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# Triterpenoidal lupin saponins from the Chilean legume *Lupinus oreophilus* Phil.

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**Abstract**

Two lupin saponins, 3β,21α,22β,24-tetrahydroxyolean-12-en-3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl-21-*O*-α-L-arabinopyranoside and 3β,21α,22β,24-tetrahydroxyolean-12-en-3-*O*-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl-21-*O*-α-L-rhamnopyranoside, along with eight other saponins and one triterpene previously reported from other legumes, were isolated from the aerial parts of *Lupinus oreophilus* collected in northern Chile. The structures of the isolated compounds were established with the help of extensive spectroscopic techniques.


*Keywords:* *Lupinus oreophilus*; Leguminosae; Structure elucidation; Triterpene saponins

## 1. Introduction

Lupins, especially in the Andean region of South America, have been used as a source of protein and oil for a long time. For this reason, they have recently attracted attention as an alternative source of protein for human consumption. A trend that has developed as a result is the promotion of lupin protein extract as a food ingredient. Furthermore, several studies showing the presence of phytates (Trugo et al., 1993), alkaloids (Wink et al., 1995) and saponins (Hudson and El-Difrawi, 1979), among others, in lupins and their possible role as "antinutrients" (Cheeke and Kelly, 1989; Muzquiz et al., 1989; Periago et al., 1997) has lent support to the promotion of the use of lupin protein extract instead of the whole seed as a protein source in the human diet and animal feed. The presence of antinutritional constituents, especially alkaloids, has led to the development of a "sweet" variety of some lupins containing very low levels of alkaloids through breeding experiments.

Though there exist data to show that a few of the compounds identified as being present in lupins may be antinutritional, a detailed investigation showing antinutritional property, if any, at levels naturally found in lupins is generally lacking. In fact, identification of anti-inflammatory (Jang et al., 2002) and cancer chemopreventive (Itoigawa et al., 2000) properties of flavonoids, and the hepatoprotective (Kinjo et al., 1999) effect of saponins and hypoglycemic (Mohamed et al., 1993) properties of alkaloids found in lupins are a few examples that show the potential functional role other constituents of lupins can play if incorporated into the human diet.

As a result, *Lupinus oreophilus* Phil. (Leguminosae), a wild lupin not previously chemically characterized, was selected for investigation as part of the International Cooperative Biodiversity Group (ICBG) program "Bioactive Agents from Dryland Biodiversity of Latin America". Herein we report on the isolation of 11 triterpene derivatives and the structure determination of two novel saponins found in the methanol extract of the aerial part of the plant.

## 2. Results and discussion

The dried and powdered aerial parts of *L. oreophilus*, collected in the district of Arica in northern Chile, was extracted and partitioned as described in the Experimental

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section. Successive chromatography of the *n*-butanol fraction using silica, Sephadex LH-20, centrifugal TLC and reversed phase HPLC afforded compounds **1**–**11**. The structures of these isolated compounds were established through analysis of their NMR, MS and IR spectra, which enabled the characterization of compounds **5** and **11** as novel and compounds **1**–**4** and **6**–**0** as known (Arao et al., 1995; Curl et al., 1988; Jurzysta et al., 1989; Kang et al., 1988; Kitagawa et al., 1983; Mahato, 1991; Mohamed et al., 1995; Woldmichael and Wink, 2002).

