	5	78.0	78.0		
28	28.6	28.5	28.3	28.3	6	62.7	62.7		
29	17.2	17.1	17.0	17.0		β-D-Xyl			
30	19.2	19.2	16.6	16.6	1	105.8			
					2	75.7			
					3	78.1			
					4	70.9			
					5	67.6			

*C numeration according to ref. [16].

Table 2. ^{1}H NMR spectral data for sugar moieties of compounds **1**–**4** [in CD_3OD, 300 MHz δ ppm, J (Hz)]

H	**1**	**2**	**3**	**4**
	α-L-Arabinose	α-L-Arabinose	β-D-Galactose	β-D-Glucose (inner)
1	4.49 (*d*, 4)	4.45 (*d*, 5)	4.40 (*d*, 7.5)	4.44 (*d*, 7.5)
2	3.96 (*m*)	3.87 (*m*)	3.83 (*dd*, 9, 7.5)	3.57 (*dd*, 8, 7.5)
3	3.93 (*m*)	3.83 (*m*)	3.75 (*dd*, 9, 2.5)	3.71 (*dd*, 9, 8)
4	3.93 (*m*)	4.08 (*dd*, 4, 2)	4.11 (*br d*, 3)	3.47 (*dd*, 10, 9)
5	3.50 (*br d*, 10)	3.52 (*d*, 10)	3.51 (*br t*, 6)	3.29 (*m*)
	3.85 (*dd*, 10, 5)	3.85 (*dd*, 10, 3)		
6			3.72 (*m*)	3.68 (11.5, 5.5)
				3.85 (11.5, 2.5)
	α-L-Rhamnose	α-L-Rhamnose	α-L-Rhamnose	α-L-Rhamnose
1	5.13 (*br s*)	5.20 (*d*, 1.5)	5.38 (*d*, 1.5)	5.44 (*d*, 1.5)
2	3.89 (*dd*, 3, 1)	3.92 (*dd*, 3.5, 1.5)	3.95 (*dd*, 3.5, 1.5)	3.97 (*dd*, 3.5, 1.5)
3	3.67 (*dd*, 9, 3)	3.71 (*dd*, 9.5, 3.5)	3.75 (*dd*, 9.5, 3.5)	3.73 (*dd*, 9.5, 3.5)
4	3.39 (*t*, 9)	3.38 (*t*, 9.5)	3.38 (*t*, 9.5)	3.39 (*t*, 9.5)
5	3.82 (*m*)	3.85 (*m*)	4.00 (*dq*, 9.5, 6.5)	4.00 (*dq*, 9.5, 6)
6	1.22 (*d*, 6)	1.20 (*d*, 6)	1.21 (*d*, 6.5)	1.22 (*d*, 6)
	β-D-Glucose (inner)	β-D-Glucose (inner)	β-D-Glucose	β-D-Glucose
1	4.58 (*d*, 7)	4.49 (*d*, 7.5)	4.50 (*d*, 7.3)	4.52 (*d*, 8)
2	3.52 (*m*)	3.28 (*dd*, 9, 7)	3.28 (*t*, 8)	3.25 (*dd*, 9.5, 8)
3	3.35 (*m*)	3.38 (*m*)	3.34 (*m*)	3.38 (*t*, 9.5)
4	3.35 (*m*)	3.30 (*t*, nd)	3.31 (*m*)	3.30 (*m*)
5	3.55 (*m*)	3.52 (*m*)	3.30 (*m*)	3.35 (*m*)
6	3.63 (*dd*, 10, 7)	3.73 (*dd*, 11, 7)	3.67 (*dd*, 12, 4.5)	3.62 (*dd*, 11.5, 6)
	4.20 (*d*, 10)	4.14 (*dd*, 11, 1.5)	3.84 (*dd*, 12, 2)	3.90 (*dd*, 11.5, 2)
	β-D-Glucose	β-D-Glucose		
1	4.30 (*dd*, 9, 7.5)	4.34 (*d*, 8)		
2	3.21 (*t*, nd)	3.19 (*dd*, 9, 8)		
3	3.33 (*m*)	3.35, (*m*)		
4	3.29 (*m*)	3.35, (*m*)		
5	3.28 (*m*)	3.27 (*m*)		
6	3.54 (*dd*, 12, 5)	3.65 (*dd*, 11, 5)		
	3.86 (*d*, 12.5)	3.85 (*d*, 11)		
	β-D-Xylose			
1	4.68 (*d*, 7)			
2	3.34 (*m*)			
3	3.60 (*m*)			
4	3.52 (*m*)			
5	3.95 (*dd*, 11, 5)			
	3.23 (*t*, 11)			