Compound **5** was obtained as a white powder, whose HR-FABMS gave the composition $C_{48}H_{78}O_{19}$. A quick inspection of the $^1H$ and $^{13}C$ NMR spectra of the compound readily indicated the presence of three monosaccharide units through easily identifiable signals for anomeric protons and carbons. After having excluded signals due to the monosaccharide residues, the remaining 30 signals were indicative of a triterpene moiety. The pentacyclic oleanene nature of the triterpene moiety then became apparent owing to the observation of characteristic signals for two $sp^2$ carbons at δ 122.7 (CH, $C_{12}$) and 144.5 (C, $C_{13}$) in the $^{13}C$ spectrum (Connolly and Hill, 1991). Further, substitution on the oleanene skeleton was evident because of the presence in both the $^1H$ and the DEPT spectra of three oxymethine and one oxymethylene resonances not accounted for by the monosaccharide residues. Partial structures comprising the oleanene skeleton were then identified with the help of several 1D-TOCSY experiments, which gave rise to spin-systems made up of $H_{1a,b}$–$H_{2a,b}$–$H_3$, $H_5$–$H_{6a,b}$–$H_{7a,b}$, $H_9$–$H_{11}$–$H_{12}$, $H_{15a,b}$-$H_{16a,b}$, $H_{18}$-$H_{19a,b}$ and $H_{21}$-$H_{22}$ through irradiation of $H_3$, $H_5$, $H_{12}$, $H_{15b}$, $H_{18}$ and $H_{21}/H_{22}$, respectively, as these were not overlapping with other signals. Connectivities between these, as well as information on additional partial structures, were obtained from the HMBC spectrum, which, among others, confirmed the presence of a geminal dimethyl group ($C_{29}$–$C_{20}$–$C_{30}$), a geminal methyl-oxymethylene group ($C_{23}$–$C_4$–$C_{24}$) and four methyls at four quaternary carbons ($C_{10}$–$C_{25}$, $C_8$–$C_{26}$, $C_{14}$–$C_{27}$, $C_{17}$–$C_{28}$) through $^3J_{C,H}$ and $^2J_{C,H}$ correlations, respectively. These, together with comparison of chemical shifts for the aglycone region of **10**, therefore, enabled the identification of the triterpene aglycone in **5** as 3β,21α,22β,24-tetrahydroxyolean-12-en. The chemical shift assignments for the triterpene portion are as shown in Table 1.

The NMR spectra data of the monosaccharide moieties in **5**, through three-anomeric proton (*δ* 4.92, 5.49 and 5.53) and three-anomeric carbon signals (*δ* 105.2, 104.8 and 105.6) in the $^1H$ and $^{13}C$ spectra, respectively, indicated the presence of three monosaccharide units. A series of 1D-TOCSY experiments through irradiation of anomeric proton signals at GlcA-$H_1$, Gal-$H_1$, Rha-$H_1$ (at $C_{21}$) and Gal-$H_{6a,b}$, Rha-$H_6$ enabled the identification of spin systems of individual monosaccharide residues. Further confirmation for the identified systems came from an HSQC-TOCSY experiment. Analysis of data from both these experiments also led to the identification of the monosaccharide units as glucuronic acid, galactose and rhamnose as summarized in Table 2. $H_1$, $H_2$ vicinal coupling constants between 7 and 8 Hz for glucuronic acid and galactose indicated that these sugars occurred in **5** as the β-anomers in $^4C_1$ configurations. Although the observed small $H_1$, $H_2$ coupling constant of rhamnose allowed either an equatorial or axial orientation of $H_1$, the $H_1$, $C_1$ coupling constant of 171.4 Hz indicated an equatorial orientation and thus the presence of the α-anomer (Bock and Pedersen, 1974). Although the $H_4$, $H_5$ coupling constant could not be determined due to overlap of signals, the common $^1C_4$ configuration was arrived at for the rhamnose unit

Table 1
$^{13}C$ and $^1H$ NMR spectral data for the aglycone region of compounds **5** and **11**[a]

| Position | **5** | | **11** | |
|---|---|---|---|---|
| | $^{13}C$ | $^1H$ (*J* in Hz) | $^{13}C$ | $^1H$ (*J* in Hz) |
| 1 | 39.0 | 1.40 *m* | 38.7 | 1.39 *m* |
| | | 0.80 *m* | | 0.81 *m* |
| 2 | 26.8 | 2.14 *m* | 26.8 | 2.08 *m* |
| | | 1.45 *m* | | 1.29 *m* |
| 3 | 90.9 | 3.38 *dd* (11.5, 4.1) | 91.4 | 3.36 *dd* (11.3, 3.4) |
| 4 | 44.0 | | 44.0 | |
| 5 | 56.2 | 0.82 *dd* (11.5, 5.5) | 56.2 | 0.81 *d* (11.9) |
| 6 | 18.8 | 1.54 *m* | 18.8 | 1.55 *m* |
| | | 1.26 *m* | | 1.26 *m* |
| 7 | 31.2 | 1.59 *dd* (14.7, 4.4) | 31.1 | 1.60 *dd* (14.2, 4.2) |
| | | 1.01 | | 1.02 *m* |
| 8 | 40.3 | | 40.3 | |
| 9 | 47.9 | 1.54 *m* | 47.9 | 1.55 *m* |
| 10 | 36.9 | | 36.9 | |
| 11 | 24.2 | 1.78 m (2H) | 24.2 | 1.77 *m* (2H) |
| 12 | 122.7 | 5.26 *t*-like | 122.7 | 5.26 *t*-like |
| 13 | 144.5 | | 144.6 | |
| 14 | 42.2 | | 42.2 | |
| 15 | 26.7 | 1.81 *m* | 26.7 | 1.82 *m* |
| | | 0.95 *m* | | 0.95 *m* |
| 16 | 27.5 | 1.92 *m* | 27.7 | 1.94 *m* |
| | | 1.06 *m* | | 1.06 *m* |
| 17 | 39.3 | | 39.3 | |
| 18 | 43.8 | 2.53 *dd* (14.2, 2.8) | 43.8 | 2.54 *dd* (13.8, 2.8) |
| 19 | 47.5 | 2.02 *t* (14.2) | 47.5 | 2.06 *dd* (13.8, 1.7) |
| | | 1.25 *m* | | 1.26 *m* |
| 20 | 36.6 | | 36.6 | |
| 21 | 84.4 | 3.82 *s* | 85.9 | 3.86 *s* |
| 22 | 78.8 | 3.92 *s* | 78.5 | 4.02 *s* |
| 23 | 22.8 | 1.33 *s* (3H) | 23.2 | 1.33 *s* (3H) |
| 24 | 63.6 | 4.28 *d* (14.2) | 63.7 | 4.25 *d* (14.2) |
| | | 3.38 *d* (14.2) | | 3.24 *d* (14.2) |
| 25 | 15.8 | 0.72 *s* (3H) | 15.9 | 0.71 *s* (3H) |
| 26 | 17.0 | 0.92 *s* (3H) | 17.0 | 0.90 *s* (3H) |
| 27 | 26.7 | 1.24 *s* (3H) | 27.0 | 1.24 *s* (3H) |
| 28 | 22.2 | 1.25 *s* (3H) | 22.3 | 1.27 *s* (3H) |
| 29 | 31.1 | 1.01 *s* (3H) | 31.4 | 1.02 *s* (3H) |
| 30 | 21.8 | 1.37 *s* (3H) | 23.2 | 1.42 *s* (3H) |

[a] Assignments based on $^1H$, $^{13}C$, DEPT, HSQC, HMBC and selective 1D-TOCSY experiments.

Table 2
$^{13}C$ and $^{1}H$ NMR spectral data for the monosaccharide region of compounds **5** and **11**[a]

| Position | **5** | | **11** | |
|---|---|---|---|---|
| | $^{13}C$ | $^{1}H$ (*J* in Hz) | $^{13}C$ | $^{1}H$ (*J* in Hz) |
| GlcA at $C_3$ | | | GlcA at $C_3$ | |
| 1 | 105.2 | 4.92 *d* (7.3) | 105.6 | 4.93 *d* (7.3) |
| 2 | 80.9 | 4.29 *dd* (8.7, 7.3) | 78.6 | 4.55 *dd* (8.2, 7.3) |
| 3 | 78.2 | 4.31 *t* (8.7) | 76.7 | 4.54 *dd* (8.8, 8.2) |
| 4 | 73.8 | 4.49 *dd* (9.6, 8.7) | 73.0 | 4.49 *t* (8.8) |
| 5 | 77.3 | 4.51 *d* (9.6) | 77.2 | 4.52 *d* (8.8) |
| 6 | 172.2 | | 172.2 | |
| Gal at GlcA-$C_2$ | | | Gal at GlcA-$C_2$ | |
| 1 | 105.6 | 5.53 *d* (7.8) | 101.9 | 5.77 *d* (7.6) |
| 2 | 72.8 | 4.42 *dd* (9.6, 7.8) | 77.9 | 4.54 *dd* (8.3, 7.6) |
| 3 | 75.6 | 4.09 *d* (9.6) | 76.9 | 4.10 *dd* (8.3, 1.8) |
| 4 | 71.3 | 4.42 *br s* | 71.4 | 4.38 *br s* |
| 5 | 77.4 | 3.99 *br s* | 76.8 | 3.92 *br s* |
| 6a | 62.8 | 4.45 *d* (11.5) | 61.7 | 4.39 *d* (11.1) |
| 6b | | 4.35 *d* (11.5) | | 4.29 *d* (11.1) |
| Rha at $C_{21}$ | | | Rha at Gal-$C_2$ | |
| 1 | 104.8 | 5.49 *br s* | 102.6 | 6.28 *br s* |
| 2 | 72.6 | 4.69 *br s* | 72.6 | 4.79 *br s* |
| 3 | 72.9 | 4.58 *d* (9.6) | 73.0 | 4.63 *d* (9.2) |
| 4 | 74.1 | 4.32 *dm* (9.6) | 74.5 | 4.32 *t* (9.2) |
| 5 | 70.6 | 4.52 *m* | 69.6 | 4.96 *m* |
| 6 | 18.7 | 1.64 *d* (6.4) | 19.4 | 1.77 *d* (6.1) |
| | | | Ara at C-21 | |
| | | | 107.2 | 4.91 *d* (7.1) |
| | | | 73.7 | 4.35 *dd* (7.1, 9.0) |
| | | | 74.7 | 4.20 *dm* (9.0) |
| | | | 69.5 | 4.33 *m* |
| | | | 67.2 | 4.33 *dd* (12.6, 3.3) |
| | | | | 3.85 *dd* (12.6, 3.3) |