101.4, corresponding to attached protons at δ 4.40 (*d*, J = 7.5 Hz), 4.50 (*d*, J = 7.3 Hz) and 5.38 (*d*, J = 1.5 Hz), respectively. Evaluation of spin–spin couplings and chemical shifts allowed identification of one α-L-rhamnose, one β-D-glucose and one β-D-galactose (Table 2).

Sequencing of the osidic chain was performed using ROESY and HMBC experiments. Observation of an Overhauser effect in the ROESY spectrum between H-3 of the genin and H-1 of the galactose, as well as strong correlation in the HMBC spectrum between C-1 of galactose and H-3 of the aglycone, confirmed the attachment of the sugar chain to C-3 of the genin. The HMBC spectrum also exhibited intense long-range correlations between H-1 of the rhamnose and C-2 of the galactose and between H-1 of the glucose and C-3 of the galactose. In addition, ROESY correlations were observed between H-1 of the rhamnose and H-2 of the galactose at δ 3.83 and between H-1 of the glucose and the H-3 of the galactose at δ 3.75. Thus, compound **3** is a 3-*O*-α-L-rhamnopyranosyl(1 → 2)-[β-D-glucopyranosyl(1 → 3)]-β-D-galactopyranosyl derivative.

Comparison of the ^{13}C NMR spectrum of **3** with those of **1** and **2** showed general good agreement, except for the signals pertaining to the D-ring and the side chain (C-20 to C-27). The signals at δ 133.5 (C), 122.7 (CH), 111.0 (C), 89.5 (CH), 90.0 (CH), 79.0 (C) and 77.6 (CH) were assigned to a double bond, a ketal carbon and four carbons bearing oxygen functions, respectively. Most of the ^{13}C NMR signals of the aglycone were attributed through two- and three-bonds ^{1}H–^{13}C couplings from the eight methyls observed in the HMBC spectrum. The ^{1}H–^{1}H cor-

relations observed in the COSY spectrum allowed determination of the side chain sequence. The vinyl proton H-24 at δ 5.21 (*br t*, $J = 6.5$ Hz) showed long-range couplings with the two terminal vinyl methyls at δ 1.66 (*br s*) and 1.62 (*br s*) and vicinal correlations with the two methylene protons H_s-23 at δ 2.24 (*m*). These methylene protons were coupled with the methine proton H-22 at δ 3.81 (*br t*, $J = 8$ Hz) and with the two vinyl methyls through a long-range coupling. The methine proton H-22 had a correlation with the carbon signal at δ 89.5 in the HMQC spectrum and a $^3J_{H\text{-}C}$ coupling with the methine carbon at δ 122.7 in the HMBC spectrum. These results were consistent with a five-membered ring including C-16, C-17, C-20, C-22 and an oxygen between C-16 and C-22, according to literature data for (20*R*,22*R*)-16β,22:16α,18-diepoxydammar-24-ene-3β,20-diol [5].

The intense correlations observed in the HMBC spectrum between the singlet proton at δ 3.92 (H-15) and carbons at δ 111.0 (C-16), 53.8 (C-14), 42.3 (C-8) and 9.9 (C-18), as well as the direct heteronuclear coupling between this proton and the lowfield carbon at δ 77.6, indicated the presence of a hydroxyl group at C-15. The relative (and absolute) configurations at C-15, C-16, C-20 and C-22 were assigned on the basis of through-space interactions in the ROESY spectrum (Fig. 2). The configurations of H-13 and Me-18 were assigned to be β and α, respectively, on biogenetic grounds. The ROE effect between Me-18 α and H-17 indicated that H-17 was α (axial). The coupling constant between H-13 and H-17 was largest in this case ($J_{H\text{-}13/H\text{-}17} = 11.5$ Hz) than this one observed for jujubogenin ($J_{H\text{-}13/H\text{-}17} = 9$ Hz and 7 Hz for jujuboside A and C, respectively). This phenomenon was due to modification of the dihedral angle defined by atoms H-13, C-13, C-17 and H-17.

The correlations between Me-21/H-17, H-22, H-23α and between H-15β/Me-30, H-13 in the ROESY experiment indicated the absolute configuration at C-15, C-20 and C-22 to be 15*R*, 20*R* and 22*R*, respectively. The presence of an epimerizable hemiacetal function at C-16 allows a more stable *cis* five-membered ring fusion and, therefore, a C-16*R* configuration. Thus, the genin of **3** is (15*R*,16*R*,20*R*,22*R*)-16β,22-epoxy-dammar-24-ene-3β,15α,16α,20β-tetraol

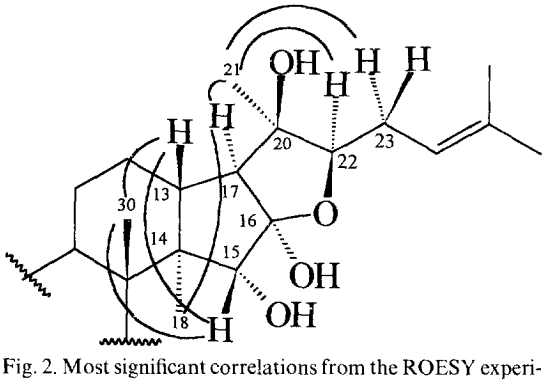


Fig. 2. Most significant correlations from the ROESY experiment for compounds **3** and **4**.

for which the trivial name lotogenin is proposed. Saponin **3** is 3-*O*-α-L-rhamnopyranosyl (1 → 2)-[β-D-glucopyranosyl (1 → 3)]-β-D-galactopyranosyl lotogenin.

Compound **4** was an amorphous powder which showed the same positive quasimolecular ion-peak as **3** at *m/z* 968 $[M+Li]^+$, analysed as $C_{48}H_{80}O_{19}Li$. The ^{13}C NMR spectrum of **4** was almost superimposable on that of **3**, except for the sugar moieties. These data suggested that **4** and **3** possessed the same aglycone. The ^1H, ^{13}C and ^1H–^1H COSY spectra indicated three sugar residues containing two β-D-glucoses and one α-L-rhamnose (Tables 1 and 2). The ^1H and ^{13}C chemical shifts for terminal rhamnose and terminal glucose were very close to those found for saponin **3** (Tables 1 and 2). Moreover, the β-D-galactopyranosyl unit in **3** has been replaced by a β-D-glucopyranosyl unit in **4**. The sugar sequence was confirmed by HMBC and ROESY experiments as in **3**. The anomeric protons at δ 4.52 (terminal glucose) and 5.44 (terminal rhamnose) showed long-range heteronuclear correlations with the carbons of inner glucose at δ 88.7 (C-3) and 77.7 (C-2), respectively. In addition, there were ROE effects between H-1 of the terminal glucose and H-3 of the inner glucose and between H-1 of the rhamnose and H-2 of the inner glucose. Consequently, compound **4** is 3-*O*-α-L-rhamnopyranosyl (1 → 2)-[β-D-glucopyranosyl (1 → 3)]-β-D-glucopyranosyl lotogenin (lotoside II).

Two points in this study must be emphasized. Firstly, CPC using linear gradient elution is confirmed to be a good technique for the isolation of polar compounds like saponins. Secondly, the isolation of saponins from a plant of the *Zizyphus* genus is not surprising, but it is remarkable to find a genin with a new skeleton such as lotogenin.

EXPERIMENTAL

General. ^1H and ^{13}C NMR were recorded at 300 and 75 MHz, respectively. 2D experiments were performed using standard Bruker microprograms. ROESY experiments were performed with a single long pulse of 200 msec. Positive FAB-MS was measured on a VG instrument type Autospec mass spectrometer. The CPC apparatus was a HPCPC Sanki Series fitted with a column presenting a total int. vol. of 240 ml. Detection was monitored by an ELSD Varex type ELSD II A.

Plant material. Root bark of *Z. lotus* was collected in March 1994 at the locality of Cherahil near Monastir, in Tunisia, and identified by Prof. Nabli, University of Tunis. A voucher specimen is deposited at the Herbarium of the Department of Pharmacognosy, Faculty of Pharmacy, Monastir.