[a] Assignments based on $^{1}H$, $^{13}C$, DEPT, HSQC, HMBC and selective 1D-TOCSY experiments.

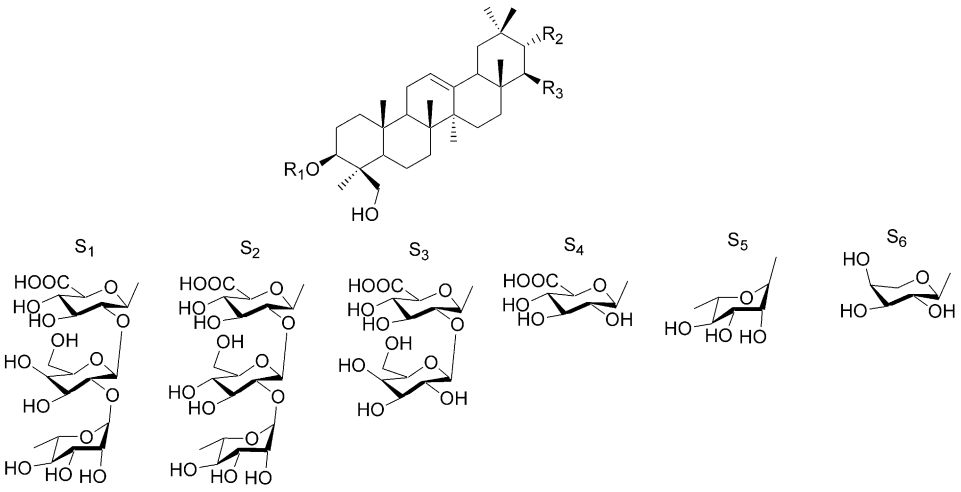
based on lack of NOE effects at $H_3$ and $H_5$ on irradiation of $H_1$ in a selective 1D-NOE experiment. Sites of attachment and sequence in the monosaccharide chain were obtained from an HMBC experiment, which provided cross-peaks between $H_3$ and GlcA-$C_1$, between Gal-$H_1$ and GlcA-$C_2$ and between $C_{21}$ and Rha-$H_1$. This was also confirmed by a selective irradiation of monosaccharide anomeric protons in a selective 1D-NOE experiment. Irradiation of GlcA-$H_1$, Gal-$H_1$ and Rha-$H_1$ produced NOE effects, among others, at $H_3$, GlcA-$H_2$ and $H_{21}$, respectively, and finally led to the structure of **5** as 3β,21α,22β,24-tetrahydroxyolean-12-en-3-*O*-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl-21-*O*-α-L-rhamnopyranoside.