Extraction and isolation. Dried, powdered root bark (400 g) was extracted in a Soxhlet apparatus with 3.9 l hexane and then with 3.2 l $CHCl_3$. The air-dried plant was macerated in 4.5 l MeOH, for 48 hr, at room temp. After evapn of MeOH, 73 g syrupy residue was obtained. Part of this residue (70 g) was dissolved in

MeOH (200 ml) and then 1.25 l Me_2CO was added. The ppt was recovered by filtration, dried and suspended in 200 ml MeOH. Insoluble material was collected by centrifugation, then dried under red. pres. to afford 7.6 g reddish powder; 5 g of which was dissolved in H_2O and dialysed against H_2O in seamless cellulose tubing. After 3 days, the content of the tube were lyophilized to yield 2 g pale brown powder which was first fractionated by CC on silica gel. Frs of 50 ml were collected by eluting with $CHCl_3$–MeOH–H_2O mixt [60:40:0 (frs 1–8), 60:40:1 (frs 9–13), 30:20:1 (frs 14–29)]. Frs 6–16 contained saponins mixts. Fr. 11 (63 mg) was purified by CPC, using the biphasic ternary system EtOAc–*n*-BuOH–H_2O and a gradient run in normal phase and ascending mode. The composition of the stationary phase was a mixt. of EtOAc–*n*-BuOH–H_2O (1:1:18). The mobile phase corresponded to a linear gradient of EtOAc–*n*-BuOH–H_2O from the initial mobile phase: EtOAc–*n*-BuOH–H_2O (95:1:4) to the final mobile phase: EtOAc–*n*-BuOH–H_2O (20:23:7) with a duration of 4 hr. The flow rate was 4 ml min^{-1} and the rotation speed was 1300 rev min^{-1}, leading to 75% retention of stationary phase in the column and 37 bars of back-pressure. A flow splitter with a restriction was installed at the outlet of the HPCPC, the main line (92% of the flow) going to a fr. collector, the other line (8% of the flow) going to the ELSD. The temp. of the nebulizer was set at 118.5°. The sample was dissolved in 5 ml of stationary phase and injected through a Rheodyne injector with a 5-ml sample loop. 90 frs of 12 ml were obtained and frs 21–29 yielded **4** (4 mg), frs 30–39 yielded **3** (7 mg), frs 45–53 yielded **2** (10 mg) and frs 57–66 yielded **1** (17 mg).

Jujuboside A (**1**). $[\alpha]_D^{20}$ −37 (MeOH; *c* 0.58); positive FAB-MS *m/z*: 1245 $[M+K]^+$, 1229 $[M+Na]^+$; ^1H NMR (CD_3OD): δ0.74 (H-5, *dm*, *J* = 8 Hz), 0.86 (Me-29, *s*), 0.88 (Me-19, *s*), 0.89 (H-9, *m*), 0.93 (H-1, *m*), 1.00 (Me-28, *s*), 1.01 (H-17, *d*, *J* = 9 Hz), 1.13 (Me-30, *s*), 1.13 (Me-21, *s*), 1.15 (H-15, *m*), 1.35 (H-22, *dd*, *J* = 11, 2.5 Hz), 1.50 (H-22′, *m*), 1.50 (H-7, *m*), 1.55 (H-7′, *m*), 1.55 (H-6, *m*), 1.67 (Me-27, *d*, *J* = 1 Hz), 1.68 (H-2, *m*), 1.70 (H-1, *m*), 1.71 (Me-26, *d*, *J* = 1 Hz), 1.81 (H-2′, *m*), 2.05 (H-15, *d*, *J* = 8 Hz), 2.48 (H-13, *m*), 3.05 (H-3, *dd*, *J* = 10, 5 Hz), 3.93 (H-18, *d*, *J* = 7 Hz), 40.2 (H-18′, *m*), 4.67 (H-23, *m*), 5.15 (H-24, *br d*, *J* = 10 Hz); for sugar moiety: Table 2; ^{13}C NMR (CD_3OD): Table 1.