Compound **11** was also obtained as an amorphous white powder and its molecular formula was established as $C_{53}H_{86}O_{23}$ based on quasi-molecular ion peaks in its HR-FABMS. The $^{1}H$ and $^{13}C$ spectrum of **11** showed signals due to seven tertiary methyls, a secondary methyl, three oxymethylenes, four anomeric resonances and a further 14 oxymethines along with a trisubstituted olefin proton. Detailed analyses of the 1D-TOCSY, HSQC and HMBC spectra allowed the assignment of all the $^{1}H$ and $^{13}C$ NMR signals (Tables 1 and 2) and indicated **11** to be a saponin composed of a triterpene aglycone identical to that of **5**, 3β,21α,22β,24-tetrahydroxyolean-12-en, and four monosaccharide units identifiable as β-D-glucuronic acid, β-D-galactose, α-L-rhamnose and arabinose. The $H_1$, $H_2$ vicinal coupling constant of 6.9 Hz, observation of NOE effects at $H_2$ and $H_3$ through irradiation of $H_1$ and $H_5$, respectively, and impediment to magnetization transfer beyond $H_3$ on irradiation of $H_1$ in arabinose in a selective 1D-TOCSY experiment all confirmed the presence in **11** of the α-anomer in the $^{4}C_1$ configuration (De Tommasi et al., 1998). Sequence and site of attachment of monosaccharides was determined by the long-range correlations between $H_3$ and GlcA-$C_1$, Gal-$H_1$ and GlcA-$C_2$, Rha-$H_1$ and Gal-$C_2$ and between $H_{21}$ and Ara-$C_1$. Similarly, NOE effects produced at $H_3$, GlcA-$H_2$, Gal-$H_2$ and $H_{21}$ upon irradiation of the anomeric proton signals GlcA-$H_1$, Gal-$H_1$, Rha-$H_1$ and Ara-$H_1$, respectively, also confirmed observations made from the HMBC spectrum and confirmed sites of attachment and sequence in the monosaccharide chain. From these data, the structure of **11** was determined as 3β,21α,22β,24-tetrahydroxyolean-12-en-3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl-21-*O*-α-L-arabinopyranoside.

## 3. Experimental

### 3.1. General

IR (as a film on a diamond cell) was measured on a Thermo Nicolet Avatar 360 FT-IR spectrometer. An IonSpec Fourier Transform Mass Spectrometer was used in recording HR-MALDI and ESI mass spectra. NMR spectra ($^{1}H$, selective 1D-NOE, $^{13}C$, DEPT-135, DEPT-90, HSQC, HMBC, DQF-COSY, ROESY) were recorded using either a Bruker DRX-500 or DRX-600 spectrometer in pyridine-$d_5$. Chemical shifts were expressed in ppm (δ) using partially deuterated solvent chemical shifts at δ 150.3 ($^{13}C$) and δ 8.74 ($^{1}H$) as reference for $^{13}C$ and $^{1}H$ NMR signals, respectively. The mixing times used in acquiring selective 1D-TOCSY spectra were 60.9, 71.0 and 81.2 ms while in selective 1D-NOE experiments these were 30 and 35 ms. Mixing time employed in the HSQC-TOCSY experiment was 70 ms. Purification of the extract was carried out using low pressure column chromatography with Sephadex LH-20 (32–63 μm, SAI). Further purification of column fractions was then carried out using an Analtech centrifugal TLC system composed of RHSY solvent pump and 8 mm rotors. Compounds were finally isolated with the help of a Varian Star semiprep HPLC system equipped with 230 pump, and a 310 variable wavelength detector.




Compounds

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $R_1$ | H | $S_4$ | $S_3$ | $S_3$ | $S_3$ | $S_1$ | $S_1$ | $S_2$ | $S_2$ | $S_1$ | $S_1$ |
| $R_2$ | H | H | H | OH | $OS_5$ | H | OH | H | H | $OS_5$ | $OS_6$ |
| $R_3$ | OH | OH | OH | OH | OH | OH | OH | OH | =O | OH | OH |

### 3.2. Plant material

*Lupinus oreophilus* Phil. was collected in December 1995, in the district of Arica, at a location called Laderas Lago Chungara, in Chile (18° 15′ S; 69° 10′ W) by Gloria Montenegro. A voucher specimen (No. 0707) has been deposited at the Universidad Católica de Chile, Santiago, Chile. Intellectual Property Rights Agreements for plant collections and collaborative research have been fully executed between the University of Arizona and P. Universidad Católica de Chile.

### 3.3. Extraction and isolation

Powder (400 g) of the aerial part of *L. oreophilus* was extracted with methanol (2×1l). The methanol extract was filtered and partitioned with hexane (2×1l). The methanol fraction was found to be turbid and was thus centrifuged at 3000 *g*. The supernatant was then concentrated under reduced pressure to about 300 ml and was diluted to 1000 ml with water. The aqueous solution was then partitioned with *n*-butanol. Concentration of the butanol layer under reduced pressure gave a viscous mass, which was applied onto a low-pressure Sephadex LH-20 column. The column was eluted with methanol (1l) and 50 ml fractions were collected. Fractions 5–16 were found to contain triterpenes and saponins while 20–29 and 30–38 primarily contained flavonoids. Combined fractions 5–16 were then further purified using centrifugal TLC with stepped gradient of dichloromethane-methanol (100:0, 95:5, 9:1, 85:15, 8:2, 7:3, v/v) to yield 2 subfractions designated SF-1 and SF-2. Purification of saponins in SF-2 was carried out using a Büchi medium pressure RP-18 column chromatography system [solvent—methanol:0.15% trifluoroacetic acid (TFA) in water, 70:30 for 3 min and a continuous gradient to 100:0 in 15 min; Flow rate—15 ml/min]. This yielded four subfractions SF-3, SF-4, SF-5, SF-6 each containing two–five compounds. SF-3 gave rise to **8** (70 mg, $R_t = 10.4$ min), **9** (6.1 mg, $R_t = 11.7$ min) and **3** (9.4 mg, $R_t = 14.4$ min) upon HPLC purification (Column— Reliasil, C-18, 10 μm, 250×10 mm, Column Engineering, Ontario, Canada; Solvent— acetonitrile: 0.15% trifluoroacetic acid (TFA) in water, 55:45 for 3 min and a continuous gradient to 70:30 in 13 min; Flow rate—5.2 ml/min; Detection— 200 nm). HPLC purification (Column— Reliasil, C-18, 10 μm, 250×10 mm; Solvent— acetonitrile:0.15% trifluoroacetic acid (TFA) in water, 45:55 for 5 min and a continuous gradient to 60:40 in 15 min; Flow rate— 5.2 ml/min; Detection— 200 nm) of SF-6 gave **6** (28.3 mg, $R_t = 10.4$ min) and **3** (9.4 mg, $R_t = 14.1$ min). Components of SF-5 were also purified with HPLC under same conditions to give **6** (7.1 mg, $R_t = 9.9$ min), **7** (10.6 mg, $R_t = 12.2$ min) and **4** (2.4 mg, $R_t = 16.5$ min). Finally, SF-4 were also purified under same conditions using a MeCN:water linear gradient (30:70 for 5 min then to 60:40 in 20 min) giving **11** (1.6 mg, $R_t = 15.4$ min), **10**

(5.2 mg, $R_t = 16.4$ min), **5** (2.0 mg, $R_t = 17.2$ min), **4** (3.5 mg, $R_t = 17.9$ min) and **3** (1.9 mg, $R_t = 18.9$ min). The subfraction SF-1 was further purified on centrifugal TLC with a step gradient of hexane:acetone (75:25, 60:40, 40:60 and 10:90). This purified fraction was then run on HPLC (Column— Reliasil, ODS-2, 10 μm, 250×10 mm; Solvent— acetonitrile:0.15% trifluoroacetic acid (TFA) in water, 60:40 for 5 min and a continuous gradient to 100:0 in 20 min and at 100:0 for 5 min; Flow rate— 5.2 ml/min; Detection— 200 nm) to yield compounds **1** (1.7 mg, $R_t = 25.8$ min) and **2** (2.3 mg $R_t = 18.3$ min).

*3.3.1. 3β,21α,22β,24-tetrahydroxyolean-12-en-3-*O*-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl-21-*O*-α-L-*rhamnopyranoside *(**5**), white amorphous powder*

HR-MALDI/TOF $m/z$ 981.5193 ($[M + Na]^+$, monoisotopic calc. 981.5013), HR-ESI $m/z$ 957.5120 ([M-H], monoisotopic calc. 957.5037), $C_{48}H_{78}O_{19}$. IR $\nu_{max}$ ($cm^{-1}$) 3370 (OH), 2946 (CH), 1675 (COOH), 1431, 1044. $^{13}$C-NMR (150 MHz, $CDCl_3$) and $^1$H-NMR (600 MHz): see Tables 1 and 2.

*3.3.2. 3β,21α,22β,24-tetrahydroxyolean-12-en-3-*O*-α-L-rhamnopyranosyl-(1→2)-β-D-galactopyranosyl-(1→2)-β-D-glucuronopyranosyl-21-*O*-α-L-arabinopyranoside (**11**), white amorphous powder*

HR-MALDI/TOF $m/z$ 1113.4988 ($[M + Na]^+$, monoisotopic calc. 1113.5433), HR-ESI $m/z$ 1089.5350 ([M-H], monoisotopic calc. 1089.5457), $C_{53}H_{86}O_{23}$. IR $\nu_{max}$ ($cm^{-1}$) 3357 (OH), 2945 (CH), 1676 (COOH), 1349, 1027. $^{13}$C-NMR (150 MHz, $CDCl_3$) and $^1$H-NMR (600 MHz): see Tables 1 and 2.

NMR, MS, and IR data for compounds **1**–**4** and **6**–**10** can be obtained from the authors directly.

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