Jujuboside C (**2**). $[\alpha]_D^{20}$ −48 (MeOH; *c* 0.66); positive FAB-MS *m/z* (rel. int.): 1097 $[M+Na]^+$(8), 1096 (15), 949 (7), 455 (100); ^1H NMR (CD_3OD): δ0.73 (H-5, *dm*, *J* = 9 Hz), 0.84 (Me-29 *s*), 0.87 (Me-19, *s*), 0.98 (H-1, *m*), 1.00 (Me-28, *s*), 1.00 (H-17, *d*, *J* = 7 Hz), 1.13 (Me-30, *s*), 1.13 (Me-21, *s*), 1.19 (H-15, *m*), 1.33 (H-22, *m*), 1.44 (H-7, *m*), 1.46 (H-22′, *m*), 1.54 (H-7′, *m*), 1.54 (H-6, *m*), 1.65 (H-2, *m*), 1.67 (Me-27, *d*, *J* = 1 Hz), 1.71 (Me-26, *br s*), 1.82 (H-2′, *m*), 2.05 (H-15, *d*, *J* = 8.5 Hz), 2.48 (H-13, *m*), 3.10 (H-3, *dd*, *J* = 10, 4 Hz), 3.87 (H-18, *d*, *J* = 9 Hz), 4.02 (H-18′, *d*, *J* = 8 Hz), 4.67 (H-23, *ddd*, *J* = 10, 8, 2 Hz), 5.15 (H-24, *dt*, *J* = 8, 1 Hz); for sugar moiety: Table 2; ^{13}C NMR (CD_3OD): Table 1.

Lotoside I (**3**). $[\alpha]_D^{20}$ −6 (MeOH; *c* 0.33); positive FAB-MS (+LiCl) *m/z*: 968.2 $[M+Li]^+$; ^1H NMR (CD_3OD): δ0.74 (H-5, *br d*, *J* = 10 Hz), 0.84 (Me-29 *s*), 0.89 (Me-19, *s*), 0.94 (Me-18, *s*), 1.00 (H-1, *m*), 1.03 (Me-28, *s*), 1.13 (Me-30, *s*), 1.20 (H-6, *m*), 1.24 (Me-21, *s*), 1.30 (H-9, *m*), 1.50 (H-7, *m*), 1.51 (H-6′, *m*), 1.52 (H-7′, *m*), 1.62 (Me-27, *br s*), 1.66 (H-2, *m*), 1.66 (Me-26, *br s*), 1.86 (H-17, *d*, *J* = 11.5 Hz), 1.93 (H-2′, *m*), 2.10 (H-13, *m*), 2.24 (H_s-23, *m*), 3.10 (H-3, *dd*, *J* = 11.5, 4 Hz), 3.81 (H-22, *br t*, *J* = 8 Hz), 3.92 (H-15, *s*), δ5.21 (H-24, *br t*, *J* = 6.5 Hz); for sugar moiety: Table 2; ^{13}C NMR (CD_3OD): Table 1.

Lotoside II (**4**). $[\alpha]_D^{20}$ −8 (MeOH; *c* 0.58); positive FAB-MS (+LiCl) *m/z*: 968 $[M+Li]^+$; ^1H NMR (CD_3OD): δ0.76 (H-5, *br d*, *J* = 11 Hz), 0.85 (Me-29 *s*), 0.89 (Me-19, *s*), 0.94 (Me-18, *s*), 0.97 (H-1, *m*), 1.02 (Me-28, *s*), 1.13 (Me-30, *s*), 1.20 (H-6, *m*), 1.24 (Me-21, *s*), 1.31 (H-9, *m*), 1.50 (H-7, *m*), 1.50 (H-6, *m*), 1.61 (Me-27, *d*, *J* = 1 Hz), 1.65 (Me-26, *d*, *J* = 1 Hz), 1.68 (H-2, *m*), 1.68 (H-12, *m*), 1.88 (H-17, *d*, *J* = 11 Hz), 1.94 (H-2′, *m*), 1.96 (H-12, *m*), 2.05 (H-13, *m*), 2.25 (H_s-23, *m*), 3.19 (H-3, *dd*, *J* = 11.5, 3.5 Hz), 3.79 (H-22, *dt*, *J* = 7, 1.5 Hz), 3.92 (H-15, *s*), 5.21 (H-24, *br t*, *J* = 7 Hz); for sugar moiety: Table 2; ^{13}C NMR (CD_3OD): Table 1.

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